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# Heavy Metals in Waste

Final Report

February 2002

COWI A/S, Denmark

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## Preface

### Background

The presence of heavy metals in waste as a result of their uses in modern society is matter of ever-growing concern to both politicians, authorities and the public in the 15 Member States of the European Union.

The strategy for minimisation of the effects of heavy metals in waste is partly to reduce today and future environmental and human exposure to the heavy metals in the waste, partly to reduce the content of heavy metals in products marketed.

In the Member States of the European Union, the treatment of waste is regulated by a number of directives, which define the scope and stipulate general rules for the treatment of waste containing heavy metals. In the aim of increasing the recycling of materials, among these heavy metals, regulation of the treatment of composite waste products as electronics, vehicles and batteries has been put into force (or are at the stage of proposal). A number of directives today regulate the content of the heavy metals cadmium, mercury and lead in marketed products in order to reduce their use.

Among Member States, there are significant differences in attitude as to the necessity of further reduction of the content of heavy metals in products and waste.

### Purpose

The overall objective of the present project is to present information concerning sources of heavy metals to waste, harmful effects of heavy metals, the problems posed by the disposal and recycling of heavy metals and heavy metal containing products, and to assess the options for substituting the heavy metals.

### Study team

The following team has contributed to the solving of this assignment: Ole Holm (Project Director), Erik Hansen (Project Manager), Carsten Lassen, Frank Stuer-Lauridsen and Jesper Kjølholt, COWI Consulting Engineers and Planners.



## Table of Contents

<b>Preface</b>	<b>1</b>
<b>1 Summary and discussion</b>	<b>5</b>
<b>2 Harmful effects to humans and the environment</b>	<b>9</b>
2.1 Lead	9
2.1.1 Humans	9
2.1.2 Environment	11
2.2 Mercury	12
2.2.1 Humans	12
2.2.2 Environment	14
2.3 Cadmium	15
2.3.1 Humans	15
2.3.2 Environment	16
2.4 Chromium	17
2.4.1 Humans	17
2.4.2 Environment	18
<b>3 Sources of heavy metals to waste</b>	<b>20</b>
3.1 Lead	22
3.2 Mercury	29
3.3 Cadmium	35
3.4 Chromium	38
3.5 Obstacles for increased collection and recycling of heavy metals	42
<b>4 Pathways of the heavy metals by waste disposal and recovery</b>	<b>45</b>
4.1 Incineration	46
4.1.1 Slag	48
4.1.2 Flue gas cleaning residues	50
4.2 Landfilling	51
4.3 Recycling	54
4.3.1 Sorting and separation activities	54
4.3.2 Fate of heavy metals by recycling of other metals	55
4.3.3 Recovery of heavy metals	56
4.3.4 Recycling of plastics, glass and organic waste	57

<b>5</b>	<b>Substitution</b>	<b>59</b>
5.1	Principal options for substitution	59
5.2	Costs of substitution	69
	<b>References</b>	<b>72</b>
	<b>Annex 1 Parameters determining evaporation and diffusion of heavy metals</b>	<b>80</b>

## 1 Summary and discussion

The aim of this report has been to demonstrate the existing knowledge regarding the harmful effects of heavy metals, the principal routes for the metals via waste management systems to the environment and the strength and weaknesses of recycling and substitution as options for risk reduction.

### Harmful effects

Mainly related to the heavy metals lead, mercury and cadmium but covering other heavy metals like chromium as well extensive documentation of the potential harmful effects to humans and the environment is available. Generally heavy metals have each their story. Common to lead, mercury and cadmium is that neither has any known useful function in biological organisms.

### Lead

Lead is causing concern in particular due to the possible impacts on children. Lead influences the nervous system, slowing down neural response. This influences learning abilities and behaviour. Children are exposed to lead right from their birth, as children in the embryonic stage receive lead from their mothers through the blood. Children are, furthermore, exposed to lead via dust and soil contaminated by deposition from air and other sources.

In the environment lead is known to be toxic to plants, animals and microorganisms. Effects are generally limited to specially contaminated areas.

### Mercury

Concerning mercury the primary focus is on methyl mercury originating from the diet in particular through the consumption of fish and fish products. In humans methyl mercury affects among other organs also the brain, and it is documented that (as for lead) children in the embryonic stage receive mercury via the placenta causing persistent effects on children's mental development.

In the environment animals placed high in the food chain and in particular the marine food chain are assumed exposed to mercury poisoning due to the ability of methyl mercury to concentrate via the food chain. However, notable effects on microorganisms are believed to take in large parts of Europe in forest soils dominated by organic material.

### Cadmium

Cadmium accumulates especially in the kidneys leading to dysfunction of the kidney with increased secretion of e.g. proteins in urine (proteinuria) and other effects. Intake of cadmium is generally based on the diet, in particular vegetables and corn products. The concern of this pathway is based on the knowledge that an increase in the content of cadmium in agricultural soil will result in an increased uptake of cadmium by plants. However, for smokers also the use of tobacco is of concern.

In the environment cadmium is reported toxic to especially animals and microorganisms. Also for animals kidney damage is the dominating effect. Concerning microorganisms cadmium is known to significantly influence leaf litter decomposition.

Chromium	Chromium differs from the 3 other heavy metals discussed here by being essential in form of Cr(III) to humans and animals. The most widespread human effect is chromium allergy caused by exposure to chromium (especially Cr(VI) compounds) in the working environment. Chromium compounds are also assumed to cause cancer. Environmentally Cr(VI)-compounds are generally considered the most toxic.
Sources to waste	<p>The content of heavy metals in waste is primarily a consequence of the intended use of heavy metals in industrial products. At the end of their useful life all products will end up in waste to the extent they are not attractive for recycling. Heavy metals may, however, also be lost to waste during production and use phases. Losses in the manufacturing process are often disposed of as manufacturing waste, while products may be exposed to wear and tear inclusive corrosion during the use phase.</p> <p>Identification of the actual sources for heavy metals observed in different waste types and waste products may only be done with some uncertainty. E.g. a lead atom in flue gas cannot tell whether it originates from lead pigments in plastic or a lead battery been disposed of as combustible waste. A useful tool in this context is Substance Flow Analysis, which based on a knowledge on applications for the substance in question and flow patterns for relevant products allows for the development of a realistic picture of significant sources for different waste types. The analysis of sources to waste has focused on solid waste.</p>
Lead	It is characteristic for lead, that many different products containing lead will end up in waste management systems and be a source of lead to incineration plants and/or landfills. Important sources include (reference is made to table 3.3): Plastics, fishing tools, lead crystal glass inclusive cathode ray tubes, ceramics, solders, pieces of lead flashing and many other minor products. To these waste types must be added residues from metal shredding, steel reclamation and cable reclamation.
Mercury	Important sources for mercury to waste include (reference is made to table 3.10, 3.12 and 3.13): Dental amalgam, measurement and control devices inclusive thermometers, batteries, tubes and lamps etc. It is interesting to note the significant differences between countries, which may be explained by differences in regulation as well as tradition.
Cadmium	For cadmium the picture is somewhat simpler, as the use of cadmium has been restricted for some years and NiCad batteries today is the all-dominating product. However, to understand the picture of sources to incineration plants, it is necessary to remember uses as pigments and stabilisers in plastic as well as plating on steel, which have been significant uses 1-2 decades ago. Many of the relevant cadmium products were quality goods with an expected lifetime of 10-20 years or even more (e.g. PVC-window frames). Such goods are only slowly released to waste. Concerning landfills table 3.20 indicates that manufacturing waste is a source of the same magnitude as industrial products in municipal waste.

## Chromium

The environmental concerns related to chromium are focused on applications like tanning, wood preservation and pigments and dyes for plastics, paint and textiles. Chromium alloys and in particular stainless steel are by far the dominating field of application for chromium, but normally not regarded as a serious waste problem due to the high value of chromium alloys, which motivates collection for recycling. One may, however, pay attention to that many types of stainless steel are not magnetic and cannot be separated from waste streams by magnetic separation.

## Fate by waste treatment and disposal

Modern waste treatment technology have developed to ensure that the immediate release of heavy metals to the environment (air, water) from waste treatment facilities inclusive incineration plants in general today are small. An exemption may be mercury, which due to its very volatile nature is extremely difficult to retain. However, also for mercury the dominating part of the content in combustible waste will be collected with residues – slag and flue gas cleaning residues. The basic problems related to these residues can be summarised to:

- Lack of space for landfills are forcing some countries to utilise the residues for civil works and similar purposes, but the content of heavy metals in residues constrains this kind of material recycling.
- No matter whether the residues are utilised for civil works or placed in landfills the overall consequence is a continued creation of heavy metal stocks in the European society. This process cannot be considered sustainable taking into account the potential for future release to environment either by leaching or by more drastic geological events as e.g. a new Ice Age.

The issues related to landfilling in several ways resemble the issues of disposal of incineration residues. Although the mobility of heavy metals inside landfills is low, and a complete wash-out of a specific metals may require a time of hundreds to thousands of years and in special cases even more, no evidence exist that landfills can be regarded as a permanent containment of heavy metals.

Thus the basic question to be considered is: For how long into the future are we responsible for the consequences of our actions of today?

## Recycling

Recycling may be a way to significantly reduce the loss of heavy metal to the environment and at the same time avoid that new metal enter into circulation. However, the concept of recycling covers an array of very different activities.

Dedicated recycling of heavy metals may be carried out rather efficiently with very small losses to the environment and residues, assuming that proper technology are applied. The main problem here is to ensure an effective collection of item made of heavy metals. The fact is that effective collection only will work for items present in such a quantity and condition that collection is feasible.

Reality is that significant quantities of heavy metals will never be collected for recycling by the present waste management systems. Thus recycling will not

prevent a continued release to the environment of heavy metals in circulation in the technosphere.

Regarding recycling of other metals, heavy metals are present as contaminants requiring special pollution prevention operations and special disposal of residues. To some extent the heavy metals will be integrated in the metals in question, e.g. chromium and nickel will be integrated in steel.

Continued recycling of plastics only exist for few products like boxes for beer and soft water bottles. Apart from such product recycling will typically only delay the disposal of the heavy metals in question for a single product generation.

Systems are being developed for recycling of cathode ray tubes. Apart from this lead crystal glass will mainly be source for lead contamination of ordinary secondary glass and may be a source for lead emission from glass manufacturing as well as from landfills at the time of final degradation of the glass matrix.

Recycling of organic materials to be utilised as soil improvement media will lead to dispersal of heavy metals present in other waste types, e.g. plastics, contaminating the organic material.

#### Substitution

Substitution is the option left, when recycling cannot solve the problem. By substitution pollution is prevented at the source, as it is avoided that heavy metals are taken into the manmade circulation.

Alternatives have been developed for many of the applications of lead and nearly all applications of mercury and cadmium, while the development regarding chromium so far has focused in particular on tanning and wood preservation. The knowledge available with respect to alternatives has been presented in table 5.1-5.4.

The costs of substitution vary between applications and may range from below zero to a much higher price level. It is, however, always possible to discuss, what should be included in such cost estimates. Attention is e.g. drawn to the fact, that in order to restrict emissions of heavy metals to the environment by waste treatment and disposal processes, significant costs are paid by local governments or other parties to control operations and special treatment and disposal activities. Such costs are generally not included in estimates for costs of substitution.

## 2 Harmful effects to humans and the environment

Mercury, lead, cadmium and chromium all pose a number of undesired properties that affect humans and the environment. In the following is presented a review of the key harmful effects to humans and the environment, and the main concerns associated with the four heavy metals. This review is focused on the routes of exposure relevant for waste treatment and disposal operations as outlined in chapter 4. The review should not be regarded as a general review of the heavy metals in question as some direct routes of exposure related to specific uses, like e.g. lead additives in gasoline, are not discussed.

### 2.1 Lead

Lead in the environment is mainly **particulate bound** with relatively low mobility and bioavailability. Lead does, in general, not bioaccumulate and there is no increase in concentration of the metal in food chains.

Lead is not essential for plant or animal life.

The following information has largely been extracted from the IPCS monographs /WHO 1989a; WHO 1995/ unless otherwise indicated.

#### 2.1.1 Humans

In the general non-smoking adult population, the major exposure pathway is from food and water. Airborne lead may contribute significantly to occupational exposure and exposure of smokers.

**For infants and young children lead in dust and soil often constitutes a major exposure pathway** and this exposure has been one of the main concerns as to the exposure of the general population. The intake of lead will be influenced by the age and behavioural characteristics of the child and the bioavailability of lead in the source material. Baseline estimates of potential exposure of children to dusts, including intake due to normal hand-to-mouth activity, are 0.2 g/day for children 1–6 years old when both indoor and outdoor ingestion of soil and dust is considered, but for some children it may be up to 5 g/day (RTI 1999).

In adult humans approximately 10% of the dietary lead is absorbed. However, in infants and young children as much as 50% of dietary lead is absorbed, although absorption rates for lead from dusts/soils and paint chips can be lower depending upon the bioavailability. Depending upon the type of lead compounds, particle size, and solubility in body fluids, up to 50% of inhaled lead compounds may be absorbed.

Organic lead is more bioavailable and toxic than inorganic lead, but the primary source of organic lead has been leaded petrol, now phased out from the market in the EU.

Absorbed lead is rapidly taken up into blood and soft tissue, followed by a slower redistribution to bone. Bone accumulates lead during much of the human life span and may serve as an endogenous source of lead that may be released slowly over many years after the exposure stops.

In humans, lead can result in a wide range of biological effects depending upon the level and duration of exposure. Effects may range from inhibition of enzymes to the production of marked morphological changes and death. Such changes occur over a broad range of doses. For neurological, metabolic and behavioural reasons, children are more vulnerable to the effects of lead than adults.

**Of particular concern for the general population is the effect of lead on the central nervous system.** Epidemiological studies suggest that low level exposure of the foetus and developing child may lead to reprotoxic effects, i.e. damage to the learning capacity and the neuropsychological development /Goyer 1986/. Studies of children indicate a correlation between higher lead contents in the blood and a lower IQ. Slowing of nerve conduction velocity has been found at low lead blood levels. Impairment of psychological and neurobehavioural functions has also been found after long-term lead exposure of workers.

Lead has been shown to have effects on haemoglobin synthesis and anaemia has been observed in children at lead blood levels above 40 µg/dl.

Lead exposure is associated with a small increase in blood pressure. There is no evidence to suggest that any association of lead blood levels with blood pressure is of major health importance.

Lead is known to cause kidney damage. Some of the effects are reversible, whereas chronic exposure to high lead levels may result in continued decreased kidney function and possible renal failure. Renal effects have been seen among the general population when more sensitive indicators of function were measured.

The reproductive effects of lead in the male are limited to sperm morphology and count. In the female, some adverse pregnancy outcomes have been attributed to lead. Lead does not appear to have deleterious effects on skin, muscle or the immune system.

The evidence for carcinogenicity of lead and several inorganic lead compounds in humans is inadequate /WHO 1995/. Classification of IARC is class 2B *'The agent (mixture) is possibly carcinogenic to humans. The exposure circumstance entails exposures that are possibly carcinogenic to humans'* /IARC 1987/.

### 2.1.2 Environment

In the environment lead binds strongly to particles, such as soil, sediment and sewage sludge. Because of the low solubility of most of its salts, lead tends to precipitate out of complex solutions. It does not bioaccumulate in most organisms, but can accumulate in biota feeding primarily on particles, e.g. mussels and worms. These organisms often possess special metal binding proteins that removes the metals from general distribution in their organism. Like in humans, lead may accumulate in the bones.

The distribution of lead within animals is closely associated with calcium metabolism. In shellfish, lead concentrations are higher in the calcium-rich shell than in the soft tissue. In dolphins, lead is transferred from mothers to offspring during foetal development and breast-feeding.

#### Mammals and birds

In all species of experimental animals studied, including non-human primates, lead has been shown to cause adverse effects in several organs and organ systems, including the blood system, central nervous system, the kidney, and the reproductive and immune systems. There are many reports of lead levels in wild mammals, but few reports of toxic effects of the metal in the wild or in non-laboratory species.

Lead shot and lead sinkers have been recognised as sources of severe lead contamination for birds via their gizzards. However, this effect is related to specific products and not to waste treatment activities.

#### Microorganisms

In general, inorganic lead compounds are of lower toxicity to microorganisms than are trialkyl- and tetraalkyllead compounds. There is evidence that tolerant strains exist and that tolerance may develop in others. Lead compounds are in general not very toxic to microorganisms and lead compounds have contrary to mercury and chromium compounds not been used as biocides.

#### Other aquatic organisms

One of the most important factors influencing the aquatic toxicity of lead is the free ionic concentration and the availability of lead to organisms. Lead is unlikely to affect aquatic plants at levels that might be found in the general environment.

In communities of aquatic invertebrates, some populations are more sensitive than others and community structure may be adversely affected by lead contamination. However, populations of invertebrates from polluted areas can show more tolerance to lead than those from non-polluted areas. In other aquatic invertebrates, adaptation to low oxygen conditions can be hindered by high lead concentrations. Young stages of fish are more susceptible to lead than adults or eggs. Typical symptoms of lead toxicity include spinal deformity and blackening of the tail region. The maximum acceptable toxicant limit for soluble species of inorganic lead has been determined for several species under different conditions and results ranging from 0.04 mg/litre to 0.198 mg/litre. Organic compounds are more toxic to fish than inorganic lead salts. There is evidence that frog and toad eggs are sensitive to nominal lead concentrations of less than 1.0 mg/litre in standing water and 0.04 mg/litre in flow-through sys-

tems; arrested development and delayed hatching have been observed. For adult frogs, there are no significant effects below 5 mg/litre in aqueous solution, but lead in the diet at 10 mg/kg food has some biochemical effects.

#### Other terrestrial organisms

The tendency of inorganic lead to form highly insoluble salts and complexes with various anions together with its tight binding to soils, drastically reduces its availability to terrestrial plants via the roots. Lead is taken up by terrestrial plants through the roots and to a lesser extent through the shoots.

Translocation of the ion in plants is limited and most bound lead stays at root or leaf surfaces. As a result, in most experimental studies on lead toxicity, high lead concentrations in the range of 100 to 1,000 mg/kg soil are needed to cause visible toxic effects on photo synthesis, growth, or other parameters. Thus, lead is only likely to affect plants at sites with very high environmental concentrations.

Ingestion of lead-contaminated bacteria and fungi by nematodes leads to impaired reproduction. Caterpillars that are maintained on a diet containing lead salts show symptoms of toxicity leading to impaired development and reproduction. The information available is too meagre to quantify the risks to invertebrates during the decomposition of lead-contaminated litter.

## 2.2 Mercury

Mercury is a peculiar metal. Most conspicuous is its fluidity at room temperature, but more important for the possible exposure of man and the environment to mercury are two other properties:

- Under reducing conditions in the environment, ionic mercury changes to the uncharged elemental mercury which is **volatile** and may be transported over long distances by air.
- Mercury may be chemically or biologically transformed to methylmercury and dimethylmercury, of which the former is **bioaccumulative** and the latter is also **volatile** and may be transported over long distances.

Mercury is not essential for plant or animal life.

### 2.2.1 Humans

The main human exposure to mercury is via inhalation of the vapour of elemental mercury and ingestion of mercury and methylmercury compounds in food.

Mercury and its compounds are toxic to humans. The toxicity varies among the different types of mercury. Generally, organic forms are much more toxic than the inorganic forms.

## Methylmercury

**Methylmercury represents the most important toxic impact of mercury to humans.** It is present worldwide and the general population is primarily exposed to methylmercury through their diet, in particular through the consumption of fish and fish products. Most of the total mercury in fish is in the form of methylmercury (may be close to 100% for older fish, especially in predatory species). Due to long-range atmospheric and aquatic transport of mercury, methylmercury is also present in the environment in remote areas without local or regional mercury sources. This implies that population groups particularly dependent on – or accustomed to – marine diets, for instance the Inuits of the Arctic, as well as populations depending on fishing and marine hunting anywhere else on the globe, are particularly at risk. /AMAP 1998/.

The high toxicity of methylmercury is well documented. Methylmercury has been found to have adverse effects on several organ systems in the human body as well as in animals. These include the central nervous system (mental retardation, deafness, blindness, impairment of speech etc.) and the cardiovascular system (blood pressure, heart-rate variety and heart diseases). Research on animals has given evidence of effects on the immune system and the reproduction system. Recently, an extensive evaluation of the toxicological effects of methylmercury was performed under the U.S. National Research Council /NRC, 2000/. Here, it was concluded that the effects on the developing nervous system in unborn and newborn children are the most sensitive, well-documented effects judged from the evidence from human epidemiological studies and animal studies.

Methylmercury in our food is rapidly absorbed in the gastrointestinal tract (stomach and intestine), readily crosses the placental barrier and enters the brain. A series of large epidemiological studies have recently provided evidence that methylmercury in pregnant women's marine diets appears to have subtle, persistent effects on the children's mental development (cognitive deficits) as observed at about the age of school start /NRC, 2000/.

The U.S. EPA has calculated from dietary statistics that as many as 7% of U.S. women of childbearing age exceed what is regarded as safe exposures /U.S. EPA 1997/.

Methyl mercury is classified by /IARC 1993/ as Class 2B *'The agent (mixture) is possibly carcinogenic to humans. The exposure circumstance entails exposures that are possibly carcinogenic to humans.'*

## Inorganic mercury

The general population is primarily exposed to inorganic mercury through the diet and dental amalgam /WHO 1991/.

Acute inhalation exposure to mercury vapour may be followed by chest pains, dyspnoea, coughing, haemoptysis, and sometimes interstitial pneumonitis leading to death (WHO 1991). The central nervous system is the critical organ for mercury vapour exposure. Subacute exposure has given rise to psychotic reactions characterised by delirium, hallucinations, and suicidal tendency.

The kidney is the critical organ following the ingestion of inorganic divalent mercury salts. Occupational exposure to metallic mercury has been associated with the development of proteinuria, both in workers with other evidence of mercury poisoning and in those without such evidence (WHO 1991).

Metallic mercury and inorganic mercury compounds are classified by the International Agency for Research on Cancer as Class 3 '*The agent (mixture, or exposure circumstance) is unclassifiable as to carcinogenicity in humans*' (IARC 1993/).

### 2.2.2 Environment

#### Birds and mammals

Experiments on certain groups of animals have shown that the central nervous system and the kidneys are the organs most vulnerable to damage from methylmercury and inorganic mercury exposure (AMAP 1998/). Effects include neurological impairment, reproductive effects, liver damage and significant decreases in intestinal absorption. These effects may appear at animal tissue concentrations above 25-60 mg/kg wet weight (AMAP 1998/). Birds fed inorganic mercury show a reduction in food intake and consequent poor growth (WHO 1991/). Adverse effects on birds hatching have been observed at above 2 mg/kg wet weight (free ranging birds and experimental) (AMAP 1998/). Other more subtle effects on enzyme systems, cardiovascular function, blood parameters, the immune response, kidney function and structure, and behaviour have been reported.

#### Other aquatic organisms

The organic forms of mercury are generally more toxic to aquatic organisms than the inorganic forms. Aquatic plants are affected by mercury in the water at concentrations approaching 1 mg/litre for inorganic mercury, but at much lower concentrations of organic mercury (WHO 1991/). High concentration of inorganic mercury affect macroalgae by reducing the germination (AMAP 1998/). Aquatic invertebrates vary greatly in their susceptibility to mercury. Generally, larval stages are more sensitive than adults. A wide variety of physiological and biochemical abnormalities has been reported after fish have been exposed to sublethal concentrations of mercury, although the environmental significance of these effects is difficult to assess. Reproduction is also affected adversely by mercury (WHO 1991/).

#### Other terrestrial organisms

Plants are generally insensitive to the toxic effects of mercury compounds. Mercury is, however, accumulated in taller plants, especially in perennials (Boening et al 2000/). The primary effect in plants is associated with the root tips (Boening et al 2000/).

#### Microorganisms

Mercury is toxic to microorganisms. Inorganic mercury has been reported to have effects at concentrations of the metal in the culture medium of 5 µg/litre, and organomercury compounds at concentrations at least 10 times lower than this (WHO 1991/). Organomercury compounds have been used as fungicides. These effects are often irreversible, and mercury at low concentrations represents a major hazard to microorganisms. Subtle, but notable impacts are believed to take place in large parts of Europe in forest soils dominated by or-

ganic material – and potentially in many other locations in the world with similar characteristics /Maag & Hansen 2001a/. The microbiological activity in soil is vital to the material balances for carbon and nutrients in the soil and is affecting trees and soil organisms, which form the basis for the terrestrial food chain.

## 2.3 Cadmium

Cadmium and cadmium compounds are, compared to other heavy metals, relatively **water soluble**. They are therefore also more mobile in e.g. soil, generally more bioavailable and tends to **bioaccumulate**.

Cadmium is not essential for plant or animal life.

The following information has largely been extracted from the IPCS monographs /WHO 1992a; WHO 1992b/ unless otherwise indicated.

### 2.3.1 Humans

The major route of exposure to cadmium for the non-smoking general population is via food; the contribution from other pathways to total uptake is small. Tobacco is an important source of cadmium uptake in smokers, as tobacco plants like other plants accumulate cadmium from the soil.

Data from experimental animals and humans have shown that absorption via lungs is higher than gastrointestinal absorption (via the stomach). Up to 50% of the inhaled cadmium may be absorbed. The gastrointestinal absorption of cadmium is influenced by the type of diet and nutritional status. On average, 5% of the total oral intake of cadmium is absorbed.

A major part of cadmium in the human diet comes from agricultural products. **The pathway of human exposure from agricultural crops is susceptible to increases in soil cadmium** as increase in soil cadmium contents, e.g. due to cadmium in soil amendment products, result in an increase in the uptake of cadmium by plants.

Cadmium accumulates in the human body and especially in the kidneys. According to the current knowledge **kidney damage (renal tubular damage) is probably the critical health effect**, both in the general population and in occupational exposed workers /Järup *et al* 1998/. The accumulation of cadmium in the kidney (in the renal cortex) leads to dysfunction of the kidney with impaired reabsorption of, for instance, proteins, glucose, and amino acids. It is estimated that 1% of all smoking women Sweden with low body iron stores in may today experience adverse kidney effects due to the cadmium load /Järup *et al* 1998/.

Both human and animal studies indicate that skeletal damage (osteoporosis) may be a critical effect of cadmium exposure, but the significance of the effect in the Swedish population is according to /Järup *et al* 1998/ still unclear.

Other effects of cadmium exposure are disturbances in calcium metabolism, hypercalciuria and formation of renal stones.

The International Agency for Research on Cancer (IARC) classifies cadmium in Class 1 '*The agent (mixture) is carcinogenic to humans. The exposure circumstance entails exposures that are carcinogenic to humans.*' /IARC 1993b/. Occupational exposure is linked to lung cancer and prostate cancer. According to a recent review, the epidemiological data linking cadmium and lung cancer are much stronger than for prostatic cancer, whereas links between cadmium and cancer in liver, kidney and stomach is considered equivocal /Waalkes 2000/.

### 2.3.2 Environment

Cadmium is readily accumulated by many organisms, particularly by microorganisms and molluscs where the bioconcentration factors are in the order of thousands. Soil invertebrates also concentrate cadmium markedly. Most organisms show low to moderate concentration factors of less than 100.

#### Birds and mammals

Chronic cadmium exposure produces a wide variety of acute and chronic effects in mammals similar to those seen in humans. Kidney damage and lung emphysema are the primary effects of high cadmium in the body.

Kidney damages have been reported in wild colonies of pelagic sea birds having cadmium level of 60-480 µg/g in the kidney /WHO1991/.

#### Microorganisms

Cadmium is toxic to a wide range of microorganisms as demonstrated by laboratory experiments. The main effect is on growth and replication. The most affected soil microorganisms are fungi, some species being eliminated after exposure to cadmium in soil. There is selection for resistant strains of microorganisms after low exposure to the metal in soil.

#### Other aquatic organisms

In aquatic systems, cadmium is most readily absorbed by organisms directly from the water in its free ionic form Cd (II) /AMAP 1998/.

The acute toxicity of cadmium to aquatic organisms is variable, even between closely related species, and is related to the free ionic concentration of the metal. Cadmium interacts with the calcium metabolism of animals. In fish it causes lack of calcium (hypocalcaemia), probably by inhibiting calcium uptake from the water. Effects of long-term exposure can include larval mortality and temporary reduction in growth /AMAP 1998/.

Sublethal effects have been reported on the growth and reproduction of aquatic invertebrates; there are structural effects on invertebrate gills. There is evidence of the selection of resistant strains of aquatic invertebrates after exposure to cadmium in the field. The toxicity is variable in fish, salmonoids being particularly susceptible to cadmium. Sublethal effects in fish, notably malformation of the spine, have been reported. The most susceptible life-stages are the embryo and early larva, while eggs are the least susceptible. Cadmium is toxic

to some amphibian larvae, although some protection is afforded by sediment in the test vessel.

#### Other terrestrial organisms

Cadmium affects the growth of plants in experimental studies, although no field effects have been reported. Stomatal opening, transpiration, and photosynthesis have been reported to be affected by cadmium in nutrient solutions, but metal is taken up into plants more readily from nutrient solutions than from soil. Terrestrial plants may accumulate cadmium in the roots and cadmium is found bound to the cell walls /AMAP 1998/.

Terrestrial invertebrates are relatively insensitive to the toxic effects of cadmium, probably due to effective sequestration mechanisms in specific organs. Terrestrial snails are affected sublethally by cadmium; the main effect is on food consumption and dormancy, but only at very high dose levels.

Cadmium even at high dosage does not lethally affect birds, although kidney damage occurs. Cadmium has been reported in field studies to be responsible for changes in species composition in populations of microorganisms and some aquatic invertebrates. Leaf litter decomposition is greatly reduced by heavy metal pollution, and cadmium has been identified as the most potent causative agent for this effect.

## 2.4 Chromium

Chromium occurs in a number of oxidation states, but Cr(III) (trivalent chromium) and Cr(VI) (hexavalent chromium) are of main biological relevance. There is a great difference between Cr(III) and Cr(VI) with respect to toxicological and environmental properties, and they must always be considered separately.

Chromium is similar to lead typically found **bound to particles**. Chromium is in general not bioaccumulated and there is no increase in concentration of the metal in food chains.

Contrary to the three other mentioned heavy metals, Cr(III) is an essential nutrient for man in amounts of 50 - 200 µg/day. Chromium is necessary for the metabolism of insulin. It is also essential for animals, whereas it is not known whether it is an essential nutrient for plants, but all plants contain the element.

The following information has largely been extracted from the IPCS monographs /WHO 1988/ unless otherwise referenced.

### 2.4.1 Humans

The kinetics of chromium depends on its oxidation state and the chemical and physical form within the oxidation state. Most of the daily chromium intake is ingested with food and is in the trivalent form. About 0.5-3% of the total intake of trivalent chromium is absorbed in the body. The gastrointestinal absorption

of Cr(VI) is 3-5 times greater than that of trivalent forms; however, some of it is reduced by gastric juice.

Skin exposure of the general public to chromium can occur from contact with products containing chromium e.g. leather or preserved wood or chromium containing soil. Airborne chromium may contribute significantly to occupational exposure.

**In general, Cr(III) is considerably less toxic than Cr(VI). Cr(VI) has been demonstrated to have a number of adverse effects ranging from causing irritation to cancer.**

Effects in humans occupationally exposed to high levels of chromium or its compounds, primarily Cr(VI) by inhalation, may include irritating respiratory effects, possible circulatory effects, effects on stomach and blood, liver and kidney effects, and increased risk of death from lung cancer /RTI. 2000/.

Evidence from studies on experimental animals shows that Cr(VI), especially those of low solubility, can induce lung cancer. Trivalent chromium is not considered to be carcinogenic. There is, according to the IPCS monograph, insufficient evidence to implicate chromium as a causative agent of cancer in any organ other than the lung. Classification according to IARC is class 1 '*The agent (mixture) is carcinogenic to humans. The exposure circumstance entails exposures that are carcinogenic to humans*' (IARC 1990). Many chromium compounds are classified in the EU for their carcinogenic and mutagenic effects.

Both Cr(III) and Cr(VI), when injected at high levels parenterally in animals, shows effects on the embryo, with the hexavalent form accumulating in the embryos to a much greater extent than the trivalent. Effects on embryos from chromium exposure have not been reported for human subjects. Chromosome aberrations have been observed in some humans occupationally exposed to Cr(VI) compounds and other substances.

Exposure to Cr(VI) and Cr(III) compounds can be associated with allergic responses (e.g., asthma and dermatitis) in sensitised individuals. Chromium eczemas are often observed in the general population, due to exposure to chromium in products used in daily life. People who work with material containing mere traces of chromium salts are more at risk than workers who occasionally come into contact with high concentrations of chromium salts.

#### **2.4.2 Environment**

Hexavalent chromium is in general more toxic to organisms in the environment than the trivalent chromium. Almost all the hexavalent chromium in the environment is a result of human activities. In this oxidation state, chromium is relatively stable in air and pure water, but it is reduced to the trivalent state when it comes into contact with organic matter in biota, soil, and water.

Microorganisms	<p>Hexavalent chromium is toxic to microorganisms; a property utilised in chromium-based biocides. In general, toxicity for most microorganisms occurs in the range of 0.05 - 5 mg chromium/kg of medium. Trivalent chromium is less toxic than hexavalent. The main features are inhibition of growth and inhibition of various metabolic processes such as photosynthesis or protein synthesis. The toxicity of low levels of hexavalent chromium (1 mg/kg) indicates that soil microbial transformations, such as nitrification, may be affected.</p>
Other aquatic organisms	<p>Chromium can make fish more susceptible to infection; high concentrations can damage and/or accumulate in various fish tissues and in invertebrates such as snails and worms. Reproduction of the water flea <i>Daphnia</i> was affected by exposure to 0.01 mg hexavalent chromium/litre. Hexavalent chromium is accumulated by aquatic species by passive diffusion.</p> <p>In general, invertebrate species, such as polychaete worms, insects, and crustaceans are more sensitive to the toxic effects of chromium than vertebrates such as some fish. The lethal chromium level for several aquatic and terrestrial invertebrates has been reported to be 0.05 mg/litre.</p>
Other terrestrial organisms	<p>Although chromium is present in all plants, it has not been proved to be an essential element for plants. Several factors affect the availability of chromium for the plant, including the pH of the soil, interactions with other minerals or organic chelating compounds, and carbon dioxide and oxygen concentrations. Little chromium is translocated from the site of absorption; however, the chelated form is transported throughout the plant. Chromium in high concentrations can be toxic for plants, but a specific pattern of chromium intoxication has not been demonstrated. The main feature of chromium intoxication is chlorosis, which is similar to iron deficiency.</p>

### 3 Sources of heavy metals to waste

Heavy metals entering the technosphere will sooner or later be discharged to the environment or end up in waste. Heavy metals may end up in solid waste during all life cycle phases of the products as illustrated in the figure below. The term ‘the technosphere’ will be applied here, and should be considered equal to other terms like ‘the economy’, ‘the physical economy’ or ‘the Society’. The figure below shows the overall flows, in practice each step on the figure may consist of several minor steps. Steps related to treatment of waste water are e.g. not indicated on the figure.

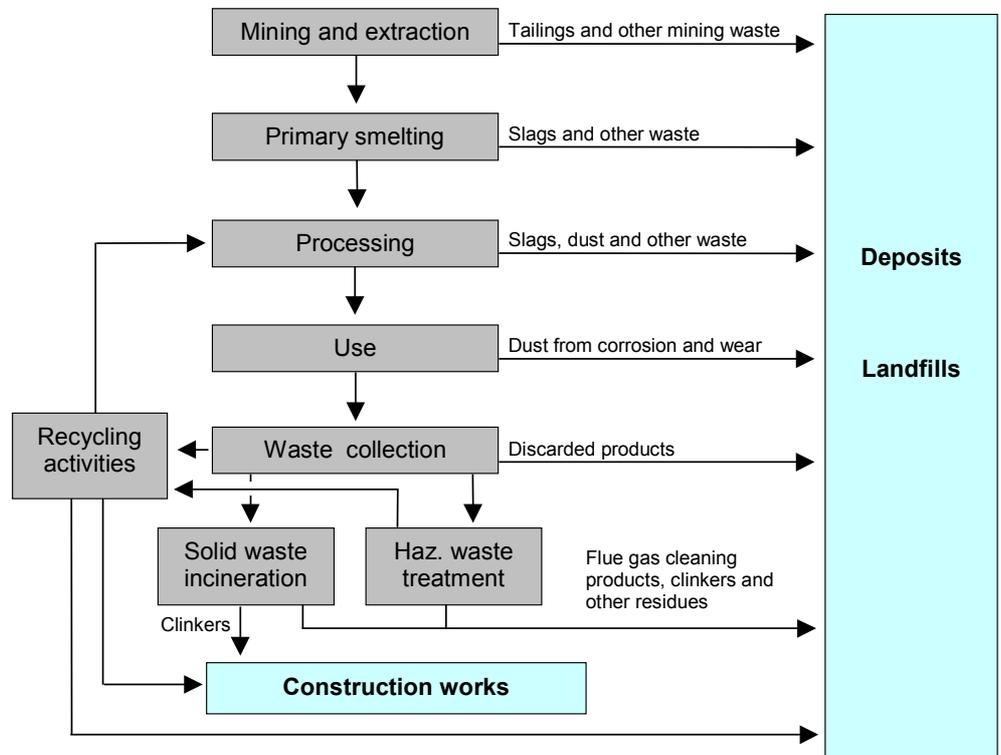


Figure 3.1 Schematic illustration of the overall flow of heavy metals to waste

Only few detailed analyses of the flow of the metals through the technosphere of the Member States are available for each heavy metal. It is thus difficult to give a uniform description for all heavy metals and make detailed comparisons between Member States. The selection of Member States for the examples presented has been determined by the availability of detailed analyses. In general, only very few studies regarding the turnover of heavy metals in Member States in Southern Europe have been available.

For most applications of heavy metals, the applications are estimated to be the same in all Member States, but the consumption pattern may be different. For some applications which during the last decade has been phased out in some Member States, there may, however, today be significant differences in uses. In such cases comparisons between studies not having the same year of reference will be difficult.

- Mining and extraction** By mining and extraction a part of the heavy metals will end up in tailings and other waste products. Waste from mining and processing is not specifically addressed in the present project. A significant part of the turn over of the four heavy metals with mining waste actually concerns the presence of the heavy metals in waste from extraction of other metals like zinc, copper and nickel. It should, however, be kept in mind that mining waste is generated independent of the subsequent application of the heavy metal.
- Primary smelting and processing** A minor part of the heavy metals will end up in waste from the further processing of the metals. Waste from these production processes has been briefly addressed to the extent studies were available.
- Use phase** A small part of the heavy metals may be lost from the products during use by corrosion and wear. The lost material may be discharged to the environment or end up in solid waste either as dust or indirectly via sewage sludge. Sources of discharges of the heavy metals to the environment and wastewater are not specifically addressed in this study.
- Disposal of discarded product** The main part of the heavy metals will still be present when the discarded products are disposed off. The heavy metals will either be collected for recycling or disposed of to municipal solid waste incinerators (MSWI) or landfills. A minor part will be disposed of as chemical waste and recycled or landfilled via chemical waste treatment.

Only very few and incomplete analyses exist of the content of heavy metals containing products in household waste and other complex waste fractions. The reason is that heavy metals are typically heterogeneously distributed in the waste and it is necessary to sort very large amounts of waste to get results of a satisfactorily statistical significance.

Based on the knowledge of the application of the heavy metals and disposal pattern of the heavy metal containing products, it is possible to point out which products may end up in solid waste. For the quantification of the sources, it is in addition necessary to have knowledge of the consumption of the heavy metals by application both today and in the past. It has only been possible to identify rather few studies from the Member States where the sources of heavy metals to solid waste is quantified on the basis of a comprehensive substance flow analyses (SFAs). The following chapter is based on these studies.

As many products containing heavy metal last for many years - especially those used for infrastructure and in the building sector - analyses of present days sources of heavy metals to waste may underestimate the contribution from these products. To the extent information is available, products for which the

waste volumes must be expected to increase significantly in the future is indicated.

- Waste treatment** The flow of the heavy metals by solid waste treatment is discussed further in Chapter 4.
- Recycling** Recycling both includes direct recycling of heavy metals and heavy metal containing alloys (e.g. brass or stainless steel) and heavy metals following other materials being recycled as steel or zinc. Recycling will be further discussed in Chapter 4.

### 3.1 Lead

- Global consumption** The global consumption of lead has during the period 1970 to 2000 increased from 4.5 million tonnes to 6.5 million tonnes /LDA 2001/. The consumption by end uses in the OECD countries in 1970, 1990, and 1998 is shown in Table 3.1.

As indicated significant changes in the overall use pattern include increased consumption for batteries and decrease in the areas of e.g. cable sheeting and petrol additives.

*Table 3.1 Lead consumption by end uses in OECD countries (derived from /OECD 1993; LDA 2001\*/. All figures in tonnes Pb/year*

Application	1970 (%)	1990 (%)	1998 * (%)
Batteries	39	63	75
Cable sheeting	12	5	1
Rolled/extruded lead (mainly sheets)	12	9	6
Ammunition	4	3	3
Alloys	7	4	3
Lead compounds	11	10	9
Petrol additives	10	2	1
Miscellaneous	5	4	2
Total OECD (tonne)	3,050	3,365	5,238 *
Total World (tonne)	4,502	5,627	6,018

\* Designated "Western World" in the reference; the consumption pattern is assumed to be identical to OECD countries.

The overall consumption pattern for metallic lead seems to be quite similar at least in the Northern Europe though there are some major differences in the use of lead sheets in the building industry. Due to tradition and the style of buildings, the consumption of lead sheets for building in for example Sweden /Hedemalm 1994/ is significantly lower than the OECD average whereas it is relatively high in Denmark /Lassen & Hansen 1996/ and the UK /Scoullon et al.

2001/. It has not been possible to obtain detailed information on lead consumption in Member States in Southern Europe.

For the main use of lead compounds, which are lead oxides for cathode ray tubes and crystal glass and stabilisers for PVC, only minor differences between Member States is expected. For minor uses, e.g. lead pigments there may be more significant differences as the use of these pigments to a large extent is phased out in some countries.

## Applications

In the aim of identifying sources of lead in waste, a more detailed list of applications with indication of anticipated main pathways for disposal of the discarded products is shown in Table 3.2. Similar tables are shown for the other heavy metals in the succeeding sections, and the following interpretation applies to all tables.

The disposal pattern may vary among countries and the indicated disposal pattern represents the authors' rough estimate on the typical disposal pattern. The number of '+' indicates the disposal pattern within each product group where +++ represents the major disposal pathway. The number of + does not give any indication of quantities between the groups.

The table distinguishes between four routes of disposal:

- Municipal solid waste incineration (MSWI) or landfilling on sanitary landfills.
- Recovery including recovery by processing of residues from metal reclamation. Products, which are collected as hazardous waste, but subsequently recovered, are indicated as recovered.
- Chemical waste disposal including disposal at landfills for hazardous waste and hazardous deposits e.g. in mines.
- Emission to the environment during use or direct losses to the environment by end of life of the products. Minor releases during use or losses by the end of life may occur for a significant part of the applications, but only applications where a substantially part of the products is disposed of by this route are indicated.

A part of the heavy metals disposed of to MSWI will end up in residues and may after incineration be disposed of as hazardous waste. It is in the table, however, still be indicated as disposed of to MSWI.

Similarly, all heavy metals will ultimately end up in the environment, but only products, for which emission to the environment during use or direct losses to the environment by end of life is a significant disposal pathway, have a + in the column 'Emitted or lost directly to the environment'.

Table 3.2 Applications of lead and disposal pathways for lead products

Product group	Comment	Disposal or recovery of discarded products			Emitted or lost directly to the environment
		MSWI or sanitary landfills	Recovery	Chemical waste disposal	
<b>Metallic uses</b>					
Batteries	Lead content of lead batteries is app. 55-60%	+	+++		
Cables sheeting	Today mostly used for cables in the ground or undersea, Significant amount of lead sheeted cables used both in the ground and in-door are still in service	+	++		+++ Left in the ground or sea-floor
Sheets for buildings	Lead sheets are used in building and construction industry mainly for flashing and weathering protection.	+	+++		+ Corrosion
Sheets for chemical industry	Lead sheet can be used for watertight linings for tanks and vessels		+++		
Leaded window frames	Extruded lead frames holding stained glass Also available as self-adhesive extruded lead tape	+++	+		
Solders for electronics	Solders for electronic typically contain 40 % lead, alloyed with tin	++	++ EEE waste		
Solders for other applications	Solders are used for many applications: plumbing, light bulbs, cans, etc. The lead content vary from 35% to 99%	++ Solders for light bulbs, cans etc.	+ With zinc and other metals. Recycled from filter dust		
Ammunition	Lead is used in shots, bullets and other types of ammunition	+ Shot in game. Shot and bullets used on shooting ranges	+ Shot and bullets used on shooting ranges		+++
Fittings, bearings etc. of lead alloys	Lead is used in brass, steel and aluminium to improve the machineability of the materials. Brass used for fittings, taps etc. contains typically 2-3% lead. Bronze for bearings often contain between 5 and 20% lead	+ Small parts + Slag from recycling processes	+++	+ Dust from manufacturing processes	
Zinc coating (hot galvanisation)	Zinc coating may contain a few percent lead.	+	+++ Recycled from filter dust		
Weights for fishing tools and anchors	Lead weights are used for small sinkers by anglers and for weights on fishing nets used for professional fishing	++	++		++
Balance weights for vehicles Plating of gasoline tanks	Lead weights for balancing of wheels	+	+++		+
Keels	Lead is used in keels for yachts		+++		

Product group	Comment	Disposal or recovery of discarded products			Emitted or lost directly to the environment
		MSWI or sanitary landfills	Recovery	Chemical waste disposal	
Lead tubes for drain and water pipes Lead joints for pipes	Lead is hardly used for lead pipes today, but significant amount of lead pipe work are still in service	+	++		
Radiation shielding	Used both in protective walls, aprons and foils for X-ray films	+ Aprons and foils	+++		
Other: Toys, curtains, candlesticks, foils, organ pipes etc.	Tin-lead alloys (pewter) containing 5-50% lead are used for miniatures (toy), candlesticks, tableware, organ pipes etc. Lead strings are used for curtains. Lead foil is used for decorative means,	+++	+ Relevant for organ pipes		
<b>Uses as chemical/mineral</b>					
Gasoline additives	Lead in gasoline additives is nearly 100% phased out in the EU				+++
PVC stabiliser	About 0.7-2% Pb as stabiliser in many types of rigid PVC for out-door use	+++	+		
Pigments in plastic	Lead chromate for yellow and red colours contains 64% lead	+++			
Pigments in paint and ceramics	Lead chromate for yellow and red colours contains 64% lead Lead carbonate previously used for white colours	+++		+	
Siccative in paint	Lead naphthenate in concentrations of 0.5-2% used as siccative in alkyd-paint	+++			
Rust-inhibitive primers; miniate	Red lead (Pb <sub>3</sub> O <sub>4</sub> ) used in some rust-inhibitive primers used e.g. for maintenance of old iron-constructions	+ Slag from steel reclamation	+++ Recycled from filter dust from steel reclamation	+	+
Lubricants	Lead naphthenate may be used as a lubricant	?			
Cathode ray tubes	The neck and funnel of cathode ray tubes contains about 25% lead whereas the faceplate contains 2-3% lead in the form of lead silicates	++	++ EEE waste		
Other applications of lead crystal glass	Crystal glass contains 24-36% lead oxide, PbO, semicrystal glass contains 14-24% PbO Lead silicate glass is used in fluorescent tubes and light bulbs	+++			
Glazing	Lead silicate (PbSiO <sub>3</sub> ) used for glazing in tableware and	+++			

Note: The number of + indicates the disposal pattern within each product group and does not give any indication of quantities among the groups.

\* Only applications where a substantially part of the products are emitted is indicated.

## Sources of lead to waste, the Netherlands

The contribution of the basic metal industry and the lead recycling industry to the total amount of lead in solid waste is apparent from the assessment of sources of lead to landfills in the Netherlands (Table 3.3). The table is based on a comprehensive analysis of the flow of a number of heavy metals through the Dutch technosphere /Annema et al. 1995/. The analysis of the lead flow shows that the main sources of lead to landfills in 1990 were basic metal industry, household waste and building waste. Of the total turnover of about 80,000 tonnes lead, 9,400 tonnes was accumulated in the technosphere and 12,400 was accumulated in landfills and residues used for construction work or discharged to the environment. The origin of the lead disposed of from the basic metal industry was lead in 210,000 tonnes zinc ore imported for primary production on zinc. The analysis does not provide a detailed assessment of the sources of lead to large household waste.

Table 3.3 Sources of lead to landfills in the Netherlands 1990 (derived from /Annema et al. 1995/)

Source	Tonnes Pb/year	%
Basic metal industry	6,368	63
Secondary lead industry	234	2.3
Lead chemicals industry	65	0.6
Food industry	5	0.05
Sewage sludge	67	0.7
Large household waste	2,323	23
MSW residues *	577	6
Transport	151	1.5
Building waste	272	2.7
Dredged sediment	105	1.0
Total	10,167	100

\* In addition, 746 tonne lead followed the residues used for road construction work and 21 tonnes was emitted to the air. In total, the waste disposed of to MSWI contained must have contained some 1,300 tonnes lead.

## Sources of lead to waste, Denmark

A detailed assessment of the sources of lead to solid waste in Denmark is shown in Table 3.4. The table shows by application the consumption volumes and estimated direct sources of lead to MSWI and landfills. In addition, residues from other waste treatment processes are shown. The sources of lead for these other treatment processes are indicated in the table notes. It should be noted that lead and lead containing copper alloys are exported for recycling abroad and the waste generated by the recycling process consequently not included in the assessment. It is noted that Denmark does not have any primary metal industry and only hosts relatively few large metal-processing industries.

Use of lead chemicals accounted for more than 40% of the total input to MSWI or landfills even though these uses only accounted for 8% of the total consumption. At that time, the recycling of PVC, cathode ray tubes and electronic products was insignificant. It should be noted that recycling of cathode ray tubes and lead solder with electronics has increased in recent years.

Table 3.4 *Lead consumption by application area and sources of lead to solid waste in Denmark 1994 (Derived from /Lassen and Hansen 1996/)*

Application area	Consumption		Total to MSWI or landfill	
	tonnes Pb/year	% of total	tonnes Pb/year	% of total
<b>Metal</b>				
Batteries	8,100-8,900	48	<100	2
Flashing and sheets	2,600-3,700	18	50-200	5
Cable sheets	2,000-2,300	12	6-23	0.6
Fishing tools (sinkers)	375-725	3.6	230-300	11
Ammunition	350-460	2.7	10-15	0.5
Roofs	250-400	2	-	-
Solders	260-380	2	120-210	7
Other alloys	150-300	1.3	-	-
Balancing weights	200-250	1.3	-	-
Keels	50-150	0.6	-	-
Seals	5	<0.1	5	0.1
Lead foil for flower decorations and toys (miniatures)	5.5-12	<0.1	5.5-12	0.4
Curtains, wine bottle foils, and other products of metallic lead	80-270	1.0	10-100	2
<b>Chemicals/minerals</b>				
Cathode ray tubes (lead glass)	550-900	4	450-750	25
Ceramics (glazing)	25-150	0.5	25-150	4
Glass others than cathode ray tubes	70-80	0.4	50-100	3
Pigments in paint and plastic	35-110	0.4	150-250	8
Stabilisers in PVC	300-400	2	30-100	3
Gasoline additives	2-10	<0.1	-	-
Other chemicals	12-40	0.2	-	-
<b>Trace element and contaminant</b>	40-80 * <sup>1</sup>	0.3	2-14 * <sup>2</sup>	0.3
Waste from cable reclamation			10-13	0.5
Shredder fluff * <sup>2</sup>			200-1,000	25
Residues from steel reclamation * <sup>3</sup>			45	2
Sewage sludge * <sup>4</sup>			3	0.1
Residues from chemical waste treatment * <sup>5</sup>			97	2
<b>Total (round)</b>	<b>15,000-20,000</b>	<b>100</b>	<b>1,500-3,500</b>	<b>100</b>

Notes: Percentages based on averages

- \*<sup>1</sup> Exclusive lead as trace element in fuels and residues from power production
- \*<sup>2</sup> The sources of lead in shredder fluff were accumulators, balance weights, solders, pigments, PVC, lead linings, etc.
- \*<sup>3</sup> The sources of lead following steel scrap are rust-inhibitive primers, pigments and siccatives, zinc coatings, etc.
- \*<sup>4</sup> The main sources of lead to waste water were corrosion from sheets and roofs and atmospheric deposition.
- \*<sup>5</sup> The sources of lead in chemical waste were pigments, waste oils (gasoline additives) and waste from foundries and other metal processing industries.

The recycling of PVC has also increased, but still only a minor part of the lead-containing PVC is recycled in Denmark. The disposal of lead with PVC was much lower than the consumption due to the fact that PVC at present is accumulating in the technosphere. The waste amounts must be expected to increase in the coming years.

Of the metallic uses, fishing tools contributes significantly to the total. This source must be expected to be of less significance in many Member States. Lead batteries were estimated to be a minor source because of a very high recycling rate. It may, however, account for a significant part of lead in shredder fluff although the batteries have to be removed before shredding. In other Member States this source will be of higher significance as e.g. the recycling rates has been reported to be down to 75% in Portugal (1997) and about 90% in the UK /Scoullos et al. 2001/.

Table 3.5. *Inflow and accumulation of lead in Stockholm 1995 /Sörme et al., in press/\**

Goods	Accumulated 1995		Inflow 1995	
	tonnes Pb	%	tonnes Pb/year	%
Power cables	22,000	42.1	2.4	<1
Tube and pipe joints	9,400	18.3	0	0
Tele cables	8,900	17.1	0	0
Batteries	7,800	14.9	1,300	84
Keels	1,100	2.1	10	<1
Crystal glass	970	1.9	60	3.9
Chimney collars	630	1.2	10	<1
PVC; cables pipes and floors	590	1.1	46	1.5
Cathode ray tubes	440	<1	80	5.2
Radiation protection, hospitals	220	<1	0	0
Balance weights	30	<1	24	1.6
Miniature steel bridges	28	<1	1.4	<1
Light bulbs/fluorescent tubes	29	<1	13	<1
Printed circuit boards (solders)	20	<1	2	<1
Wood preservative, 'Falu-Red'	4	<1	1	<1
Petrol	0	0	0.14	<1
Sinkers, sports fishing	0	0	5	<1
Ammunition	0	0	6	<1
<b>Total</b>	<b>52,000</b>	<b>100</b>	<b>1,600</b>	

\* Reference is made to the most recent paper where some of the figures have been revised in comparison to the original report.

Accumulation in the technosphere, Sweden

Lead has been used for many years and a very significant amount is today accumulated in the technosphere. Even when applications are phased out, waste of lead products may be generated for many years to come from this pool.

The most comprehensive study on the accumulation on heavy metals in the technosphere has been carried out with Stockholm (0.7 million inh.) as study object /Lohm et. al 1997; Sörme et al., in press/. About 52,000 tonnes lead are estimated accumulated in the Stockholm technosphere corresponding to about 30 times the actual annual inflow (consumption) as shown in Table 3.5. Unfortunately, the outflow from the pool to waste is in the study not quantified by application area. The assessment demonstrates the large pool of lead accumulated in the infrastructures as cables and pipes.

### 3.2 Mercury

#### Global consumption

The global mercury demand decreased over the period 1990 to 1996 by 2,019 tonnes from 5,356 tonnes to 3,337 tonnes /Sznoppek & Goonan 2000/. Of the 3,337 tonnes, 1,344 tonnes was used in the chlor-alkali industry, 100 tonnes was used for gold extraction, 1,061 tonnes ended up in products and 832 tonnes was added to stocks. It should be noted that the uncertainty on the total consumption volumes is higher than indicated by the accuracy of these figures.

The amount ending up in products decreased over the 6-years period from 1,818 tonnes to 1,061 tonnes. A detailed assessment of the Global or European consumption of mercury by application area does not exist.

It is difficult to give an updated picture of the mercury consumption because the consumption pattern in many countries has changes significantly the recent years.

The most recent assessments of the use of mercury by application area are from the Nordic Countries where mercury during the last decade has been phased out for most applications.

#### Change in mercury consumption 1982/83 to 2000, Denmark

The changes in mercury consumption in Denmark from 1982 to 2001 are shown in Table 3.6. The assessment for 2001, which is based on quite rough estimates, shows that dental amalgam account for the main part of the intentional mercury consumption, and that mercury is still present in light sources, measuring and control equipment and laboratory chemicals. The unintentional turnover of mercury as natural contaminant in fuels, cement, etc. exceeded in 2001 the intentional uses of mercury.

#### Change in mercury consumption, Sweden

The same changes in consumption pattern has been seen in Sweden where the consumption of mercury exclusive the use in the chlorine-alkali industry decreased from 9 tonnes per year in 1991/1992 to about 2 tonnes in 1997 (Table 3.7). The main application areas in 1997 were dental amalgams and batteries, which counted for about 80% of the total consumption.

Table 3.6 *Changes in annual consumption of mercury in Denmark (derived from /Hansen 1985; Maag et al. 1996; Maag et al 2001a/)*

Application	Consumption (tonnes Hg/year)		
	1982/83	1992/93	2001 *
Chlor-alkali production	3.00	2.50	0
Dental amalgam	3.10	1.80	0.90
Mercury-oxide batteries	2.40	0.36	0
Other batteries	2.30	0.28	0
Electric and electronic switches	0.34	0.30	0
Light sources	0.14	0.17	0.17
Medical thermometers	0.75	0.05	0
Other thermometers	1.55	0.10	0
Other measuring and control equipment	0.53	0.50	0.3
Laboratory chemicals	0.50	0.09	0.09
Other intended uses	1.48	0.03	0.03
<b>Sub-total, intentional uses</b>	<b>16.09</b>	<b>6.18</b>	<b>1.5</b>
Impurities in consumed fuels, minerals and bulk materials (non-intended mobilisation)	1.96	1.80	1.8
<b>Total *4</b>	<b>18.05</b>	<b>7.98</b>	<b>3.3</b>

Note: Only average figures are presented. The 2001 figures are based on rough estimates.

Table 3.7 *Changes in the consumption of mercury in Sweden 1991/92 to 1997, exclusive mercury for chlorine-alkali production (derived from /KEMI 1998/)*

Application	1991/92		1997	
	tonnes Hg/year	%	tonnes Hg/year	%
Dental amalgam	1.7	19	1.0	45
Batteries	2.3	26	0.8	36
Switches, measuring and control equipment	4.5	51	0.2	9
Light sources (lamps)	0.3	3	0.15	7
<b>Total</b>	<b>8.8</b>		<b>2.2</b>	

These changes may, however, not be general for all Member States, as the changes in consumption pattern in the Nordic Countries has been driven by more strict regulation than in most other countries.

Change in mercury consumption, the U.S.A.

The most comprehensive studies on the mercury flow with changes over time have been carried out in the U.S.A. Although at the other side of the Atlantic, the changes of consumption among industrial sectors in the U.S.A. still gives an indication of the overall changes. From 1990 to 1996, the total consumption decreased about 50% including a total phase-out of mercury in paint and bat-

teries. The assessment demonstrates contrary to the reported changes in Denmark and Sweden, that switches and measurement and control devices in 1996 still accounted for a very significant part of the total consumption.

Table 3.8 *Reported consumption of mercury in the USA in 1990 and 1996 (derived from Sznopce and Goonan 2000).*

Application	1990		1996	
	tonnes Hg/year	%	tonnes Hg/year	%
Chlorine-alkali production	247	35	136	37
Dental amalgams	44	6	31	8
Laboratory analyses	32	5	20	5
Measurement and control devices	108	15	41	11
Wiring devices and switches	70	10	49	13
Electric lighting	33	5	11	3
Paint (fungicides)	14	2	0	0
Batteries	105	15	0	0
Other	58	8	84	23
<b>Total</b>	<b>711</b>		<b>372</b>	

Note: 'Reported consumption' refers according to the authors to collected data from surveyed respondents and represents the mercury metal purchased from producers by non-producers. Imports and exports of mercury incorporated in products were not included in the assessment. Except for the wiring devices and switches sector, which may be of some importance to the actual materials balance, the authors of the reports estimate that imports and exports are approximately equivalent or negligible.

Applications of mercury

Applications of mercury with indication of the anticipated disposal pathway for discarded products are shown in Table 3.9. Reference is made to section 3.1 and Table 3.2 for further explanation.

Table 3.9 *Applications of mercury and disposal pathways for mercury products*

Product group	Comment	Disposal or recovery of discarded products			Emitted or lost directly to the environment *
		MSWI or sanitary landfills	Recovery	Chemical waste disposal	
<b>Metallic uses</b>					
Chlor-alkali industry	Mercury used as electrode in the production of chlorine and alkali		+	+	
Dental amalgams	Mercury accounts for 44-51% by weight of dental amalgams	++ Lost teeth	++ Dental waste	+ Dental waste and lost teeth	++ By burial or cremation
Thermometers	Mercury used as expanding liquid	+++		+	+
Tilt switches and wiring devices	Mercury used as conductive liquid in tilt switches of water pumps, cars, flashlight, etc.	++ residues from recycling activities	+	+	

Product group	Comment	Disposal or recovery of discarded products			Emitted or lost directly to the environment *
		MSWI or sanitary landfills	Recovery	Chemical waste disposal	
Manometers, relays, measuring devices and control equipment	Mercury used as conductive or expanding liquid Electrochemical properties used in i.a. calomel electrodes	++	++	+	
Gold mining	Gold can be dissolved in mercury Not relevant in EU Member states				+++
<b>Use as chemical/vapour</b>					
Batteries, button cells	The mercury content of mercury oxide button cells is about 30% whereas silver oxide cells may contain up to 1% mercury	++	+	++	
Other batteries	Alkaline batteries have formerly contained mercury, but alkaline batteries are today "mercury free" in OECD countries	+++		+	
Paints	Mercury has formerly been used as pigment in paint, The use today in the EU is assumed to be insignificant	+++			
Fluorescent tubes and bulbs High-voltage discharge lamps	Mercury vapour emits light when charged	++	+	+	+ When tubes or lamps are broken
Laboratory chemicals	A number of compounds, e.g. mercury sulphate, mercury oxide, mercury nitrate are used as laboratory chemical			+++	
Pesticides and biocides	Formerly widely used as biocide and pesticide. The use today in the EU is assumed to be insignificant				+++

Note: the number of + indicates the disposal pattern within each product group and does not give any indication of quantities among the groups. For more details: see the body-text just before Table 3.2.

\* Only applications where a substantially part of the products are emitted is indicated.

#### Accumulation in the technosphere, the U.S.A

The studies from the U.S.A. also give a very detailed view of the accumulation of mercury in the technosphere and outflow to MSWI and landfill (reference is made to Table 3.10). The assessment demonstrates large stocks of mercury in measurement and control devices, switches, etc. from which the mercury over a long period of time will be disposed of to MSWI and landfills. The assessment does not include waste from production processes as the waste generation is reported together with the direct emission to the environment.

#### Accumulation in the technosphere, Sweden

In the assessment of the flow of heavy metals in Stockholm described in the previous section, the pool of wiring devices and switches is estimated to be insignificant, which reflects that the use of mercury for wiring by tradition has been less used in Sweden. In 1995 dental amalgams in the teeth of the popula-

tion accounted for the major part of mercury accumulated in Stockholm (reference is made to Table 3.11).

Table 3.10 *Reported consumption, stocks and disposal of mercury in the USA 1996. All figures in tonnes Hg/ year (Sznoppek and Goonan 2000)*

Application	Inflow, consumption	Stocks		Outflow, disposal	
			%	Secondary production	MSWI, land or landfill
Chlorine-alkali production	136	3,050	44.9	7	18
Dental amalgams	31	236	3.5	46	5
Laboratory analyses	20	66	1.0	26	3
Measurement and control devices	41	331	4.9	54	54
Wiring devices and switches	49	2,670	39.3	16	16
Electric lighting	11	64	0.9	3	20
Batteries	0	32	0.5	2	16
Other	84	349	5.1	11	101
Unaccounted, unknown	?	?	?	282	114
<b>Total</b>	<b>372</b>	<b>6,800</b>		<b>446</b>	<b>358</b>

Table 3.11 *Inflow and accumulation of mercury in Stockholm 1995 (Sörme et al., in press)*

Goods	Accumulated 1995		Inflow 1995	
	tonnes Hg	%	tonnes Hg/year	%
Dental amalgams	4.9	72	0.23	49
Electric equipment, instruments	1.0	15	0.003	<1
Thermometers, fever	0.40	5.5	0	0
HgO- batteries	0.33	4.8	0.2	44
Thermometers, others	0.25	2.2	0	0
Fluorescent tubes	0.07	1	0.03	6.6
<b>Total</b>	<b>6.8</b>	<b>100</b>	<b>0.46</b>	

#### Sources of mercury to waste, France

An assessment of sources of mercury to waste in France in 1993 (Table 3.12) demonstrated that zinc and lead metallurgy, thermometers, dental amalgams, and batteries were the main sources /Groupe de travail de l'AGHTM 1999/. The study does not include a detailed assessment of the consumption of mercury in France and it is consequently not possible to compare the consumption and disposal patterns. The assessment does among other sources not include switches and wiring devices. In 1993, only a minor part of the mercury-containing waste in France was recycled. The recycling may, however, have increased during the last years.

Table 3.12 Sources of mercury to waste in France 1993 (except the chlorine-alkali industry) /Groupe de travail de l'AGHTM 1999/\*

Source	Waste (tonnes Hg/year)	%	Of which is recycled (tonnes Hg/year)
Zinc and lead metallurgy	18	40	0.86
Thermometers	9	20	0.5
Dental amalgams	9	20	1.3
Batteries	6.8	15	0.5
Laboratory analyses	0.9	2.0	0
Fluorescent tubes	0.8	1.8	0.1
Barometers	0.4	0.9	0.04
High-voltage discharge lamps	0.2	0.4	0.02
<b>Total</b>	<b>45</b>	<b>100</b>	<b>2.8</b>

The assessment is stated not to include the following sources: electric contacts, old paint, explosives and fireworks, mirrors, gold washing and wastes from polluted industrial sites including mercury accumulated in metal and concrete structures. It is estimated that the 'diffuse' flow of mercury disposed of from stocks at laboratories and other professional users represents a few tonnes per year.

Sources of mercury to waste, the Netherlands

Mercury is present as impurity in zinc-ore and the assessment of the sources of mercury to landfills in the Netherlands, demonstrates that production of zinc accounted for about 70% of the mercury disposed of to landfills.

Table 3.13 Sources of mercury to landfills in the Netherlands 1990 (derived from /Annema et al. 1995/

	Tonnes Hg/year	%
Primary zinc production	17	70
Basic metal industry	0.8	3.3
Chlorine-alkali industry	0.004	0.02
Lamp production	0.7	2.9
Petrochemical and other industry	0.13	0.5
Other industry	0.31	1.3
Large household waste	2.3	9.4
Power plants	0.11	0.5
Dentists (amalgam)	0.25	1.0
Hospitals and laboratories	0.6	2.5
Sewage sludge	0.6	2.5
MSW residues *	0.14	0.6
Dredged sediment	1.5	6.1
<b>Total</b>	<b>25</b>	<b>100</b>

\* In addition, 0.2 tonne mercury followed the residues used for road construction work and 1.5 tonnes was emitted to air from MSWIs.

### 3.3 Cadmium

#### Global consumption

The general trend in the global cadmium consumption the last two decades has been a steep increase in the use of cadmium for batteries and a decrease in the use for other applications. Batteries accounted in 1990 for 55% of the total Western World consumption and for about 73% of the estimated EU consumption in 2000 (Table 3.14). Although the use of cadmium for pigments, PVC stabilisers and plating in some countries by the large has been phased out, these applications at the EU level still account for a significant part of the total cadmium consumption in 2000.

Table 3.14 Cadmium consumption by end-uses in Western World 1990 (derived from /OECD 1993/) and the EU about 2000 (derived from /Scoullos et al 2001/)

Application	Western World 1990 * <sup>1</sup>		EU about 2000 * <sup>2</sup>	
	tonnes Cd/year	%	tonnes Cd/year	%
Ni-Cd batteries	9,100	55	1,900	73
Pigments	3,300	20	300-350	12
Stabilisers	1,650	10	150	6
Plating	1,320	8	200	8
Alloys	500	3	30-40	1
Other	660	4	-	-
Total	16,500	100	1,930-1,990	100

\*<sup>1</sup> The figures in tonnes is calculated from the distribution represented in percentages in the reference.

\*<sup>2</sup> The figures for consumption are derived from a diagram showing the Cd flows in EU. The flow diagram is indicated as a preliminary draft. The report text states that Ni-Cd batteries account for 78% of the total consumption of end products. The consumption is here calculated from the flow diagrams indication of consumption, import and export of cadmium with batteries.

#### Consumption by application area, Greece

Substance flow analyses from Member States in Southern Europe are rare, but for cadmium, the total consumption in 1993 and 1997 in Greece has been assessed by /Scoullos and Karavoltos 2001/. Reference is made to Table 3.15.

The total cadmium consumption increased from 27 in 1993 to 66 tonnes in 1997 due to increased consumption of Ni-Cd batteries. The share of the Ni-Cd batteries to the total consumption increased from 71% to more than 90%. The share of pigments and stabilisers decreased accordingly, but in terms of tonnes the consumption of PVC stabilisers was at the same level whereas the consumption with pigments was halved.

#### Denmark

In a study of the cadmium flow in Denmark 1996, the batteries accounted for more than 90% of the total intentional consumption, while pigments and stabilisers in imported products was estimated to account for a few percent /Drivsholm et al 2000/. The Danish study in addition pointed at a possible significant consumption of cadmium with silver jewellery.

#### Germany

The consumption pattern of cadmium in Germany 1994 by the large followed the general pattern for the Western World /Balzer & Rauhaut 1996/. In the

German study, it was in addition specified that the use of cadmium for colouring of glass accounted for about 2% of the total cadmium consumption.

Table 3.15 *Cadmium consumption in Greece 1993 and 1997 (derived from /Scollos and Karavoltso 2001/).*

Application	1993		1997	
	Tonnes Cd/year	%	Tonnes Cd/year	%
Ni-Cd batteries	27	71	66	92
Pigments	8.6	22.5	3.9	5.4
PVC stabilisers	1.2	3.2	1.2	1.7
Plating	1.2	3.2	0.2	0.3
Alloys	-	-	-	-
Total	38	100	71.5	100

\* The figures have been derived from the diagrams of cadmium consumption and the total volume indicated in the discussion chapter.

#### Cadmium as impurity

All heavy metals are present as trace element in fossil fuels, mineral raw materials, food, etc. and there will be an unintentional turn over of the heavy metals with all nearly all products. Beside the intentional use of cadmium, the turnover of cadmium as impurity in zinc and fertilisers has been substantial and has attracted much attention. The turnover with zinc and fertilisers has decreased significantly by refining and changes in raw materials, and will not be discussed further.

#### Accumulation in the technosphere, Sweden

Even in countries where the consumption of cadmium with pigments and stabilisers has decreased there may still be a large pool of cadmium accumulated in the technosphere with these products as demonstrated in the Stockholm study (Table 3.16). Pigments and stabilisers in 1995 accounted for one third of the cadmium accumulated in the technosphere.

Table 3.16 *Inflow and accumulation of cadmium in Stockholm 1995 /Lohm et al. 1997/*

Goods	Accumulated 1995		Inflow 1995	
	tonnes Cd	%	tonnes Cd/year	%
Stabilisers, plastics	30	25	0.16	1.8
Batteries – closed	30	25	6.4	73
Impurities in zinc	20	17	?	?
Batteries – open	16	13	1.6	18
Pigments, plastics	10	8.4	0.08	<1
Surface plating	10	8.4	0.16	1.8
Alloys	3	2.5	0.4	4.5
Total	120		8.8	

\* Only average figures are shown.

## Applications of cadmium

Applications of cadmium with indication of the anticipated disposal pathway for discarded products are shown in Table 3.17. Reference is made to section 3.1 and Table 3.2 for further explanation. Ni-Cd batteries, stabilisers and pigments should be considered obvious candidates to be the main sources of cadmium to waste, when discarded products are considered.

Table 3.17 Application of cadmium and disposal pathways for cadmium products

Product group	Comment	Disposal or recovery of discarded products			Emitted or lost directly to the environment *
		MSWI or sanitary landfills	Recovery	Chemical waste disposal	
<b>Metallic uses</b>					
Plating and coating	Plating and coating on iron, steel, aluminium and brass Used mainly in electrical, electronic automobile and aerospace industry	+++ Residues from metal reclamation	+ With metals Recycled from filter dust		
Silver-cadmium alloys	Silver jewellery often contains small amount of cadmium. Some silver jewellery may contain up to 30% Cd.	++	++		
Copper-cadmium alloys, solders and other alloys	Copper with 0.6-1.2% cadmium used for wires for railway traction Cd containing solders are used for soldering aluminium (40% Cd in solder) and steel Cadmium is used on some bearing alloys and fusible alloys	+ Minor parts + Residues from metal reclamation	+ With metals Recycled from filter dust		
<b>Use as chemical/mineral</b>					
Ni-Cd batteries	Sealed cells (closed batteries) are used for electronics and vehicles Vented cells (open batteries) are mainly used for power backup	++	++	+	
PVC stabiliser	About 0.7-2% Cd as stabiliser in many types of rigid PVC for out-door use	+++	+		
Pigments	Pigments are used in plastic (main use), ceramics, glass and paint	+++	+ Transport		
Photovoltaic cells	Cadmium telluride and cadmium sulfide are used in some types of photovoltaic cells	?			

Note: The number of + indicates the disposal pattern within each product group and does not give any indication of quantities among the groups. For more details: see the body-text just before Table 3.2.

- Only applications where a substantially part of the products are emitted is indicated.

## Sources of cadmium to waste, EU level

At the EU level, industrial sources are estimated to account for about 60% of the total sources of cadmium to landfills (Table 3.18). Around half of this contribution is associated with the intentional use of cadmium e.g. cadmium processing, iron and steel processing (cadmium in scrap) and a small part of the non-ferrous metals processing (cadmium alloys).

Cadmium in discarded products disposed off with municipal solid waste and mixed waste fractions is estimated to account for some 40% in total. Of these the main part was disposed of directly to landfills reflecting the overall treatment of municipal waste in the EU (1995 figures are used in the study).

Table 3.18 Sources of cadmium to waste disposal in the EU about 2000\*<sup>1</sup> (derived from /Scoullas et al 2001/)

	Tonnes /year * <sup>2</sup>	% of total
Cadmium processing	400 (approx.)	16
Coal ash	113	4
Sewage sludge	70	3
Phosphate processing	60	2
Iron and steel processing	230	9
Cement production	280	11
Non-ferrous metals processing	419	17
<b>Total industrial sources</b>	<b>1,572</b>	<b>62</b>
Municipal waste or mixed, direct input to landfills	800	32
MSWI ashes	150	6
<b>Total municipal waste or mixed</b>	<b>950</b>	<b>38</b>
	2,522	

\*1 The table text in the report designate the geographic area "Europe", but the figures refers according to the report text only to the EU.

\*2 Only average values are indicated. The report contains uncertainty ranges for only a few of the sources, indicating the total figures to be more precise than judged by the authors of this report.

### 3.4 Chromium

#### Global consumption

Chromium is extracted from chromite ore. World mine production of chromite has increased from 13.0 million tonnes ore in 1990 to 13.7 million tonnes in 2000 /Papp 1994, USGS 2001/. In terms of chromium, the mine production increased from 3.9 to about 4.1 million tonnes chromium. The consumption of chromium has been less studied than the other heavy metals covered by this project, and it has not been possible to identify detailed analyses of the changes in chromium consumption by application areas from the Member States.

#### Chromium metal

In 1998, production of chromium alloys from ferrochromium accounted for about 85% of the global chromite consumption /Roskill 2000/. Stainless steel accounted for the main part of the consumption of ferrochromium. The World production of stainless steel in 1998 is estimated at about 16.4 million tonnes, containing about 2.9 million tonnes of chromium. Of these 42% originated from recycled scrap. A variety of alloys contain chromium including iron, cobalt, copper, nickel and titanium alloys /Papp 1994/. In terms of volumes, the steel alloys (beside stainless steel) are of most significance. Foundry applications accounted for around 5% of the chromite consumption.

**Refractories** Chromite-containing refractories are used to line furnaces and kilns for production of copper, nickel, cement and glass /Papp 1994/. The refractories accounted in 1998 for 2% of the global chromite consumption /Roskill 2000/. The chromite refractories do not enter into the final products.

**Chemicals** Chromium chemicals accounted for 8% of the global chromite consumption (Roskill 2000) corresponding to some 300,000 tonnes chromium per year. The use of chromium compounds has attracted most attention, as some of these are very toxic dependent on the oxidation state of the metal (see section 2.4). Chromium can display a number of oxidation states, but compounds with trivalent chromium, Cr(III), and hexavalent chromium, Cr(VI), are the most significant by an economic perspective. The distinction between the oxidative states is, however, complicated by the fact that the chromium may be oxidised during the application. Cr(VI) may e.g. be transformed to Cr(III).

There is an intensive production of chromium compounds in Europe and Europe is net exporter of chromium compounds. The total use of chromium (VI) compounds in the EU is estimated at 17,000 tonnes of chromium trioxide and 25,000 of dichromates (as sodium dichromate dihydrate) /EU 2000/.

**Consumption of chromium compounds, Sweden** An indication of the use of chromium compounds by application area can be obtained from an assessment of chromium use in Sweden (Table 3.19). It is noted in the assessment that the registered consumption of chromium compounds for tanning is far below the net import of chromium with leather products estimated at 150-200 tonnes Cr/year. The inflow of chromium to Stockholm 1995 (Table 3.21) shows that stainless steel is estimated to account for some 87% of the inflow, whereas preserved wood and pigments each account for around 3% of the total and chromium plated products and leather products each account for about 2%. It seems, however, that the study is missing the use of chromium in other steel alloys than stainless steel.

*Table 3.19 Major applications of chromium registered in the Swedish Product Register and the pesticide division of KemI 1992 /Palm et al. 1995/*

Application	Registered consumption tonnes Cr
Leather tanning	13-43
Metal plating	29-46
Metal surface treatment	28-52
Raw materials for synthesis	116
Colours and pigments	74-109
Wood preservatives	608
Total (major uses)	868-974

**Applications** The applications of chromium with indication of anticipated disposal pattern are listed in the following Table 3.20. Reference is made to section 3.1 and Table 3.2 for further explanation.

Table 3.20 Application of chromium and disposal pathways for chromium products

Product group	Comment	Disposal or recovery of discarded products			Emitted or lost directly to the environment *
		MSWI or sanitary landfills	Recovery	Chemical waste disposal	
<b>Metallic uses</b>					
Stainless steel	Average Cr content of stainless steel is about 17%	+ Kitchen ware and other small items	+++		
Other alloys	Chromium is used in a variety of alloys - often at a content of less than 1%	+ small items	+++		
Plating	Chromium is used in layers of approximately 0.2-1.2 µm for decorative coating on steel, coppers alloys and plastics  Chromium is used in layers of 2.5-500 µm for hard chromium plating of steel  Chromium compounds are used for the plating, but the finished products contain chromium as metal	+ Peels, dust, plastics  + May end up in filter dust and slag from secondary metal production	+		
<b>Use as chemical/mineral</b>					
Colours and pigments	Various chromium compounds used - both Cr(III) and Cr(VI)  Used for plastics, ceramics, corrosion inhibition	+++		+	
Textile dyes	Various chromium compounds used - both Cr(III) and Cr(VI)	+++		+	
Leather tanning	Various chromium compounds used - both Cr(III) and Cr(VI)	+++		+	
Wood preservatives	Cr(VI) is used for preservatives	++		(+)	+
Metal surface treatment	Chemicals do not end in the finished products			+	
Refractories	Lining furnaces and kilns for production of copper, nickel, cement and glass	+++			
Laboratory chemicals	Many different chemicals			++	
Catalysts	Are typically returned to the manufacturer for regeneration and from here to recovery.		+		

Note: The number of + indicates the disposal pattern within each product group and does not give any indication of quantities among the groups. For more details: see the body-text just before Table 3.2.

\* Only applications where a substantially part of the products are emitted is indicated.

### Consumption and accumulation, Sweden

The inflow to and accumulation in the technosphere of Stockholm demonstrate that stainless counted for 87% of the inflow and 81% of accumulated chromium in 1995. The assessment also includes the unintentional use in concrete and the stainless steel thus represents a higher percentage of the intentional consumption. It seems, however, that chromium in other alloys is missing in the assessment. Products containing stainless steel should be assumed generally to have a long life, and chromium chemicals may account for a larger part of the chromium that are disposed of today.

*Table 3.21 Inflow and accumulation of chromium in Stockholm 1995 /Sörme et al. in press/*

Goods	Accumulated 1995		Inflow 1995	
	tonnes Cr	%	tonnes Cr/year	%
Stainless steel	4,500	81	310	87
Impregnated wood	520	9.3	13	3.6
Concrete **	230	4.1	5	1.4
Leather furniture and shoes	120	2.2	6	1.7
Chromium plated products	76	1.4	6	1.7
Paints and pigments	73	1.3	7	2.8
Vehicles, cars, exhaust	50	<1	10	2
<b>Total</b>	<b>5,600</b>		<b>360</b>	

\* Only average figures are shown. The total is estimated at 3,000-11,000 tonnes.

\*\* Chromium is present as natural contaminant in the concrete.

*Table 3.22 Sources of chromium to landfills in the Netherlands 1990 (derived from /Annema et al. 1995/)*

Source	Tonnes Cr/year	%
Basic metal industry	36	3.1
Chromium production	12	1.0
Paint industry	3.2	0.3
Paint application	7.8	0.7
Wood preservation	1.8	0.2
Leather industry	98	8.4
Graphic industry	1	0.1
Food industry	5	0.4
Sewage sludge	17	1.5
Large household waste	828	71
MSW residues *	1	0.1
Transport	3.3	0.3
Dredged sediment	154	13
<b>Total</b>	<b>1,168</b>	<b>100</b>

- In addition, 85 tonnes chromium followed the residues used for road construction work.

Sources of chromium to landfill, the Netherlands

The assessment from the Netherlands (Table 3.22) demonstrates the significance of the leather industry as a source of chromium to landfill. The main part of chromium is, however, supplied by large household waste, which supposedly includes leather and steel furniture and the like.

### 3.5 Obstacles for increased collection and recycling of heavy metals

Recycling of the heavy metals is generally regarded as a preferred action compared to incineration or landfilling as recycling may reduce the loss of heavy metals to the environment and at the same time avoid that virgin inter into circulation. However, in case the use of the metal is banned and the metal is in the process of being phased out, a time will come when the option of recycling no longer should be considered an appropriate action and thus ruled out in favour of incineration or landfilling /Hansen 2000/. No matter whether recycling is the preferred option or not, a number of obstacles to increased collection and recycling of the heavy metals exists.

The overall precondition for any successful collection and recycling operation is that the metal of concern is available in such a quantity and condition that separation, collection and recycling are feasible.

Separation may take place by the consumer or by professionals at waste separation or treatment facilities. The key issues related to efficient separation and collection are **identification**, **convenience** and **efforts required**.

Identification

Identification of the relevant products by the consumer must be easy and not give rise to misunderstanding. Whereas some types of products can easily be identified (e.g. batteries), other products may not be identified without assistance from experts (e.g. different plastics or nuts and bolts with special plating). Even if classification, labelling and information may facilitate the process, one cannot expect the consumer to distinguish between many similar products. It is e.g. well known that many consumers are unable to distinguish between alkaline batteries and ordinary dry batteries in spite of the fact that alkaline batteries are labelled. The consumer may be trained to be aware of certain products, but this training may take several years to accomplish. In fact, separation at the consumer level generally cannot be expected to go further than the screening level. This means that the consumer can be taught to separate out electronics, batteries, tyres, batteries and the like, but not to distinguish between different items within each of these groups and not to dismantle the individual products.

Identification of products by specially trained people at a central waste separation or treatment facility may allow for fine separation, e.g. dismantling of electronics and separation of batteries, capacitors etc. In principle, separation may in this case be carried out as detailed as necessary.

Convenience

Convenience is a matter of the effort required by the consumer in undertaking the separation and delivering the items to the right place. As a general rule, inconvenient systems will never be effective, as a certain number of consumers

will not invest the effort needed. However, the borderline between convenience and inconvenience is not fixed and will among others depend on

- the extent to which the solid waste system already includes separation at the source (by the consumer).
- how easy it is for the consumer to do things the wrong way.
- the motivation and incentives for carrying out separation (deposits for example increase the incentives).

The issue of convenience may be summarised in the following statements:

- If the separation system can be organised so that it is convenient for the ordinary citizen, motivation through information may be adequate.
- If the separation system is inconvenient for the ordinary citizen, economic incentives will probably be necessary.

#### Efforts required

The issue of the efforts required relates to the separation process itself. Even if the products may be identified, they may not be easily separated (e.g. lead solders used in electronics) or the separation process may be costly. Generally, separation is an option to consider for substances used in a limited number of products where the substances are present in relatively high concentrations. If a substance is used in many different materials and products (e.g. additives in plastics) and is present in relatively low concentration in the products, separation may be complicated and costly, and large scale arrangements and treatment facilities may be necessary.

Focusing on the heavy metals lead, mercury, cadmium and chromium the main obstacles to increased collection and recycling may be illustrated and summarised as follows:

#### Lead

Commercial collection systems exist for lead-acid batteries as well as sheets, pipes, roof plates and similar products available in large quantities. However, collection efficiency for these types of products is seldom 100%. As an example minor lead parts will follow the window frame, when workmen remove lead flashing from window frames.

For products containing small lead metal parts like foils, miniatures, curtains and candlesticks, and small electric products containing lead solders, neither collection arrangements nor the value of the lead motivates separation. The products easily find their way to the refuse bin or the bulk waste container in the household or company, as it is the most convenient solution.

Lead crystal glass could be separated, but generally collection systems are not prepared for separation of other items than cathode ray tubes from television and computer screens, which are collected together with electrical and electronic waste.

Lead compounds used in paint (siccatives and pigments), plastics (pigments and stabilisers), ceramics (pigments and glazing) are difficult to identify and in no way feasible to extract. Due to the variation of additives among products and manufacturers, continuous recycling of plastic products is typically only feasible, if the products can be returned to the manufacturer.

#### Cadmium

Collection and recycling arrangements only exist for cadmium in Ni-Cd batteries and some alloys. The present collection requirement for batteries is 75% of the potential. The main obstacles are deemed to be the lack of proper identification and inconvenient arrangements for collection leading to batteries being disposed of with ordinary solid waste.

Cadmium used as chemical compounds for pigments and stabilisers in plastics and other products is difficult to recognise and in no way feasible to extract. Due to the variation of additives among products and manufacturers, continuous recycling of plastic products is typically only feasible, if the products can be returned to the manufacturer. Items on which cadmium is used for plating will be collected together with other types of steel scrap and cannot without extreme efforts be separated. By recycling of steel scrap, cadmium will dominantly end up and be collected with filter dust from flue gas cleaning. To the extent zinc is extracted from filter dust some cadmium may follow zinc as an impurity. Extraction of cadmium is at the moment not feasible.

#### Mercury

Metallic mercury, mercury products and mercury compounds are partly collected for recycling and partly collected for disposal as hazardous waste. The collection efficiency for mercury is in general high, but losses cannot be avoided.

Mercury button cell batteries incorporated in photographic equipment may be disposed of together with the equipment, as the owner may not pay attention to the need of removing the battery before disposal. Thermometers, switches, monitoring and control equipment containing mercury may break, e.g. by being dropped on the floor or by shredding of cars and refrigerators whereby mercury is released. Similarly, mercury lamps and fluorescent tubes may break releasing the content of mercury to the ambient air.

Filters on sewage outlets at dentists are never 100% effective, while dental amalgam installed in teeth is released by cremation as well as by burial. Dentists may also hand over the tooth removed to the patient, who will later direct it to the dustbin.

#### Chromium

Apart from catalysts, chromium in alloys and chromium plating on metal, products containing chromium are generally not collected for recycling. This applies to products like tanned leather, preserved wood, chromium-plated plastic items as well as items coloured or painted with chromium pigments. Chromium-plated iron and steel may be collected for recycling of iron/steel. However, the process does not allow recovery of chromium metal, which dominantly is incorporated into the secondary iron and steel produced. Stainless steel and other alloys are relatively costly materials and will normally be collected apart from minor items, for which collection is not feasible.

## 4 Pathways of the heavy metals by waste disposal and recovery

Strategies for treatment of heavy metals in waste has apart from recycling until now been based on two basic principles: dilution and retention.

Due to the elemental nature of the metals they will remain after treatment of the waste, and will sooner or later be released to the environment. To prevent human and environmental exposure to the heavy metal at levels where harmful effects may occur, the metals are either diluted in large quantities of media or the release of the metals is retained. During the last decades there have been a tendency away from the dilution strategy toward the retention strategy, e.g. exemplified by the application of flue gas cleaning technology.

The basis for the retention strategy is that by retaining the heavy metals they can be released over time at a controlled and environmentally acceptable rate. This strategy may quite well apply to degradable substances or a situation where a limited amount of contaminated waste is produced within a limited space of time. But what will happen if there is a continued production of contaminated persistent waste over a wider space of time?

As consequence of the retention strategy, most effort has been put into studying emissions and leaching from waste on a relatively short time-scale and decisions are taken based on a relatively narrow time perspective. But in fact the actual releases of heavy metals from waste deposits are inversely proportional with the retention time. By retaining the emission, the environmental burden of the waste produced today is actually put on our descendants.

In the following the fate of heavy metals by waste management will be described in outline. A particular emphasis will be put on the long-term perspective.

Except for mercury, the heavy metals do not naturally occur in the environment in metallic form. Heavy metals in the waste will sooner or later - dependent on the treatment method - be transformed into other chemical or physical forms. All the heavy metals can exist in a wide variety of physical and chemical forms and several forms will coexist in a certain media. The distribution on the different forms (speciation) is important for the transport and the bioavailability of the metals. Physical/chemical conditions such as pH, redox potential, alkalinity and the occurrence of organic and inorganic compounds in the media play an important role in the speciation. Parameters of importance for understanding the evaporation, atmospheric transport and diffusion of heavy metals is discussed in Annex 1, which serves as background information for the following chapter.

## 4.1 Incineration

The total quantity of waste incinerated in the EU is not available from official statistical sources /EEA 1998/. All data on waste is associated with major uncertainties, but it is estimated that a total of 1,300 million tonnes of solid waste is generated each year in the EU /EEA 2000/. This is mainly from manufacturing, construction & demolition and mining /EEA 1998/. Municipal waste constitutes approximately 15% of the total waste. Of the municipal waste approximately 2/3 is landfilled, 17% is incinerated and 10% is recycled. Based on this some 33 million tonnes municipal waste should be incinerated. Data reported to the OECD indicates a total annual incineration of municipal solid waste of about 26 million tonnes (referenced in /EEA 2000b/. This must be taken as the minimum quantity. In several countries, reported quantities of incinerated waste are higher because other waste types - industrial and commercial waste - are incinerated as well. It should be noted that considerable quantities of waste are incinerated in cement kilns, steel ovens and industrial boilers. Major variations exist among the countries regarding the fraction of the waste incinerated. In Denmark approximately 20% of the total waste amount is incinerated, whereas only 1 and 4% of the waste is incinerated in Ireland and Germany, respectively /EEA 1998/.

The purposes of incineration are basically to reduce the volume of the waste, to utilise the energy content and to destroy harmful organic compounds and microorganisms in the waste. As regards some of the heavy metals in the waste, incineration unfortunately rather mobilise the metals in the waste and accelerate the release of the metals to the environment.

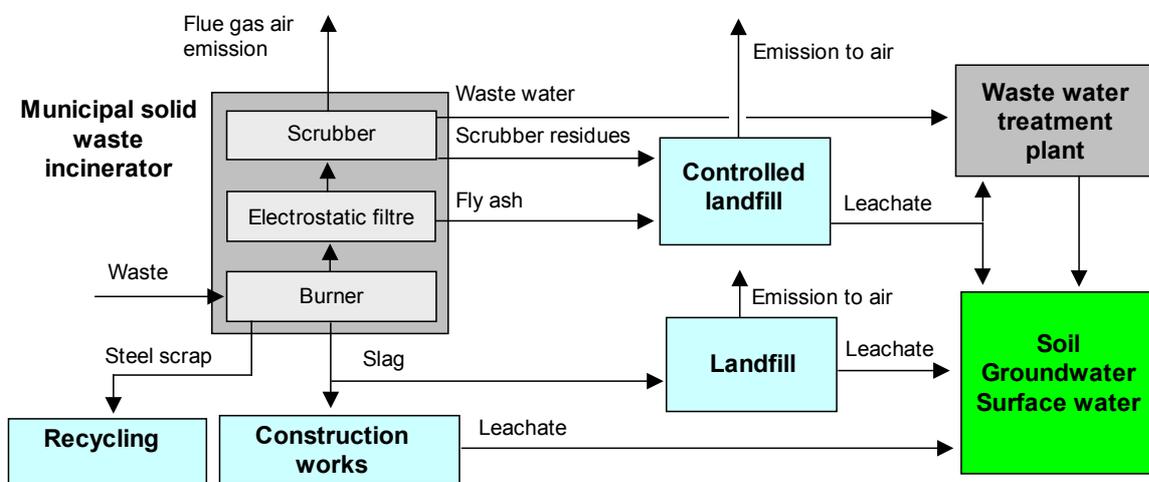
The incineration process typically takes place at temperatures around 1000°C, at which temperature organic materials will burn and be mineralised. At this temperature metals will - dependent on their physical properties - vaporise, melt or remain at metallic form.

The fate of the heavy metals by the incineration will also depend on the actual process, especially the flue gas cleaning technology. A schematic view of the flow of heavy metals through an incinerator using wet scrubber for flue gas cleaning is shown in Figure 4.1. It should be noted that many incinerators of this type in addition may have carbon filter and specific processes for further treatment of the residues e.g. by gypsum precipitation, and washing and stabilisation of the residues.

The outlets from the incineration process can be divided into the flue gas, flue gas cleaning residues, slag (clinker) and steel scrap. The partitioning of the heavy metals between the outlets will be process dependent and different for the four heavy metals. The route of steel scrap for recycling is only important for chromium that is a minor constituent of many steel alloys. Steel scrap will not be further discussed.

The distribution of the heavy metals between the different outlets is illustrated in the tables 4.1 and 4.2 with examples from an Austrian and a Danish incinerator.

Figure 4.1 Schematic view of the flow of heavy metals by incineration using wet acid gas cleaning process



The distribution of heavy metals in outlets from the Austrian MSWI plant Spittelau is shown in Table 4.1. The data represent a situation where only clean household waste was incinerated, but the distribution is not significantly different when mixed MSW is incinerated /Schachermayer et al. 1995/. More generally, the composition of waste seems not to have a significant influence on the partitioning of the metals in the single incinerator /Morf et al. 2000/. The study does not include chromium. Less than 1% of all heavy metals was emitted to the air. It is clearly demonstrated that lead will tend to end up in the slag. Cadmium, which evaporates during the incineration, will due to its tendency to adhere to particles mainly end up in the electrostatic precipitator dust. Mercury tends to be on the vapour phase and ends up mainly in the filter cake from the denox flue gas cleaning system.

Table 4.1 Heavy metals in outlets from MSWI plant Spittelau incinerating clean household waste /Schachermayer et al.1995/

Metal	Percentage of total outlet to:				
	Emission to air	Electrostatic filter dust	Waste water	Flue gas cleaning filter cake	Slag
Mercury	<1	30	<1	65	5
Lead	<1	28	<1	<1	72
Cadmium	<1	90	<1	<1	9

The results indirectly demonstrate that the main part of the mercury in the waste may be emitted to air in MSWI without acid flue gas cleaning. The emission of mercury from MSWIs seems in general to be highly dependent on the applied flue gas cleaning technology as indicated by /Maag et al. 1996/. The average emission from MSWI with dry and semidry flue gas cleaning systems in Danish incinerators shown to be 3 to 4 times higher than the emission from incinerators with a wet process (as the incinerator in Table 4.1).

The partition of three heavy metals from the Danish MSWI plant Amagerforbrænding with semi-dry flue gas cleaning process demonstrates the significance of the emission of mercury (Table 4.2). Neutralisation of acid gasses in this plant is accomplished by spraying a slurry of lime into the flue gas. This spray process creates solid dry particles that are collected in filter bags.

*Table 4.2 Heavy metals in outlets from MSWI plant Amagerforbrænding incinerating clean household waste /Amagerforbrænding 2001/*

Metal	Percentage of total outlet to:			
	Emission to air	Waste water	Flue gas cleaning residue	Slag
Mercury	7	>0.01	92	1
Lead	0.04	>0.01	46	54
Cadmium	0.2	0.01	94	6

The environmental concerns related to incineration have traditionally been focused on the flue gas as an important source of immediate heavy metal releases to the environment. As mentioned in Annex 1, most of the emitted heavy metals will be deposited relatively close to the incinerators although a part of the metals - and especially mercury- may be transported over long distances. It should be noted that although only a very small part of the heavy metal content of the waste is emitted to the air, emission from waste incinerators may constitute a significant part of the total air emission from a country. In the middle of the nineties waste incineration accounted for approximately 50% of total mercury (1993) and cadmium (1996) emission from Denmark and 20% of total lead emission (1994) /Lassen and Hansen 1996; Maag et al. 1996, Drivsholm et al. 2000/.

However, as the flue gas cleaning systems are improving to modern standard, disposal of slag and in particular flue gas cleaning residues are becoming major subjects of concern.

#### **4.1.1 Slag**

Slag (also designated 'bottom ash' or 'clinker') is the solidified bottom ash from the incineration.

As shown in the tables above a significant amount of the heavy metals in the waste end up in the slag. The heavy metal content of slag varies by waste type, but is in general considerable higher than the concentration in soil. The range of heavy metals in slag is show along with Dutch and Danish limit values for good soil quality in Table 4.3. It should be noted that the low values within the ranges are significantly below typical values from incineration of municipal solid waste.

Table 4.3 *Heavy metals in slag and limit values for good soil quality (after /EEA 1998; MoE 2000/)*

Heavy metal	Range in slag (mg/kg)	Limit values for good soil quality (mg/kg)	
		The Netherlands (1998)	Denmark (2000)
Mercury	0.02-7.75	0.3	0.5
Lead	98-13,700	85	40
Cadmium	0.3-70.5	0.8	0.5
Chromium	23-3,170	100	30

In general, heavy metals are strongly attached to slag partly due to the high content of alkaline material in these residues, which strongly limits the solubility of heavy metals, partly because they are integrated in a silicate matrix created during the incineration process.

The leaching of heavy metals from the slag is consequently quite low in a short-term perspective. The long-term behaviour of slag is still not known in detail. Some experiments have demonstrated that the release of e.g. lead from slag increased about a factor of 1000 when the pH of the slag - due to leaching of salts by penetrating water - decreased below a certain level /Hjelmar 1994/. The results should, however, be interpreted with care, because other chemical and physical changes of the slag will occur. Simultaneously with the leaching of salts, the silicate matrix may slowly decompose into a clay-like material with high cation-adsorbing capacity. The formation of the clay-like material must be expected to slow down the leaching rate due to the adsorption activity. The time for complete release of the heavy metals in slag must under normal conditions be expected to be in the range of many hundreds to thousands of years.

Slag may be utilised for civil works such as road construction or dumped at sanitary landfills. The term sanitary landfill is here taken to also include mono-fills and similar specialised depots for incineration residues. In densely populated countries, the mere volume of incineration residues is a strong argument for continued efforts to promote the utilisation of these residues instead of allowing residues to occupy valuable landfill capacity. The ongoing utilisation of slag for civil works should be seen in this context. Also flue gas cleaning residues would probably be utilised, if the content of hazardous compounds could be reduced.

Utilisation of incineration residues for civil works allows a minor part to be spread to the surroundings as dust during the disposal operation. Furthermore, later changes to the construction involving rearrangement of the residues will cause fractions to be released to the environment as dust, to be washed away by rain or to be mixed up with soil or other construction materials like sand and gravel.

#### 4.1.2 Flue gas cleaning residues

Flue gas cleaning residues arise from electrostatic precipitators and acid flue gas cleaning operations.

Several types of acid flue gas cleaning systems exist. They are either based on injection of dry or wet lime into the flue gas (dry and semi-dry process) or based on directing the flue gas through a scrubber with a lime solution (wet condensing process). Beside the acid flue gas cleaning systems, the incinerators may be equipped with a carbon filter for dioxins and other hazardous organic substances.

In incinerators with the dry and semidry process, the residues often consist of a mixture of the fly ash from the electrostatic precipitators and the residues from the lime injection (as the example in Table 4.2). Residues from incinerators with the wet condensing process are fly ash and a filter cake (sludge) from the scrubber (as the example in Table 4.1).

Compared to the slag, the content of heavy metals in leachate from unstabilised flue gas cleaning residues from dry and semi-dry processes is relatively high, whereas the immediate leaching from residues from the wet processes is significantly lower. Maximum concentration of heavy metals in initial leachate from MSWI residues has been reviewed by /Hjelmar 1996/ and the typical ranges for the four heavy metals are shown in Table 4.4.

Table 4.4 Maximum concentration levels of heavy metals in initial leachates from MSWI residues (after /Hjelmar 1996/)

Heavy metal	Concentration in leachates (mg/l)		
	Bottom ash (slag)	Fly ash and residues from dry and semi-dry processes	Mixture of fly ash and sludge from wet scrubbing process
Lead	1-10	10.000-100.000	0,001-0.01
Mercury	0,001-0.01	<0,001	<0,001
Cadmium	0,01-0.1	1-10	<0,001
Chromium	0,001-0.01	1-10	0,01-0.1

To reduce the release of heavy metals and other contaminants from the residues, a number of stabilisation processes have been developed. The experience with stabilisation processes has been reviewed by /Flyvbjerg and Hjelmar 1997/. In short, the main processes are:

- Stabilisation/solidification by binding the residues with cement or other binders.
- Chemical stabilisation processes where heavy metals are precipitated by addition of e.g. phosphates and sulphates.
- Thermal stabilisation processes including sintering processes (300-500°C) and melting or vitrification processes (up to 2000 °C).

Prior to the stabilisation process, the residues may be washed to reduce the content of water-soluble salts.

These residues are in many countries treated as hazardous waste and deposited on controlled landfills for hazardous waste. At the landfills the residues may be stored in big plastic bags, or they may be encapsulated in stores with top and bottom membranes. By the stabilisation processes, the immediate release of the heavy metals is decreased markedly, but in general residues stabilised with binders or chemical stabilisation processes still have to be treated as hazardous waste.

Most studies have focused on short-term releases of contaminants from the residues. The long-term behaviour of the residues is much less understood. It must be expected that leaching of the lime over time will change the chemical properties of the residues and increased leaching may occur as the pH decrease. The time required for complete release from stabilised residues must, however, be expected to be in the range of several hundred to thousand years.

If the heavy metals are not recovered from the residues, which is potentially possible but a costly and energy consuming process, the contaminants will sooner or later be released. It should be emphasised that these time perspectives mean that the dominant part of the metals in questions will be released at a time, when all leachate collection activities from the landfills probably have been discontinued for many years. In addition, the location of the depot may have been forgotten, as the area in question has been used for other purposes for a long time.

As pointed out in the start of this chapter, a controlled contaminant release strategy may quite well apply to a situation where a limited amount of contaminated waste is produced within a limited space of time. But the strategy cannot be considered sustainable if there is a continued production of contaminated waste over a wider time span.

## 4.2 Landfilling

Most waste in the EU today will be landfilled. Of the municipal waste approximately 2/3 is landfilled, and for other waste types the share will be even higher. Despite increased recycling no progress has been made in reducing landfilling from 1985-90 to 1995 /EEA 1998/. The landfills range from unlicensed simple dumpsites without any leachate control to highly controlled landfills for hazardous waste.

Not all licensed landfills are equipped with membranes and leachate collection. Wide variations exist among countries. In 1994, less than 40% of the landfills licensed for municipal waste in Ireland had liners and leachate collection, whereas landfills with liners and leachate collection account for more than 90% of landfills in operation in Austria, Belgium, Portugal and Sweden /EEA 1998/. In addition to the licensed landfills many unlicensed landfills have been reported, especially from Greece.

Heavy metals in leachate from landfills have been extensively studied and monitored. Compared to the total amount of heavy metals disposed into landfills the content of heavy metals in leachate is relatively low. The major part of the metals is retained in the landfill. As a consequence, it must be expected that leaching of heavy metals from the landfills will continue for a long time.

During the active life of a sanitary landfill, the leachate created will typically be collected and undergo some kind of wastewater treatment. For financial reasons the leachate is often treated together with municipal sewage. By this sort of treatment, a significant amount of the heavy metals present in leachate will be retained in sewage sludge, while the rest will be emitted to the water environment. The amount retained in sludge will be directed to farmland, incineration or deposited again on landfills. A cycle is therefore created that in time will allow all heavy metals in leachate to be emitted to the environment. The active life of the landfill includes the period, when waste is sent to the landfill as well as the time that follows, when no more waste is dumped and the final top cover has been established, but leachate is still collected for treatment.

/Hjelmar et al. 1994/ (quoted by /EEA 1998/) has made some model calculations on the time needed before leachate from different landfills can be released to groundwater without risk. The calculations are based on landfills with an average height of 12 m and different rates of leachate production (Table 4.5). The estimations of cause are very uncertain but indicate the relevant range of time.

*Table 4.5 Estimated time needed before leachate can be released without risk to groundwater resources /EEA 1998/.*

Rate of leachate production	Estimated time needed before leachate can be released without risk (years)			
	Hazardous waste landfill	Municipal solid waste landfill	Non-hazardous low organic waste landfill	Inorganic waste
Medium 200 mm/year	600	300	150	100
High 400 mm/year	300	150	75	50

As indicated by the model calculations it may be necessary to continue leachate collection from landfills for hundreds of years. However, hardly any landfill specialists expect that leachate collection will continue for more than 50-100 years. It may therefore be necessary to develop disposal strategies, where the contaminants after some time are allowed to leak to the surroundings.

Substantial amounts of research have been carried out on the degradation processes in the landfill; especially landfills for municipal solid waste (reviewed by /Hjelmar et al 2000/ among others). The degradation process over times lead to different stages of ageing with leachate composition quite different from the young landfill. Often, there will be great variability within the landfill body itself, resulting in different degradation phases in various parts of the landfill.

During the stage of anoxic conditions and methane production which will be reached after a short time (months), the mobility of the heavy metals is in general low due to formation of relatively insoluble compounds /Flyhammar 1997/. During the later oxidised state where the degradation of the organic material lead to formation of carbon dioxide, the mobility of the heavy metal will increase leading to higher content of heavy metals in the leachate.

The concentration of soluble metals will not only depends on the actual chemical conditions and speciation of the metals, but also the degradation or disintegration of products in which the metals are embedded. A significant part of the heavy metals in the waste will be bound in glass, plastics, slag, ceramics, steel, wood etc. Products and materials stored in a landfill should be expected to slowly disintegrate over time. Plastics will probably degrade in time due to biological and chemical processes including weathering processes. Glass is known to disintegrate over time in a humid environment. Slag from incineration plants should be expected to disintegrate into a clay-like material (reference is made to section 4.1.1). Metals should be expected slowly to be oxidised and thereby be dissolved. Wood and organic materials will decompose due to biological and chemical processes. Many of these processes are slow and strongly influenced by the presence of oxygen, water and acids. As mentioned in Annex 1, mercury may escape from the landfill due to evaporation.

Transport of heavy metals within a mature landfill can be compared to transport in soil and should thus generally be taken as a very slow process. The exact rate of transport will, however, vary with the metal in question, the composition of materials and the chemical conditions within the landfill. The time required for a complete wash-out of a specific metal may be in the range of hundreds to thousands of years or even more. For all metals, the major part cannot be expected to be washed out before long time after any leachate collection has been discontinued.

The studies of landfill ageing mainly cover what in the long time perspective must be considered the initial phases - the phases of relevance for understanding the methane production dynamics and leachate composition. Taking a closer look at older disused landfills a number of uncontrolled processes takes place. Landfills will after some time often be covered by trees with roots deep down in the former landfill and construction works may mix up the upper parts. Large parts of cities today are build on old waste dumps. The landfill will after some time become a part of the environment - a highly contaminated part of the environment. If the information systems in the future work as they do today, the information on former landfill sites may remain for the necessary hundreds to thousands of years, but actually nobody knows.

Probably these highly contaminated parts of the environment will remain and slowly be absorbed into the surroundings until major geological events occur. In the northern part of Europe this may ultimately happen when a new Ice Age leads to that the remains of landfills are eroded away by the ice and their content of e.g. heavy metals spread over large areas.

## 4.3 Recycling

Recycling operations related to heavy metals and other metals may be divided in:

- Sorting and separation activities
- The recycling operation itself.

### 4.3.1 Sorting and separation activities

Sorting and separation activities include manual sorting and dismantling, cutting, flattening and shredding. Manual sorting and dismantling may be applied to products and materials with significant value. Cutting and flattening may be used to reduce the size of large homogenous metal items (predominantly iron, steel and aluminium items), thereby making them suitable for further handling and transport.

Cutting processes and flattening will damage surface treatment slightly causing small pieces to drop to the ground and be removed as dust or by rain (e.g. relevant for chromium plating and lead/chromium-based paint). As metal scrap is often stored outside and frequently/occasionally on bare ground (this varies between countries due to national regulations and their enforcement), corrosion of surfaces will often take place leading to soil contamination in addition to small metal parts being buried in mud during rainy seasons. When acids are involved (e.g. from lead batteries), the stage may be set for significant soil pollution often leading to groundwater contamination.

Collection of metallic mercury will typically include breaking of switches, thermometers and other types of small glass containers used in measuring, monitoring and electrical equipment. The operation naturally allows some emission of mercury to air. Mercury contained in fluorescent tubes and mercury lamps are removed by cutting the glass container and emptying it by vacuum.

#### Shredding plants

Shredding plants are used for fragmenting inhomogeneous metal waste (typically cars, refrigerators and miscellaneous other items from households and companies) into small normally homogenous parts that can be separated by mechanical means such as ballistic separation, magnetic separation and occasionally also fluid separation.

By the shredding process, the temperature of the shredded items may reach several hundreds degrees. Shredding will cause emissions to air depending on the efficiency of the scrubber or other kind of air cleaning equipment. Fluids still present in the waste (e.g. mercury) will be released to the interior of the plant and either evaporate or leak to the ground or be collected as sludge. Dust from the plant will be spread to the surroundings.

Other outlets from a shredding plant include a magnetic metal fraction, non-magnetic metal fractions, sludge from washing processes, and a fluff fraction which is a mixture of plastics, insulation materials, soil etc.

The fluff fraction may be disposed of for incineration or landfilled. A quite significant amount of heavy metals follows the fluff fraction. In the middle of the nineties Danish shredder plants shredded about 300,000 tonnes waste. The fluff from the operation was estimated to contain about 0.15 tonne mercury, 200-1000 tonnes lead, and 0.5-2.5 tonnes Cd /Maag et al. 1996; Lassen and Hansen 1996; Drivsholm et al. 2000/. The emission of mercury to air from the operations was estimated at <0.05 tonne. /Maag et al. 1996/

### 4.3.2 Fate of heavy metals by recycling of other metals

Cadmium, lead and mercury may be present as contaminant in iron and steel scrap, making secondary steel production an important source of release of these metals to air. Chromium and to some extent lead is also used as alloy in steel. The heavy metals may as well be present in aluminium scrap, but compared to steel scrap the total turnover with aluminium scrap is small. Also in aluminium, chromium is intentionally used as alloy.

By steel production lead and cadmium will dominantly be oxidised and collected with flue gas cleaning residues. Mercury will either be emitted or end up in the residues.

The heavy metal content of the outlet from a Danish steel processing plant processing around 700,000 tonnes scrap in the mid nineties is shown in Table 4.6. It should be noted that the emissions to air might have been reduced during the last years compared to the figures shown in the table.

Table 4.6 Heavy metals in outlet from a Danish steel production plant /Maag et al. 1996; Lassen and Hansen 1996; Drivsholm et al. 2000/.

	Outlet in tonnes/year to:				
	Emission to air	Filter dust	Slag and other waste fractions	Waste water	Following the product
Mercury (1993) *	0.07	-	-	-	-
Lead (1994)	2.0	302	69	0.03	11
Cadmium (1997)	0.02	4.4	0.09	0.0002	≈ 0

\* Only mercury emission to air is reported.

The filter dust from steel reclamation may be processed for recovery of the metal content. Apart from the heavy metals mentioned here, the filter dust contains significant amounts of zinc, which is the main economic incentive for the recovery. Lead and cadmium is to some extent also recovered by the processes.

Only a minor part of the three heavy metals considered here will end up in the final product. It should be noted that heavy metals with higher boiling points will remain as contaminant or alloying element in the steel. This applies for copper, nickel, chromium and tin. Increasing content of especially copper and tin is considered a problem for steel recycling as the metals are undesirable and

the content increases for each lifecycle. Heavy metals present as contaminant in secondary metals will sooner or later during future life cycles be released from the secondary metal due to wear and tear.

Lead and cadmium is also present as an alloying element in various copper alloys and may thus be emitted to air, waste water or to residues from recovery activities addressing these materials.

### 4.3.3 Recovery of heavy metals

#### Lead

About 50% of global lead consumption is derived from recycled or re-used material; the figure is higher in Western Europe (60% ) and the USA (70%) /Scoullos et al 2001/. The main source of lead for recycling is lead batteries. Most lead metal scrap will be re-melted and used for production of lead alloys. Lead re-melting today is a rather centralised activity. Only one recycling plant is operating in Scandinavia.

The recovery rate is very dependent on whether lead is recovered from the residues (matte) from the secondary lead smelter. /Karlsson 1999/ has described the flow of lead containing materials in the lead battery system for Sweden. About 1% of the turnover of the secondary lead smelter ends up in the lead matte, while 0,001% is emitted to the air. The matte is exported for recovery. Karlsson estimates that the total losses to air, water and landfills by the recycling activity is about 0,06 % of the amount disposed of to recovery. It is from these model calculations obvious that it is the collection rate, which is the key parameter for the total losses in this recycling system.

Scrap lead may, however, also be used for small scale manufacturing of yacht keels, fishing equipment, roof plates and the like under conditions that is not necessarily well controlled. The emissions during these operations will be significantly higher than figures indicated above for the Swedish lead battery recycling system.

#### Mercury

According to /Masters 1997/ about 700-900 tonnes/year of mercury was recycled globally, of which about 200-400 metric tons originated from spent mercury-containing products, and the rest mainly coming from chlor-alkali facilities.

Recovery of mercury is normally done by distillation in a closed system. This process is applied to most mercury waste inclusive metallic mercury, batteries as well as residues from e.g. laboratories. The volatile nature of mercury means that the greatest concern of the distillation process as well as other collection and recovery processes generally will be paid to the risk of air emission.

An indication of the emission to air from the recovery process can be obtained from /Sznoppek and Goonan 2000/ who report that total air emission from recovery of 446 tonnes mercury in the U.S.A accounted 0.4 tonnes in 1996. It has not been possible to obtain information on the amount of mercury disposed of to landfills/deposits from the process.

**Cadmium** The total amount of cadmium recovered by recycling worldwide in 1998 is estimated at approximately 1500 tonnes /Scoullos et al 2001/. Secondary cadmium production is based on recovery of cadmium from flue gas filter dust, slag and residues arising from primary cadmium production as well as discarded materials and treatment of wastes and sludge (e.g. of steel-making). Cadmium containing products for recovery consist mainly of spent Ni-Cd batteries, electroplated coated components and alloys and anode residuals from electroplating scrap. Also in copper production a primary feed is scrap which may contain cadmium.

Most existing secondary production is from the remelt of various standard shapes from primary production, lower grade old stocks of cadmium metal and increasingly, from recycling of spent Ni-Cd batteries.

**Chromium** Chromium is mainly recycled as alloying element in stainless steel and other types of steel. The recycling operation in itself will typically be a melting operation during which the metal is diluted by virgin metal to ensure that the content of other metals acting as contaminants (e.g. copper in steel) are kept within certain limits. Melting operations generally cause air emissions besides different residues like slag and flue gas cleaning residues. Other recovery processes may, however, be employed also (reference is made to mercury above).

#### **4.3.4 Recycling of plastics, glass and organic waste**

Considerations regarding the fate of heavy metals during recycling operations may be relevant also with respect to:

- Recycling of plastics
- Recycling of glass
- Recycling of organic materials by biological waste treatment

**Plastics** Heavy metals used as pigments or stabilisers etc. in plastics will be incorporated in secondary plastic products. The use and fate of these products will thus determine the fate of the metallic compounds used in the original products.

Ongoing recycling activities regarding plastic products are focused on products made from virgin plastic mainly. Recycling of secondary plastic is insignificant, as secondary plastic is typically used for low-quality bulk products, which will be disposed of to incineration or landfilling. Thus the lifecycle of secondary plastic products is generally limited to one product generation only. Recycling may in this way delay the disposal of the heavy metals used as additives in virgin plastic by a likely maximum of 30 years (may be the case for secondary plastic turned into construction materials as a substitute for wood).

Whereas continuously recycling of plastics in principle is possible (at least for some thermoplastics), continuously recycling, however, in reality requires that the plastic is returned to the manufacturer responsible for manufacturing the original product. The reason is that only this manufacturer has the full knowl-

edge of the composition of the plastic and is able to turn it into new products of a quality equalling products made from virgin plastic. Today closed cycle recycling actually exist for a few special products, e.g. plastic boxes for beer and soft water bottles.

## Glass

Recycling of cathode ray tubes and fluorescent tubes made of lead crystal glass has been established.

Heavy metals used in ordinary consumer glass (bottles and the like) are normally limited to heavy metals like chromium, cobalt and zinc, which are used as colorants/de-colorants in glass manufacturing. However, other glass products like crystal glass and fluorescent tubes containing heavy metals may occasionally contaminate used consumer glass collected for recycling.

By glass manufacturing, heavy metals will partly be incorporated in secondary glass products and partly emitted to air or captured by flue gas cleaning. Glass is generally regarded as a very stable and inert material. Glass will, however, disintegrate in time especially in a humid environment. The time required for glass to disintegrate will be in the range of several hundred years to several thousands years depending on the conditions under which it is stored.

## Biological waste treatment of organic materials

Waste directed to biological treatment will dominantly include compostable organic waste from households, gardens and the like. However, even waste sorted at source will contain pieces of plastic, metals etc. containing heavy metals and affecting the quality of the waste product.

Pre-treatment includes one or more of the mechanical operations homogenising, magnetic separation and sifting. By magnetic separation and sifting, items containing heavy metals may be separated from the organic material and disposed of by recycling (only relevant for items removed by magnetic separation), incineration or landfilling.

The biological treatment processes involve mixing and adding of water and air (air is only relevant for the composting process). A common characteristic of both processes is that heavy metals in the original material will be well mixed with the rest of the material by dissolution, extraction or simply by being torn into small pieces during the operation. After the operation, compost will be sifted again occasionally combined with further efforts to remove small pieces of plastic, glass etc. from the matured compost. The elements removed will typically be sent to landfills or for incineration.

Concerning biofermentation, the sludge will be de-watered. Heavy metals may be discharged with the wastewater generated. Compost and biofermentation sludge is intended for land application purposes. The content of heavy metals is emitted to soil. In case the content of heavy metals is too high to allow land application, the compost/sludge may be used for daily covering at landfills.

## 5 Substitution

### 5.1 Principal options for substitution

The present status regarding development and marketing of substitutes for lead, mercury, cadmium and selected uses of chromium is indicated in the following sections. For chromium, the comments are focused on tanning and wood preservation being the only applications, for which significant efforts have been invested in developing alternatives.

The tables indicate whether substitutes are available today and whether substitutes are just potential or actual alternatives marketed. It should be noted that the tables are only listing one or few of the most promising substitutes, and that many more substitutes may be available or being developed. The tables furthermore indicate the cost level of the substitute solution as compared to the lead solution. The cost issue is, however, discussed further in section 5.2.

Substitute characteristics

Substitutes may be a substitute on the substance or material level, meaning a substance/material is replaced by another substance/material providing more or less the same characteristics. E.g. lead for flashing purposes may be replaced by soft zinc. It is however very seldom that alternatives will be perfect substitutes. Most often, substitutes will represent a trade off between relevant characteristics inclusive costs.

Another type of substitute is the alternative that represents another way of fulfilling the same function. To illustrate such substitutes, a good example is the electronic thermometer that has replaced the traditional mercury thermometer for most applications.

‘Must have’ versus ‘nice to have’ characteristics

Assessing the suitability of substitutes it is often relevant to distinguish between ‘must have’ and ‘nice to have’ characteristics, as ‘nice to have’ characteristics are frequently based on tradition or consumer preferences, but in no way essential to the use of the product. A relevant example is pigments in plastics.

Prior to the Danish cadmium ban from 1983, many household items were marketed in warm red and yellow colours. After the ban was established colours like white, brown and purple began to dominate. In this case, a wish for a specific colour must be described as a “nice to have” characteristic.

However, pipelines for natural gas made of HDPE were granted dispensation for the use of cadmium pigments, as cadmium yellow in this case was regarded as a safety colour and thus a “must have” characteristic.

Development of substitutes

For applications where no alternative exist or research is ongoing, it is not possible to state precisely, when alternatives are available and ready for being marketed, as this depends heavily on the demand for substitutes. Experience related to substitution of the heavy metals considered in this report, as well as ozone-depleting substances, indicates that the necessary time for development of new technology and modification of manufacturing equipment will generally

not exceed 10 years (e.g. /Hansen & Thomsen 1988/). This estimate is based on the assumption that the principles for the new technology are well known. It should be noted that no guaranty can be issued for the new technology developed to be cheaper or in all respect environmentally more friendly than the existing technology. E.g. lead cable sheaths could be avoided in all electric cables for ground purposes if a solution with aluminium sheathing is adopted. Unfortunately, aluminium sheathing suffers from electrical turbulence leading to around 5% higher internal resistance, again leading to increased power consumption and related environmental impacts (/NKT 97/ - reference is made to table 5.1).

Table 5.1 Options for substitution of lead with initial indication of level of expenses relative to Pb-technology

Application	Alternatives	Level of expenses relative to lead technology *1	Extension of alternatives
Batteries	Lithium-ion-polymer batteries or other types.	"+" - Compared to the lead-acid battery will the lithium-ion-polymer battery cost 6 times more but last 2-3 times longer /Danionics 1998/.	On research/product development level. Price difference so far prevents further development. The lead-acid battery is generally unchallenged on the market for all major fields of application (starter batteries, traction, and emergency power).
Cable sheathing	PE/XLPE – Polyethylene/cross linked polyethylene plastic to low-voltage ground cables up to 24 kV. No alternatives to lead sheaths for marine cables and high-voltage ground cables despite significant research efforts /NKT 1997/. Aluminium is rejected as an alternative to lead due to higher internal resistance (caused by electrical turbulence) /NKT 97/.	"=" – Production costs, lifetime and quality of PE/XLPE-cables deemed equal to traditional lead cables for low-voltage ground applications /Gudum et al 2001/	PE/XLPE is substituting lead in Denmark for low-voltage ground applications.  In France lead has been partly substituted for medium-voltage cables not requiring absolute long-term reliability /CECAD-plomb 1996/.
Flashing (around chimneys, windows etc.)	Alternatives may be organised as /Maag et al 2001b/: <ul style="list-style-type: none"> <li>• Pure zinc, which is soft and may be treated almost as lead</li> <li>• Aluminium (as net or wrapped) combined with rubber/polymer</li> <li>• Rigid profiles of aluminium, stainless steel or other metals</li> </ul>	"+" - Cost increase estimated at 10% of total costs installed /Gudum et al 2001/.	Aluminium solutions and some rigid profiles are already available on the market. Training in pure zinc solutions has been initiated at Danish training centres for plumbers.
Roofing plates (on historical buildings)	Many alternative roofing materials are available, but preservation of historical buildings makes substitution difficult. Lead plated steel has been proposed as an alternative.	?	No alternative has actually been marketed.
Sheets for corrosion protection in chemical industry	Acid resistant stainless steel	"+/++"	Alternative is available on the market.
Leaded window frames	None		
Solders for electronics	Lead free solders, surface-mount technology/ electrical glue.	"+" - Cost increase of tin based lead-free solders typically in the range of +20 – 50% /Brorson & Nylén 1997/.	Development is still at the research level. Electrical glue can replace solders for some applications, but not all. Lead-free solders are needed /Christensen et al 2000/.
Solders for food cans	Lead free solders, welding, gluing	"-/+" – Lead has been substituted voluntarily.	No lead soldered food containers have been produced or used in the U.S. since December 1990 /USEPA 1994/.

Application	Alternatives	Level of expenses relative to lead technology *1	Extension of alternatives
Solders for electrical bulbs	Tin-zinc solders, welding or electrical glue	?	Development is still at the research level.
Solder for auto radiators made of brass-copper	Aluminium radiators soldered by Mg-Si solder may substitute brass-copper radiators /Hedemalm 1994/	"-" – Aluminium is significantly cheaper than brass/copper.	Aluminium radiators dominate the market /Hedemalm 1994/
Solders for VVS and other applications	Alternatives vary with application. For public water supply alternative solders include tin-antimony and tin-silver	"=/+ " – The cost of solder is low compared to the overall costs of construction.	Alternatives are well established as the use of lead solders for public water supply is prohibited in some countries.
Ammunition	Steel, soft iron, wolfram, bismuth and tin may be used as alternatives to lead shot. Wolfram is used as powder in a polymer matrix.  No research seems to have been carried out regarding alternatives for other applications like bullets for rifles and pistols. In principle all non-toxic metals with a density close to or above lead could be appropriate.	"+/+" – Costs differs with substitute: Steel Shot: + 25% Tin shot: + 50-100% Wolfram/bismuth shot: + 200-400 % /Hartmann 2001/.	Lead shot is prohibited in Denmark. The market is dominated by steel shot. In forests supplying wood for veneer production only wolfram and bismuth shot are typically allowed, as steel shots in wood damage wood saws /Hartman 2001/.  Lead is so far unchallenged for other types of ammunition.
Bearings etc. of lead alloys	Babbitt metal (leaded tin bronze) for bearings may be substituted by aluminium bronze and unleaded tin bronze, assuming a lubricant can be added and the design of axles etc. allows for the higher hardness of the bearing material.	?	To the best of knowledge lead alloys are still unchallenged.
Hot dip galvanising (zinc contains 1% lead)	No knowledge of alternatives. To the best of knowledge no research for alternatives have been initiated.	?	
Weights for fishing tools and anchors	Depends on the application: <ul style="list-style-type: none"> <li>• Anglers equipment: Lead can be substituted by iron, tin or zinc etc. Tin is appropriate for split shot sinkers while iron is appropriate for most weights.</li> <li>• Lead weights on trawls may be substituted by iron chains</li> <li>• Development work is ongoing with respect to leaded robes and lines – plastic coated iron bullets seems to a promising substitute for small lead bullets in robes.</li> </ul>	"-/+/+" – Depends on application as follows: Angler split shot sinker: ~ 200 % (tin) Angler ordinary weights: ~ 50 % (zinc /iron) Weights for trawls: ~ 0% (iron) /Ponsaing & Hansen 1995/. Robes and lines: 20 – 100% /Gudum et al 2001/.	Regarding anglers equipment and trawls substitutes are available on the market. Lead free robes are being developed.  In Canadian national parks only lead-free equipment is allowed /Environment Canada 2002/.
Balance weights for vehicles	Alternatives assumed to include auto-balancing devices as well as other metal like copper tin etc. /Hedemalm 1994/.	"+"	Lead weights still dominate the market
Plating of gasoline tanks	Lead plated steel tanks can be substituted by plastic tanks	"-/="	Plastic tanks dominate the market

Application	Alternatives	Level of expenses relative to lead technology *1	Extension of alternatives
Yacht keels	Iron is used as alternative today, but only on boats not designed for racing. Other materials are available. The choice is partly a trade-off between speed and price. Iron keels require more maintenance than lead keels.	"-/+"	Iron and lead is sharing the market.
Lead tubes and joints for drain and water pipes etc.	For drains and water pipes alternatives include iron, copper and plastic pipes and joints. For corrosion resistant pipes/joints for industrial purposes alternatives include acid resistant stainless steel.	"-/+"	In many countries lead pipes have not been used for domestic water supplies for over 30 years / Scoullou <i>et al</i> 2001/. However, in France lead piping still counted for 36 % of the connecting pipes in 1996 /CECAD-Plomb 1996/.
Radiation shielding	Barium and concrete are assumed to be alternatives /Hedemalm 1994/.	?	Lead dominates the market
Other: Toys, curtains, candlesticks, foils, organ pipes etc.	Alternatives vary with application and include several other materials like plastic, tin, stainless steel, aluminium etc.	?	
Gasoline additives	Alternatives are available and widespread	?	In many countries lead additives have been completely substituted for several years.
PVC stabiliser	Substitutes are generally calcium/zinc stabilisers, which already dominate indoor applications, and has proven useful also with respect to electrical cables/wires etc. Calcium/zinc stabilisers seem to be the primary choice also for outdoor purposes. However, research/development based on organic compounds is ongoing /Gudum <i>et al</i> 2001/. Organo-tin compounds have been used for more than 40 years. However, concerns about potential risks have been raised both in Sweden, Holland and Germany /Scoullou <i>et al</i> 2001/.	"+" – The cost increase related to substituting lead compounds by calcium/zinc systems is in the range of 5-10% of the total production costs for PVC-products /Gudum <i>et al</i> 2001/.	In Denmark lead is completely replaced for indoor purposes apart from electrical cable/wires. Also outdoor products like windows are now based on lead free stabilisers. Generally, lead stabilisers are expected to be completely out of the Danish market from 2002 /Gudum <i>et al</i> 2001/.
Pigments	Many alternatives are available on the market. Ultimately, the choice is a matter of costs and the colour and other characteristics, like weather fastness, torsion stability and brilliance, preferred.	"-/++" - Other pigments providing other colours can easily be found at lower costs. Trying to develop the perfect substitute may be rather costly /Ponsaing & Hansen 1995/.	Other pigments are already widely used
Rust-inhibitive primers	Zinc phosphate or zinc oxide combined with iron oxide.	"+" – Assessment relates to cost of primer only. If the use of lead primers require heavy occupational safety protection the use of lead primers may be far more costly than other primers.	Lead based primers are almost completely substituted in Denmark.

Application	Alternatives	Level of expenses relative to lead technology *1	Extension of alternatives
Siccatives in paint	Several other siccatives are marketed. However, for special applications alternatives may be few or missing	"=/" - Compared to price of final product, cost increase for siccative must be assumed small.	Lead based siccatives are replaced by zirconium or calcium based siccatives in the USA /Hoffman 1992/. No market data for Europe are available.
Lubricants for demanding industrial applications	No precise knowledge – research should be ongoing	?	?
Cathode ray tubes	Alternatives to lead are assumed to include zirconium, strontium and barium /Hedemalm 1994/.	"+/++" - Costs of alternatives so far prevent further development.	Lead is so far unchallenged
Other applications of lead crystal glass	Alternatives depend on application /Smith 1990/: <ul style="list-style-type: none"> <li>For fluorescent tubes and light bulbs alternatives include strontium, barium, cerium etc., but alternatives are more difficult to process.</li> <li>For optical glass alternatives are assumed to include barium and zinc oxides for glass with indices of refraction below 1.6 and lanthanum for glass with indices of refraction above 1.6.</li> <li>For semi-crystal glass barium, potassium and zinc are alternatives. For whole crystal glass research is ongoing but no introduction of alternatives are likely, before the international quality systems for crystal glass are modified, as these systems require the use of lead /Gustavsson 1993/.</li> </ul>	"+" – The largest Danish manufacturer of semi-crystal glass replaced lead with barium partly to reduce the costs of emission control /Fought 1993/.	Lead is so far unchallenged apart from semi-crystal glass, in which lead by some manufacturers is replaced by barium.
Glazes and enamels	Alternative systems include alkali borosilicate glasses, zinc/strontium and bismuth glasses /Cambell 1998/.	"?"	In UK around 80% of bone china, 30 % of earthenware and 40 % of hotelware is un-leaded (1998 –figures). The trend towards substitution of lead glasses continues /Campbell 1998/.

\*1 Indication of the overall current user/consumer price levels for lead free alternatives as compared to lead technology. Price determining factors vary among the uses (expenses for purchase, use, maintenance etc.). Costs of waste disposal or other environmental or occupational health costs as well as local and central government costs and revenues are, however, not considered in the cost assessments given.

"-": lower price level (the alternative is cheaper)

"=": about the same price level

"+": higher price level

"++": much higher price levels

Table 5.2 Options for substitution of mercury with initial indication of level of expenses relative to Hg-technology

Application	Alternatives	Level of expenses relative to mercury technology *1	Extension of alternatives
Chlorine-alkaline production	Membrane-process which is a fully mature technology (and less optimal the diaphragm-process) /U.S. EPA 1993; Lindney 1997/.	"-/" - Based on /U.S. EPA 1993; Lindney 1997b/	Mercury-free technology dominates production in North America /U.S. EPA 1993 & Lindney 1997/.
Dental amalgam	Composite fillings (polymer/ceramics). (Cast fillings of ceramics, gold and others.)	"+" – Based on /KEMI 1998/	In Denmark, Sweden and the Netherlands composite fillings have largely substituted amalgam as filling material / Scoullos <i>et al</i> 2001/. Composite fillings do not require special equipment and is easy to apply, but require more time to install than amalgam.
Mercury-oxide batteries	Mercury-free dry cell batteries like alkaline, silver, zinc-air, lithium etc. Non-Cd rechargeable batteries. Generally equipment is designed to a specific type of battery.	"-/" – Alkaline batteries are normally cheaper than mercury batteries.	Mercury batteries have virtually disappeared from OECD countries /Scoullos <i>et al</i> 2001/. Based on Danish experiences, old photographic equipment should be regarded as the main use area remaining.
Other batteries	Same battery types with newer, non-Hg technology	"-/" – Vary, not much difference for consumer (Danish experience).	Substitutes are today's standard in Europe
Medical thermometers	1) Electronic thermometers 2) Glass thermometers with liquid Ga/In/Sn "alloy" is being developed /Scoullos <i>et al</i> 2001/	"=/" – The price of electronic thermometers is around 3 times as high as the price of mercury thermometers /Vejle Hospital 2001/. However, mercury thermometers breaks more easily, and the life of a electronic thermometer equals the life of several mercury thermometers /Maag <i>et al</i> 2001a/	Electronic thermometers are today's standard in the Nordic countries.
Other thermometers	Mainly electronic thermometers *2 Other Hg-free alternatives exist	Varying – not necessarily more expensive /Gustavsson 1997; Rasmussen 1992/	Consumption of mercury thermometers in Denmark has in principle ceased. However, mercury may be used for special applications inclusive calibration purposes
Measuring and control equipment	Availability of alternatives varies with the type of instrument in question. Many electronic devices are available, often with much more beneficial user facilities. Also traditional non-electronic techniques like membrane and spring manometers /-gauges /Rasmussen 1992/	Varying, often not more expensive /Rasmussen 1992/	Consumption of mercury for measuring and control equipment in Sweden has almost ceased /Maag <i>et al</i> 2001a/. No exact knowledge regarding the situation in Denmark.

Application	Alternatives	Level of expenses relative to mercury technology *1	Extension of alternatives
Electric and electronic switches	Substitutes vary according to different fields of application: 1) Larger switches for level- or position control: Rolling steel balls or metal powder in liquid suspension. 2) Micro-switches: Gold-plated micro-switches. 3) Optical switches 4) Other electronic circuits /Rasmussen 1992/	"-/+ " – Will depend on the alternative solution in each case. No significant price differences between mercury and non-mercury solutions /Maag et al 2001a/	Today's standard (in new equipment) in Sweden and Denmark among other countries
Fluorescent tubes and lamps *3	Currently no energy efficient alternatives on the market without mercury. Development is directed towards minimising the content of mercury in tubes and lamps. The present state of art equals 3 mg mercury for fluorescent tubes /Maag et al. 2001a/. Of other alternatives diode technology is considered. The final options are traditional less energy-efficient standard glow lamps and halogen lamps etc.	" =/+ " – No significant price differences between low-mercury tubes and high mercury tubes with respect to quality products. Traditional lamps correspond to a lower price plus higher energy costs.	Low content mercury lamps are available on the market.
Laboratory chemicals	Possible to restrict to few specific, controllable uses (mainly references and standard reactants)	?	Restrictions has been implemented in Sweden and Denmark
Gold extraction	1) So-called cyanide process. Used in large-scale gold extraction since the 1930s. More effective extraction /Lacerda 1997/ 2) New extraction process optimised for small-scale gold mining developed by The Imperial College Consultants, London. Currently under promotion in the Amazonas region /Scoullou et al 2001/.	1) Presumably more economically beneficial, since an almost total conversion from the Hg-process occurred long before Hg environmental concerns /Lacerda 1997/. Environmental qualities of alternative process not investigated here. 2) Presumably more economically attractive because of 40-50% better extraction efficiency than Hg-process /Scoullou et al 2001/.	
Pesticides and biocides for different products and processes.	1) Alternative products or processes not requiring chemical pesticides/biocides. 2) Easily degradable, narrow-targeted substances with minimised environmental impact.	?	Today's standard in most countries

\*1 Indication of the overall current user/consumer price levels for mercury free alternatives as compared to mercury technology. Price determining factors vary among the uses (expenses for purchase, use, maintenance etc.). Costs of waste disposal or other environmental or occupational health costs as well as local and central government costs and revenues are, however, not considered in the cost assessments given.

"-": lower price level (the alternative is cheaper)

"=": about the same price level

"+": higher price level

"++": much higher price levels

2) For some precision purposes mercury thermometers are still preferred for technical reasons (for instance for calibration of other thermometer types). The mercury consumption for these purposes is minimal. Some electronic industrial and marine thermometers need to be calibrated against a fixed reference. For some uses periodic re-calibration may be needed.

3) Other Hg-containing light sources exist, mainly for special, limited purposes and sold in much lower numbers.

Table 5.3 Options for substitution of cadmium with initial indication of level of expenses relative to Cd-technology

Application	Alternatives	Level of expenses relative to cadmium technology *1	Extension of alternatives
Plating	Zinc, aluminium, tin, nickel, silver, gold plating etc. depending on application.	? – No data are available	Since 1995 cadmium plating has been banned in EU for all purposes except aerospace, mining, offshore and nuclear activities according to Directive 91/338/EEC.
Silver-cadmium alloys	Ag-Cd alloys are used for solders and jewellery. In “Indian silver” have been observed up to 30% cadmium /Drivsholm et al 2000/. Many alternative solders exist inclusive e.g. Sn-Ag solders. Alloys for jewellery may be substituted by pure silver.	“+” - The present use of cadmium in Ag-Cd alloys partly reflects the current low world market price on cadmium.	Quality jewellery is generally not based on Ag-Cd alloys. However, sterling silver may contain up to 5% cadmium /Scoullous et al 2001/.
Copper-cadmium alloys, solders and other alloys	Alternatives depend on application: <ul style="list-style-type: none"> <li>• Cu-Cd alloys may be replaced by pure copper</li> <li>• Zn-Cd alloys for anti-corrosion anodes may be replaced by aluminium anodes</li> <li>• Pb-Cd alloys for cable sheaths may be replaced by using other types of cable sheaths like PE/XLPE-sheaths, aluminium sheaths or normal lead sheaths.</li> </ul>	“=” - The content of cadmium in the alloys is typically around 1% and other materials exist and is utilised on the market parallel to the cadmium alloys.	Alternatives are present and utilised on the market parallel to cadmium products.  In cable sheaths manufactured in Denmark cadmium is only present in special flat cables for electricity supply. The content of cadmium is below 1 %o. /Drivsholm et al 2000/.
Ni-Cd batteries	Nickel-metal hydride, lithium-ion-polymer etc.	“-/+”? Although alternatives are typically more expensive to produce, they have technical benefits. E.g. life of battery is longer, as alternatives are not suffering from the so-called memory effect *2.	Ni-Cd still dominates very power consuming applications like portable electrical tools. For other applications alternatives are slowly taking over the market (Drivsholm et al 2000).
PVC stabilisers	Depends on application. For indoor purposes substitutes have generally been calcium/zinc compounds.  For outdoor purposes and other demanding applications like electrical cables/wires the alternatives have so far been stabilisers based on lead or organic tin compounds, but research/development based on calcium/zinc compounds is ongoing (reference is made to table 5.1 regarding PVC-stabilisers for lead).	? – No data are available. For best estimate please refer to table 5.1 regarding PVC-stabilisers for lead.	In both Austria, the Netherlands, Sweden and Denmark cadmium stabilisers have been more or less completely eliminated completely from the market from the early 1990’s /Pearse 1995; Koot 1996; Jensen & Marcussen 1993; Öberg & Granath 1997/.
Pigments *3	Many alternatives are available on the market. Ultimately, the choice is a matter of costs versus colour and other characteristics preferred like weather resistance, torsion stability and brilliance.	“-/+” Other pigments providing other colours can easily be found at lower costs. Trying to develop the perfect substitute may be rather costly.	Other pigments are already widely used, e.g. the use of cadmium pigments for plastic manufacturing in the Netherlands had almost ceased by 1990 /Koot 1996/.
Photovoltaic cells	Cadmium is used in modern thinfilm cells based on CdTe, but not in traditional crystalline cells.	“=/+”	Traditional crystalline cells dominate the market today /Drivsholm et al 2000/

- \*1 Indication of the overall current user/consumer price levels for cadmium free alternatives as compared to cadmium technology. Price determining factors vary among the uses (expenses for purchase, use, maintenance etc.). Costs of waste disposal or other environmental or occupational health costs as well as local and central government costs and revenues are, however, not considered in the cost assessments given.  
 "-": lower price level (the alternative is cheaper)  
 "=": about the same price level  
 "+": higher price level  
 "++": much higher price levels
- \*2 Memory effect is a characteristic for NiCd-batteries. A NiCd-battery shall be completely emptied and completely recharged in each cycle. If not, its capacity will slowly be reduced, as it only remembers the capacity actually utilised. It is the experience of many consumers, that the effective life of NiCd batteries for this reason is shortened significantly /Drivsholm et al 2000/.
- \*3 The story and conclusions are similar to lead pigment.

Table 5.4 Options for substitution of chromium with initial indication of level of expenses relative to Cr-technology

Application	Alternatives	Level of expenses relative to chromium technology *1	Extension of alternatives
Leather tanning	Vegetable tanning and synthetic tanning (tanning with synthetic organic compounds).	"+++" – Total production costs for synthetic tanning are estimated 2-5% higher than for chromium tanning /Frendrup 1999/.	Alternative tanning techniques counts for around 20% of world production /Danish EPA 2001a/.  Synthetic tanning is anticipated to be a winner of the future /Frendrup 1999/.
Wood preservatives (CCA-preservation, CCA = copper, chromium, arsenic)	Preservatives based on copper + boron + organic preservative is deemed acceptable for wood above soil and in contact with soil and fresh water /Danish EPA 2001b/.  For wood for maritime purposes no alternatives to chromium preservatives have been developed.  Wood preserved solely by organic preservatives (trade name: Superwood) has been developed for purposes above soil /Superwood 2001/	"+++" – Wood preserved by copper/boron systems assessed as 40-50% more costly to manufacture besides that life in contact with soil may be reduced from 40-50 years to around 25 years /Collstrup 2001/.  Superwood will be marketed at same price level as copper/boron preserved wood. /Superwood 2001/.	Chromium has not been used for manufacturing preserved wood for non-maritime purposes in Denmark since 1997 /Danish EPA 2001b/.  Superwood will be marketed early 2002 /Superwood 2001/.
Stainless steel and other alloys, plating, hard metals, catalysts, refractories, laboratory chemicals	No attempts have so far been made to substitute chromium, but other materials are available on the market.	?	
Colours and pigments incl. textile dyes	Alternatives are available on the market. Ultimately, the choice is a matter of costs and the colour and other characteristics preferred.	?	

- \*1 Indication of the overall current user/consumer price levels for mercury free alternatives as compared to mercury technology. Price determining factors vary among the uses (expenses for purchase, use, maintenance etc.). Costs of waste disposal or other environmental or occupational health costs as well as local and central government costs and revenues are, however, not considered in the cost assessments given.  
 "-": lower price level (the alternative is cheaper)  
 "=": about the same price level  
 "+": higher price level  
 "++": much higher price levels

## 5.2 Costs of substitution

The costs of substitution of hazardous chemicals are an issue frequently discussed and so far no general consensus has been developed. In box 5.1 the principles accepted so far by the Danish EPA are presented.

### *Box 5.1 Assessing costs of substitution for chemicals*

Assuming that the choice has been made to estimate the economic costs of substitution by a cost-efficiency analysis, as the target is given beforehand (the anticipated level of substitution) and the analysis merely assesses the costs of achieving this target, the following cost elements should be considered /Gudum et al 2000/:

- Losses/benefits for manufacturers of the chemical and alternatives in question.
- Changes concerning costs for buyers of chemicals and other materials.
- Changes in manufacturing equipment for buyers of the chemical.
- Changes concerning labour costs for using the chemical for manufacturing or private purposes.
- Changes concerning quality and lifetime for products or tasks, for which the chemical is utilised.
- Changes concerning environmental and occupational health protection costs as well as costs for waste treatment and disposal.
- Changes in local and central government costs regarding supervision, monitoring, administration and environmental protection related to chemicals.
- Changes regarding fees and other sources of income to local and central governments.

It depends on the individual chemical, its characteristics, production and use pattern as well as legislation to what extent each of the cost elements listed above should be included. It follows from this that the actual costs of substitution may differ between countries.

Due to the general uncertainty in price trends, as well as the fact that a permanent press for increased productivity typically will result in lowering or stagnating prices for raw materials as compared to workers salary, costs estimates should only be considered valid for a rather limited number of years. Furthermore, continuing efforts to improve alternatives should be expected to pay off in the years to come regarding technical performance as well as costs.

The methodology behind the cost estimates presented in table 5.1-5.4 varies as some estimates are based on information from manufacturers and other estimates are based on the price paid by buyers of the substituted product.

The estimates should, however, be assumed in principle to fulfil the requirements outlined in box 5.1, except that costs of waste disposal or other environmental or occupational health costs as well as local and central government costs and revenues are not considered in the cost assessments given.

When it comes to environmental protection related to treatment and disposal of waste contaminated by heavy metals or other hazardous chemicals integrated in products, the costs are typically financed by local governments or by user charges or with respect to privately owned recycling companies by reduced profit. As such costs are seldom known to the company estimating the costs of substitution and are furthermore difficult to relate to the individual products, they are normally not included.

The magnitude of such costs may be illustrated by a Nordic study covering all the Scandinavian countries from 1994 /Hansen & Ponsaing 1994/. This study

has assessed the costs related to the presence of lead in a number of the most important waste products contaminated by lead. The assessment is presented in table 5.5 in a simplified version dealing with Denmark only.

As the assessment is based on figures from 1990-1993, the figures may deviate slightly from the lead figures presented in section 3. The magnitude of the calculated costs is still assumed to be realistic but, however, most likely in the low end of the real costs today.

*Table 5.5 Estimated economic costs related to the presence of lead in lead contaminated waste types/products in Denmark – the beginning of the 1990'ties 1)*

Waste types/products	Total quantity Mio. tons/year	Total content of lead Tons/year	Total Costs Mio. DKK	Unit costs DKK/kg lead
Solid waste incineration 2)	2.0	740	6.4 – 17	8.6-22
Compost 3)	0.052	0.3	0.5 – 0.8	1,700-2,500
Sewage sludge 4)	0.16	17	4.5 – 7.4	270-440
Harbour dredging 5)	3.8	88	2.1 – 10	24-120
Contaminated soil 6)	0.25	60	28 – 39	460-640
Iron and steel scarp 7)	0.6	500	24	48
Lead recycling 8)	0.011	11,500	14 – 20	2.2-3.2
<b>Total</b>	<b>6.9</b>	<b>13,000</b>	<b>80 – 120</b>	<b>6 – 9</b>

- 1) Based on /Hansen & Ponsaing 1994/. Exchange rate as per August 1994: 1 ECU = 7.5 DKK.
- 2) Costs include control of air emissions and of lead content in clinker to be used for civil works. Costs furthermore include landfilling of fly-ash and special treatment and disposal of residuals from removal of acid gasses.
- 3) Costs include sorting at the source and control of lead content in compost.
- 4) Costs include control of lead content in sewage sludge and landfilling of sewage sludge, which due to lead content cannot be utilised for soil application purposes.
- 5) Costs include control of lead content in harbour dredging and special transport and landfilling of dredging that cannot be dumped at sea.
- 6) Costs reflect investigations, removal, transport and landfilling of lead contaminated soil. It is assumed that 22% of the total amount of soil removed is done so due to lead contamination.
- 7) The costs stated reflect installation and operation of special flue gas cleaning equipment caused by the content of lead and cadmium in the flue gas.
- 8) The costs stated is related to environmental precautions by storing and transport of lead acid batteries and other types of lead scrap. For lead batteries such costs are partly covered by a special fee on new batteries, as the value of lead itself is not high enough to ensure complete collection of batteries.

The assessment is based on the precondition that the present costs related to control and other pollution prevention activities for the waste products considered are caused by those heavy metals and other chemical compounds, for which threshold limits have been established. It is thus assumed that if these metals and compounds could be removed from waste products the need for fi-

nancing control and other activities would be heavily reduced and eventually disappears. In those cases, for which it is not possible to separate the costs related to lead from the costs related to other metals and compounds, the total costs have been allocated evenly to all metals for which threshold limits have been established.

As shown in table 5.5, the total costs for the waste products in question are estimated to approx. 100 million DKK yearly. Compared to the total lead consumption in Denmark of 15,500-19,800 tons/yearly, the average can be calculated to 5.0-6.4 DKK per kg lead. This expenditure is at the same level or exceeding the world market price of lead, which at the time of study was down to 3.2 DKK/kg (as per August 1994) /Hansen & Ponsaing 1994/.

It is emphasised that the figures stated probably underestimates the total real costs related to lead. Costs related to chemical waste or solid waste being land-filled are not included. Neither are costs of administration or research included and the calculations should generally be characterised as conservative, as only costs which with certainty relate to lead are included.

The calculations presented relate only to lead and no attempt has been made to repeat the calculation for other heavy metals or hazardous chemicals. It should be understood that the costs identified cannot be eliminated before all hazardous metals and chemicals have been eliminated from products and thus also from waste and waste products. On the other hand, it should be acknowledged that - as the costs in question are never charged to the company choosing to use e.g. a heavy metal in the products - the company and the products are actually being subsidised by society.

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## Annex 1

### Parameters determining evaporation and diffusion of heavy metals

Except for mercury, the heavy metals do not naturally occur in the environment in metallic form. Heavy metals in the waste will sooner or later - dependent on the treatment method - be transformed into other chemical or physical forms. All the heavy metals can exist in a wide variety of physical and chemical states and several forms will coexist in a certain media dependent on the conditions. The distribution on the different forms is designated the 'speciation' of the element. Environmental conditions such as pH, redox potential, alkalinity and the occurrence of organic and inorganic compounds play an important role in the speciation. The speciation is particularly important for the transport and the bioavailability of the metals.

If not otherwise referenced the general information on properties in the following is extracted from the IPCS monographs for the heavy metals and /U.S. EPA 1997/. (See reference list of main report)

#### 1. Evaporation and long range transport

The most immediate release of the heavy metals from waste treatment operations to the environment is emission to the air. Depending on the properties of the metal and the type of waste and waste treatment volatile species, fugitive dust and stack emissions may be encountered. Aerosols may transport metals but do not normally occur in solid waste treatment operations.

##### Lead

The melting point of elemental lead is 328°C and the boiling point at atmospheric pressure 1,740°C. Metallic lead will melt in an incinerator whereas the evaporation will be dependent on the actual vapour pressure and retention time. Lead in flue gas is in the form of particles of inorganic compounds of lead and the major part will be trapped by electrostatic filters and bag filters.

Most lead emissions to the air are deposited near the source, although some particulate matter (< 2 µm in diameter) may be transported over long distances and results in the contamination of remote areas.

##### Mercury

Elemental mercury is a liquid metal at typical ambient temperatures and pressures. The boiling point at atmospheric pressure is 357 °C. The vapour pressure of mercury metal is strongly dependent upon temperature, and it vaporizes readily under ambient conditions. As a result of the low boiling point mercury in waste will tend to evaporate during waste incineration. Only a minor part of mercury in the stack will be on particulate form and mercury will thus only to a minor extent be trapped by electrostatic precipitators.

Elemental mercury in waste can also to some degree evaporate under normal ambient temperatures. During waste treatment processes at elevated temperatures - e.g. shredding of cars where the temperature may reach several hundreds degree - the evaporation of mercury must be considered highly significant. In large-scale landfill operations evaporation of mercury may be taken into consideration.

In addition to its elemental state, Hg(0), mercury exists in two oxidation states: Hg(I) and Hg(II). Stack emissions of mercury to the air seems to include both gaseous and particulate forms of mercury. Gaseous mercury emissions are thought to include both Hg (0) and oxidised chemical forms, while particulate mercury emissions are thought to be composed primarily of oxidised compounds due to the relatively high vapour pressure of elemental mercury. Most of the mercury emitted at the stack outlet is found in the gas phase although exit streams containing soot can bind up some fraction of the mercury.

Hg(0) has an average residence time in the atmosphere of about one year. Mercury is distributed via air over long distances and elevated levels of mercury can be found in remote areas far from the sources. Of particular concern are the elevated levels of mercury in arctic and subarctic areas /AMAP 1998/. Oxidised mercury, Hg(II) may be deposited relatively quickly by wet and dry deposition processes, leading to a residence time of hours to months. Longer residence times are possible as well; the atmospheric residence time for some Hg(II) associated with fine particles may approach that of Hg(0). Mercury released into the atmosphere from natural and anthropogenic sources deposits mainly as Hg(II), from either direct deposition of emitted Hg(II) or from conversion of emitted elemental Hg(0) to Hg(II) through ozone-mediated reduction.

Contrary the other heavy metals, a significant part of the deposited mercury may re-enter the atmosphere by evaporation. Hg(0) can be formed in soil, landfills and sewage stacks by reduction of Hg(II) compounds/complexes mediated by among others humic substances and light. This Hg will diffuse through the medium and re-enter the atmosphere.

## Cadmium

The melting point of elemental cadmium is 321°C and the boiling point at atmospheric pressure is 765°C. Metallic cadmium must be expected to vaporise under the temperatures present in a waste incinerator. The melting and boiling points are typically higher for the cadmium compounds; for cadmium chloride e.g. 568°C and 960°C, respectively. Cadmium has a relatively high vapour pressure. The vapour is oxidised quickly to produce cadmium oxide in the air. When reactive gases or vapour, such as carbon dioxide, water vapour, sulphur dioxide, sulphur trioxide or hydrogen chloride, are present, the vapour reacts to produce cadmium compounds. Cadmium in the flue gas will mainly be on particulate form as the outlet of the flue gas is close to or below 200 °C.

Cadmium can be transported by air over long distances. However, much higher air cadmium concentrations are found in areas close to major atmospheric sources of the metal. Studies of the particle size distributions of cadmium in urban aerosols generally show that the metal is associated with particulate

matter in the respirable range. The enrichment of cadmium on these smaller particles can be linked to the behaviour of the metal in thermal facilities that are sources of airborne cadmium

## Chromium

Compared to the other heavy metals, chromium has a high melting and boiling point. The melting point of elemental chromium is 1857°C and the boiling point at atmospheric pressure is 2672°C. Metallic chromium will thus not melt in an incinerator. Some of the chromium compounds, however, has considerably lower melting and boiling points.

Chromium may occur in each of the oxidation states from -2 to +6, but only the 0 (elemental), +2, +3, and +6 states are common. The most important states are trivalent Cr(III) and hexavalent Cr(VI).

The oxidation state of chromium emitted from stacks is not well defined quantitatively, but it can be assumed that the heat of combustion may oxidise an unknown proportion of the element to Cr(VI). While suspended in the air, this state is probably stable, until it settles down and comes into contact with organic matter, which will eventually reduce it to the trivalent form.

## 2 Leaching of heavy metals

The major pathway of heavy metals release from waste to the environment is leaching of metals from landfills and construction work where incineration residues has been used to surrounding soil, groundwater and surface water.

As mentioned above the heavy metals can exist in a wide variety of physical and chemical states. Different states of the metals have different solubility characteristics. The solubility of heavy metals in residues, landfills and soils is dependent on a number of physical and chemical parameters: pH, redox potential, presence of electron donors and acceptors, occurrence of organic and inorganic complexing agents, etc. The parameters influence the solubility and mobility in a very complex pattern, but a few important points will be mentioned below.

## Lead

Lead is in general not very mobile in soil. Soil pH, content of humic acids, and amount of organic matter influence the content and mobility of lead in soils. Only a very small portion of the lead in soil is present in the soil solution, which is the immediate source for lead for plant roots, but soil acidification will lead to increased mobility and bioavailability of lead. More acid conditions (lower pH) not only increase the solubility of lead, but also other heavy metals. In Europe major differences exist among regions as to soil acidity. In the northern Member States like Denmark, Sweden and Finland the soil in general have lower pH than in Member States with soils with a high alkalinity like France and the U.K. This result in regional differences in heavy metals mobility in soils and influences the assessments of the environmental impact of heavy metal load to soil.

Due to the binding capacity of the soil minerals and humus, groundwater usually contains very low concentrations of lead, and the diffusion of lead from deposits to the groundwater must be expected to be a relatively slow process.

#### Mercury

Soil conditions are typically favourable for the formation of inorganic compounds such as  $\text{HgCl}$ ,  $\text{Hg(OH)}$  and inorganic  $\text{Hg(II)}$  compounds, which form complexes with organic anions. This complexing behaviour greatly limits the mobility of mercury in soil. Much of the mercury in soil is bound to bulk organic matter and is susceptible to elution in runoff only by being attached to suspended soil or humus. As mentioned above mercury differs from the other heavy metals because the metal in significant amount can be released by evaporation of elemental or methylated mercury to the atmosphere from landfills and soils.

#### Cadmium

Soil pH is the most important factor controlling the availability of cadmium; it affects the stability and solubility of cadmium complexes, as well as nearly all adsorption mechanisms. Some of the cadmium salts, such as the sulphide, carbonate or oxide, are practically insoluble in water, but these can be converted to water-soluble cadmium sulphate, cadmium nitrate, and cadmium halogenates under the influence of oxygen and acids. The more acid the soil is, the more mobile the cadmium becomes, whereby it can be taken up by plants or leach more readily. Compared to the other heavy metals, cadmium is relatively mobile in soil and more bioavailable. Cadmium uptake from agricultural soils by the crops is a major concern, but due to the relatively high mobility of cadmium the transport of cadmium from residues and landfills to the groundwater must be expected to be a faster process than for the other three heavy metals.

#### Chromium

Both  $\text{Cr(III)}$  and  $\text{Cr(VI)}$  can exist in soil, but in normal soils reduction of  $\text{Cr(VI)}$  to  $\text{Cr(III)}$  is favoured. The environmental chemistry of chromium in soil is very complex and it is difficult to extract some general patterns. The pH of the soil affects the speciation, solubility and bioavailability of the chromium forms. The effect of pH is, however, different for the different species; acidic conditions increase the adsorption of  $\text{Cr(VI)}$  to particles whereas in decrease the adsorption of  $\text{Cr(III)}$  /Adiano 2001/.