

METAL FLOWS AND ENVIRONMENTAL IMPACT

12



Falu copper mine in mid Sweden, has a 1000 year long history with its peak in the mid 1600s when it produced some 2/3 of world copper. Today the mine and its surrounding constructions and buildings is a world cultural heritage. The disastrous environmental effects of the mine was commented on already by Linneaus as “a terrible air that killed all plants” in the surroundings. Mines are still the most serious point sources of environmental pollution in the world, as well as one of the oldest causes of environmental pollution. Copper, gold, lead, mercury, and zinc mines have the greatest impact on the environment. (Photo: Lars Rydén.)

"Metals have always existed and will forever exist, but we cannot avoid the fact that all humans and animals are affected by metals in the environment. Some metals are necessary for our wellbeing and others are detrimental to our health. Human activities of all kinds have led to metals being redistributed from sites where they are fairly harmless to places where they affect humans and animals in a negative way...."

International Working Group on Medical Geology, the IUGS
Commission on Geological Sciences for Environmental Planning
(<http://home.swipnet.se/medicalgeology/>)



Man has lived with and utilised metals since the rise of civilisation. The names for the early cultures point this out: the iron and bronze ages. Iron, copper, and tin were made into tools and weapons. But even before that, objects of gold – together with mercury the only metals seen in the environment in its metal form – and silver were part of human cultures. Later, from the Middle Ages, more metals were used for technical purposes: lead for tubes and window sealing, tin for cups and other items in the household. Mercury was used for its toxic properties, to cure infections. It may also have been mercury that was first noted for its adverse effects on health. Plating with gold was done with a mercury-gold mixture, and as a result, gold platers were often shortlived.

An average household in the mid 19th century typically owned about 8-10 kg of metals mainly as household items and jewellery. This contrasts dramatically with today's industrial society where all items of metal in a household, from the house itself to kitchen machinery and the car, certainly includes tonnes of metals, often as complex alloys. It is clear that the flow of metals in society has enlarged enormously. After fossil fuels and macronutrients, metals take the third position in the large material flows in our societies. Just as the other two categories of material flows, metal flows are non-sustainable not only because of their size but because they are based on non-renewable resources and are essentially linear. This is in itself a problem which needs to be addressed.

Metals, generally as compounds and ions, are naturally present in the environment, and several of them are essential to biological functions. Living organisms such as plants and animals get most of the metals needed for their biological functions through water or food. Sometimes there is a lack of some essential metal, e.g. iron, and we need to add it to maintain health. The situation is thus very different from organic environmental pollutants that are entirely

artificial, will eventually be broken down, and have no biological meaning, only technical or none at all.

The present use of metals in society has in many cases turned out to severely damage the environment. Toxic heavy metals, most importantly mercury, lead and cadmium, constitute one major category of environmental threats. Most of this is man-made, though there are places where these heavy metals are naturally so abundant that they reach toxic levels, and the places themselves are dangerous for humans. Metals appear in several forms often with vastly different biological effects. Metals in organic complexes are often more toxic than their dissolved inorganic ions.

Since metals are chemical elements, they never degrade, which means that they cannot be broken down or metabolised to harmless compounds, such as water and carbon dioxide, and in this way disappear. They can be washed out, be part of waste, or stored in landfills but they still remain in the environment.

Several measures may contribute to make the management of metals in society environmentally acceptable. Recycling is an important component of this. Recycling of metals is both profitable and sustainable, and it is possible to set up technical cycles with close to 100% recycling for certain areas of usage. For others such as Zn, Pb, Hg, Ti, Cu, etc., in paint or Pb in gasoline the use is dissipative. It should be noted that the use of essential metals such as copper in many cases leads to high concentrations that are toxic in the environment. An example is copper in waste water sludge, released from water tubes in our homes. Environmentally damaging use of some metals, such as use of mercury, should be discontinued since alternatives exist. In fact, the use of some metals, in particular mercury, lead, and cadmium, could be entirely discontinued. The collected metals then need to be stored forever in underground facilities, in fact corresponding to putting them back in the mines!

Authors of this chapter

Olle Selinus, Lars Hylander, Lars Rydén, and Pawel Migula, main authors; A background text was provided by the Turku team Peter Backlund, Bjarne Holmbom, and Erkki Leppäkoski.

METAL FLOWS AND ENVIRONMENTAL IMPACT

METALS – NATURAL, ESSENTIAL, AND TOXIC

Occurrence and distribution of metals	359
Review Box 12.1 Heavy metals overview	360
The biological roles of metals	360
The flow of metals in society	361

METALS AS ENVIRONMENTAL POLLUTANTS

Metals in the environment	362
Metallurgic industry	363
Metals in water – the Baltic Sea	364
Metals in atmospheric deposition	366
Methods Box 12.2 Mosses for biomonitoring	367
Metals in soil	367
Case Box 12.3 Regional geochemical mapping in the Baltic Sea region	368

THE HEAVY METALS

The forms – metallic, salts and organo-metallic compounds	369
Mercury pollution	370
Outlook Box 12.4 Mercury and gold mining	371
Cadmium – increased levels in biota	373
Methods Box 12.5 Methods and instruments used for analysis of heavy metals	375
Lead – declined levels but hazards still exist	376
Zinc – no great problem	376
Case Box 12.6 Heavy metal pollution in southern Poland	377
Chromium	377
Arsenic	378

GOOD MANAGEMENT OF METALS

Stop dissipative uses	379
Technical cycles of metals	379
Discontinue the use of toxic metals	379

METALS

NATURAL, ESSENTIAL, AND TOXIC

Occurrence and distribution of metals

Planet Earth is the ultimate source of all metals. Metals are found everywhere in the ground, the lithosphere, where they are not distributed homogeneously and occur in different chemical forms. Ore deposits are merely natural concentrations which are commercially exploitable. While such anomalous accumulations are the focus of mineral exploration the background concentrations of metals which occur in common rocks, sediments and soils are of greater significance to the total metal loading in the environment. Indeed, all known elements are present at some level of concentration throughout the natural environment. They are present in animals, plants, and minerals, and their beneficial and harmful effects have been present since evolution began.

An understanding of the nature and magnitude of these geological sources is a prerequisite for developing approaches to assessing the risk posed by metals in the environment. It is important to be able to distinguish between natural and anthropogenic contributions to metal loading. Table 12.1 shows the significant differences between different rock types and their contents of heavy metals. Concentrations of metals can range over orders of magnitude among different types of rocks. Accordingly concentrations of elements such as nickel and chromium are much higher in basalts than in granites, whereas the reverse is true for lead. In sediments the heavy metals tend to be concentrated in the fractions with the finest grain size and the highest content of organic matter. Thus, black shales tend to be enriched in these elements. In addition, a knowledge of natural processes is fundamental understand the fate of those metals which are released as a result of human activity.

There is a long series of metals, most of them unusual, some very common and many rather trivial for the environment. In this chapter we will focus on the so-called heavy metals since these may become environmentally damaging, not the least since they react with the components in living cells. Formerly heavy metals were defined as metals with a density greater than five, which explains their name, but in fact their chemical properties expressed in the periodic system, are more essential for the classification. Heavy metals form compounds with oxygen, nitrogen, and sulphur atoms, and thereby give rise to oxides, sulphides, etc. This is the form in which they exist in minerals and in ores, for example sulphide deposits. Some of these are easily dissolved in water and then the metals exist in dissolved, so called ionic, form or as inorganic and organic complexes. In the aquatic environment they are often bound to particulate matter, sediments. The dissolved forms are normally available to organisms, although some specific organisms can also utilise metals associated with particulate matter.



Figure 12.1. Traditional metal objects. A household some 150 years ago had on the average some 8 kg of metal. These may have included, as in this picture, *iron* in knives, *lead* in window sealing, *tin* for vases or cups, *gold* and *silver* in jewellery, as well as others e.g. *copper* in pots and *mercury* for disinfection. (Photo: Lars Rydén.)

A *metal* is an element which in its elemental form is a good conductor of electric current and heat.

Heavy metals previously denoted all metals with a density greater than five. Today the term is often (incorrectly) used for metals which are toxic in the environment.

Table 12.1. Metals in the lithosphere. Average abundance of some elements in the Earth's crust according to type of rock (all values in ppm, mg/kg). (Source: Thornton, 1983.)

Element	Earth's crust	Ultra-basic	Basalt	Granite	Shale	Limestone
As	1.8	1	2	1.5	15	2.5
Cd	0.2	-	0.2	0.2	0.2	0.1
Co	25	150	50	1	20	4
Cr	100	2,000	200	4	100	10
Cu	55	10	100	10	50	15
Pb	12.5	0.1	15	20	20	8
Se	0.05	-	0.05	0.05	0.6	0.08
U	2.7	0.001	0.6	4.8	4	2
W	1.5	0.5	1	2	2	0.5
Zn	70	50	100	40	100	25

Table 12.2. Biological role of metals. Diseases at state of deficiency, and toxicity caused by an excess of the same element.

ELEMENT	DEFICIENCY	TOXICITY
iron	anaemia	haemochromatosis
copper	anaemia, "sway back"	chronic copper poisoning, Wilson, Bedlington-disease
zinc	dwarf growth, retarded development of gonads, akrodermatitis enteropathica	metallic fever, diarrhoea
cobalt	Anaemia, "White liver disease"	heart failure, polycythaemia
magnesium	dysfunction of gonads, convulsions, malformations of the skeleton, urolithiasis	ataxia
chromium	disturbances in the glucose metabolism	kidney damage (nephritis)
selenium	liver necrosis, muscular dystrophy ("white muscle disease")	"alkali disease," "blind staggers"

The biological roles of metals

Most of the heavy metals are *essential* in certain amounts for biological functions of organisms (e.g., cobalt, copper, manganese, molybdenum, zinc, nickel, and vanadium). They are so called *micronutrients*. At high concentrations, however, *all* metals negatively influence organisms. The large scale introduction of heavy metals in society, the technosphere, and eventually into the biosphere, has given rise to *toxic effects* and non-sustainable flows. Cadmium, mercury, lead, copper, and some other metals have all been connected to various toxic effects in living organisms. Of these, mercury and lead do not seem to serve any biological functions in living organisms. Examples of health effects as well as toxic effects in living organisms are listed in Table 12.2.

In living cells heavy metals are bound to proteins, where they serve specific functions as components in e.g. enzymes. The copper and iron atoms in proteins give the cells their capacity e.g. to bind and transport oxygen and to oxidise the food, and thus serve key functions in the energy metabolism of the cells.

Review

Box 12.1

Heavy metals overview

Metal	Symbol	Biological role	Toxicity	Presence
Iron	Fe	Essential for all organisms Deficiencies widespread	To humans at drinking water level >200 mg/l	Common in many minerals
Copper	Cu	Essential for all organisms	Toxic at high doses	In many sulphide deposits
Zinc	Zn	Essential for all organisms	Toxicity low	In many sulphide deposits
Nickel	Ni	Essential for some organisms	Some compounds extremely toxic	In many sulphide and laterite deposits. In deep-sea nodules
Manganese	Mn	Essential for all organisms.	Mainly non-toxic	In many minerals and in deep-sea nodules
Molybdenum	Mo	Essential for all organisms except some bacteria	Considered toxic. More toxic to ruminants than to humans	In pegmatites, some copper deposits and U deposits
Cobalt	Co	Essential	Toxic in higher doses	In sulphide deposits, deep-sea nodules and U deposits
Vanadium	V	Essential for some organisms	Toxic	In many types of mineral deposits and oil deposits
Lead	Pb	Considered non-essential	Toxic	In many types of mineral deposits
Mercury	Hg	Considered non-essential	Very toxic	In some gold deposits and other sulphide deposits
Cadmium	Cd	May be essential to some animals	Toxic	In zinc and phosphorus deposits
Chromium	Cr	Essential to some organisms	Cr ⁶⁺ highly toxic	In some sulphide and platinum group deposits
Arsenic	As	Essential for some organisms (e.g. humans)	Toxic	In many types of sulphide deposits

Zinc serves as a catalyst in enzymes that are active in the build up of the hereditary material, DNA. Special metals such as molybdenum and manganese have key tasks in the photosynthesis and nitrogen metabolism. In all cases metal ions bind to oxygen, nitrogen or sulphur atoms. When heavy metals are causing toxic effects they also then bind to proteins but in ways that block the function of the target proteins. It is again their avidity for the oxygen, nitrogen or sulphur atoms in proteins that explains the toxicity.

The flow of metals in society

As opposed to living cells, society uses metals mainly in their pure metallic form and for their outstanding technical properties. A household in the Baltic Sea region today most likely has several tonnes of metals, at least if they own a car, and of great variation. This should be contrasted with the situation some 150 years ago when a family in Sweden, most likely typical for Europe, owned about 8-10 kg of metal, to be used for specific purposes. It was not only iron and steel in tools, but also tin in household items, lead in windows, gold and silver in jewellery, etc. Today about 30 metals are in general use, mostly in pure form, but mixtures of two or more metals (alloys) are common since they often have properties superior to those of the pure elements.

Metals may be categorised according to their technical use. Iron is a class in itself. Metals used mainly as alloys with iron, called ferro-alloy metals, include chromium, nickel, titanium, vanadium, and magnesium. The traditional non-ferrous metals are aluminium, copper, lead, zinc, tin, and mercury. Finally the precious or noble metals are gold and silver. All these metals, except titanium, chromium, nickel, and vanadium have been used since antiquity. The development and extensive use of computers and other electronic equipment has brought about the intensive use of several other metals. Although the quantities used are small, they may cause large environmental problems since their natural occurrence in the biosphere is extremely low.

Iron totally dominates the picture (Table 12.3). About 540 million tonnes are mined each year globally which is about 30 times more than any other metal. Second comes aluminium of which 18 million tonnes are extracted yearly. Both these are present in relatively high concentrations in the soil, are non-toxic and thus pose no special environmental problems. However, ionic aluminium in soil in higher concentrations is toxic to plants and in water aluminium ions are also toxic to fish, see Chapter 11. All other metals are mined in amounts that are 2% or less of these two together. Mined in amounts of the order of ten million tonnes annually are copper, zinc, manganese, and in amounts of one million tonnes are chromium, magnesium, and lead.

The extraction of metals often requires clearing or draining of land, and movement of large amounts of other material, so-called overburden. In addition,

Metal ions participate in many reactions in living cells. Their biological properties may be characterised by their binding abilities. Three main classes may be differentiated (Nieboer & Richardson, 1980):

- Metal ions with oxygen ligands (Ca, Mg, Mn, K, Sr, Na)
- Metal ions with sulphur or nitrogen ligands (Zn, Pb, Fe, Cr, Co, Ni, As, V)
- Metal ions showing both features (Cd, Cu, Hg, Ag)

(Non-essential elements are indicated in italics).



Figure 12.2. Gold mine in Brazil. Mines are natural deposits of metal ore in concentrations that are commercially exploitable. In this mine, mercury is used for gold production, which increases its environmental impact greatly. (Photo: Lars Hylander.)

Metal	Concentration in soils (mg/kg)	Metals mining (ktonnes/year)	In extracted fossil fuels (ktonnes/year)	Mining + fossil fuels/ continental weathering
<i>Abundant</i>				
Al	72,000	18,000	34,000	0.05
Fe	26,000	540,000	34,000	1.47
<i>Scarce</i>				
Zn	60	7,300	260	8.31
Cr	54	3,800	34	4.62
Cu	25	9,000	55	23.83
Ni	19	880	570	4.83
Pb	19	3,300	85	11.67
Cd	0.35	20	3.4	4.42
Hg	0.09	5.2	10	10.86

Table 12.3. Global flows of metals. Indicators of global anthropogenic flows of metals compared to the natural turnover. Mobilization in continental weathering is calculated using average concentration in soils (column one) and suspended sediment flux of $1.5 \cdot 10^{16}$ grams per year in rivers. (Sources: Nriagu 1990, and Azar et al., 1996.)

large amounts of tailings, slag, and waste water are often produced. Typically, extraction of one tonne of copper requires processing of about 800 tonnes of ore, and would thus leave 799 tonnes of solid waste. For five grams of gold, needed for a ring, about one cubic meter or 3-5 tonnes of ore can be required, that is close to 1 million times as much solid waste as pure metal. For iron the relative amount of waste is smaller, about six times that of the metal, but on the other hand it is extracted in much larger amounts. This extra weight is included in what is called the ecological rucksack of the metal and of course also causes environmental impacts. The extraction of copper is particularly destructive, very often leading to large intrusions into the landscape.

Metals are the third most abundant material flow, other than natural materials such as sand and gravel. First are the fossil fuels: carbon as coal, oil, and gas (Chapter 10); and second are the macro-nutrients (Chapter 9): phosphorus, sulphur and calcium. Today, in all three categories, the vast majority of the flows are linear, based on non-renewable resources, and need to be managed differently in a sustainable society. Some metals are also approaching the state when known resources are emptied.

The enormous flow of metals in society poses two environmental problems. One is the possible toxic effect of dissipated metals. The other are costs connected with the extraction and use of these large flows, in terms of use of fossil fuel, landscape intrusion, and so on. We will come back to how to approach these problems at the end of the chapter.

METALS AS ENVIRONMENTAL POLLUTANTS

Metals in the environment

Metals are emitted to the environment from many different point sources, the most important ones being industries, waste incinerators, coal power plants, traffic, and agriculture. Mines and smelters may cause very severe local contamination in their surroundings. The smelters in the former Soviet Union e.g. the nickel smelter in Murmansk, have created a veritable industrial desert in the surroundings up to at least a 15 km distance, with elevated levels of nickel, copper, and lead. Similar locally heavily polluted environments exist in Russian Karelia, and southern Poland. The smelter Rönnskärsverken on the Swedish Baltic Sea coast, previously very polluting, is today much improved. All these industries also emit large amounts of acidifying sulphuric acid and

Table 12.4. Consumption emissions of different metals. The values are expressed as estimated parts per part during a 10 year period for each kind of use. Thus 0.01 indicates a 1% loss to the environment during a 10 year period or 0.1% per year for the use given. (Karlsson, 1997.)

Use / Metal	Ag	As	Cd	Cr	Cu	Hg	Pb	Zn
metallic use	0.001	0.001	0.001	0.001	0.005	0.05	0.005	0.001
plating, coating	0.02	0	0.15	0.02	0	0.05	0	0.02
paint, pigments	0.5	0.5	0.5	0.5	1.0	0.8	0.5	0.5
electric tubes, batteries	0.01	0.01	0.02	na	na	0.2	0.01	0.01
other electric equipment	0.01	na	na	na	0.1	na	na	na
chemical uses in final production	0.4	0.05	0.15	0.05	0.05	na	0.75	0.15
chemical uses not in final production	1	na	1	1	1	1	1	1
agricultural biocides	na	0.5	na	na	0.05	0.8	0.05	0.05
non-agricultural, biocides	na	0.8	na	1	1	0.9	0.1	0.1
medical, dental	0.5	0.8	na	0.8	na	0.2	na	0.8
miscellaneous	0.15	0.15	0.15	0.15	0.15	0.5	0.15	0.15



the effects of the different components in the emissions may be difficult to differentiate.

Diffuse heavy metal sources are most important for mercury and cadmium (European Environment Agency, 1998; Stanners and Bordeau, 1995). The emissions of heavy metals to the environment in Europe, measured as air emissions, have decreased continuously from the peak years 1965-75. The introduction of modern technologies in western Europe and reconstruction of the technologically old industry in the former Eastern block have reduced emissions significantly during the 1990s.

Large amounts of metals are also released from the soil during natural weathering processes. In Scandinavia there are several examples where groundwater with extremely high contents of heavy metals from mineralisation occur naturally. Such springs can be found in several places and often the vegetation is poisoned in the outflow areas.

This release may be dramatically increased as a result of acidification or extended drainage of peat bogs by ditches. A drop in pH from seven to four increases the leaching of manganese, cadmium, and zinc from soil by a factor of about 10 (Swedish EPA, 1993). Bioavailability and sedimentation of the metals in the water body also depends on eutrophication. Increased eutrophication leads to the removal of heavy metals from the water column as they are bound to the sediments.

Metallurgic industry

The metallurgic industry is in many ways the largest industry in the region and constitutes a significant environmental problem. The environmental threat starts already when an ore is extracted at the mine. Underground mines are less destructive to the surface landscape. However, strip mining, where the ore to be extracted is found in a comparatively thin layer close to the surface, leads to the destruction of large land areas. Cases where large areas have been devastated are the strip mining of copper, and lignite or brown coal, at some sites in Poland, and, even more so, the strip mining of oil shale in Estonia.

The area of some old mines no longer in use have successfully been returned to a more natural state. Others have often been turned into lakes or underground rooms for various purposes. The ancient salt mine outside Krakow in southern

Figure 12.3. Strip mining of brown coal or lignite at Belchatow, central Poland. Coal is one of the main sources of metal pollution, as the metals in the coal, e.g. cadmium and mercury, is emitted during combustion. The Belchatow power plant, seen in the background, is the largest brown coal powered plant in Europe. (Photo: André Maslennikov.)



Figure 12.4. Oil shale mining in northwest Estonia has given rise to entire mountains of slag, which contain a considerable level of metals in a complex mixture. Metals leak to the environment with e.g. rain water and contribute to the metal contamination of the Gulf of Finland. (Photo: Rein Vålme.)

Poland is used for parties and conferences, while the old copper mine at Falun in central Sweden is a popular tourist site, now also a UNESCO World heritage site.

Mining leads to the management of large amounts of water, pumped from the mine or used in the production process. Enormous volumes of water from mines in southern Poland contain high concentrations of salts, mainly sulphates and chlorides, and heavy metals, which are drained into the rivers Wisła and Odra, which have water with a considerable salt concentration in their upper parts.

Extraction of metal, normally through reduction of the ore with carbon, requires large amounts of energy and produces enormous amounts of solid waste, as ash, slag, or tailings. Reduction of metal from sulphide ores, e.g. copper sulphides, gives rise to large amounts of sulphur compounds in effluents, flue gases, and the ashes after the process. The copper smelter in Rönnskär in northern Sweden, the titanium dioxide production plant in Pori in Finland, and the metal smelter in Harjavalta (outside Pori), were very important point sources of heavy metals and inorganic acids in the Bothnian Bay/Bothnian Sea area, but are today much improved.

The waste produced from mining is the largest amount of solid waste in society. The ecological rucksack from hard coal mining is about six times the amount of coal, and for lignite the figure is nine times. Both these activities constitute major sources for heavy metal pollution. Thus, the Polish coal mining gives rise to considerable amounts of heavy metal pollution. Slag as well as ash after coal combustion leaks heavy metals to ground and surface waters and thereby constitute a long-term environmental problem. A large source of heavy metals as well as phenol pollution is the oil shale mining in north-eastern Estonia. The intensive utilisation of the oil shale results in approximately 200,000 tonnes of fly ash (containing large amounts of heavy metals) emitted into the atmosphere per year. The most abundant metals in the flue gases are lead (36 tonnes/y), zinc (36 tonnes/y), copper (6.6 tonnes/y), cadmium (0.8 tonnes/y), and mercury (0.04 tonnes/y).

Also ordinary landfills leak considerable amounts of heavy metals. In general, waste is a troublesome source of heavy metal pollution, both when deposited and incinerated.

The metallurgic industry, producing everything from needles to ships, is thus environmentally damaging, mainly not due to the metal used but rather because of the production technologies. Fortunately the emissions from the production of metals have declined, at least in the west, and emissions today tend to emanate mostly from the consumption phase. A list of discharges from the iron, steel, and non-ferrous metal industries is given in Table 12.4.

Metals in water – the Baltic Sea

Almost all waters in Europe have an increased level of heavy metals as compared to unpolluted waters. The levels are higher in northern Europe. The concentrations of metals such as copper, cadmium, nickel, and zinc are remarkably higher in the Baltic Sea as compared to other marine environments, e.g., the North Sea and the Atlantic. The sources are transboundary air pollution, fallout of metal-containing dust, and heavy metals carried to the Baltic Sea by rivers. In many cases also the natural background contents are high, often in areas rich in mineral deposits.

Within the framework of the Baltic Marine Environment Protection Commission (HELCOM), monitoring data on riverine and direct land based waterborne pollution load have been collected and compiled three times since 1987. The aim is to evaluate the effectiveness of different measures taken to reduce pollution in the Baltic Sea and to determine the order of priority for different pollution sources.

The riverine load of heavy metals is the largest source of pollution accounting for approximately 90%, except perhaps for cadmium (Helsinki Commission, 1998). The municipal and industrial wastewater discharges together with diffuse

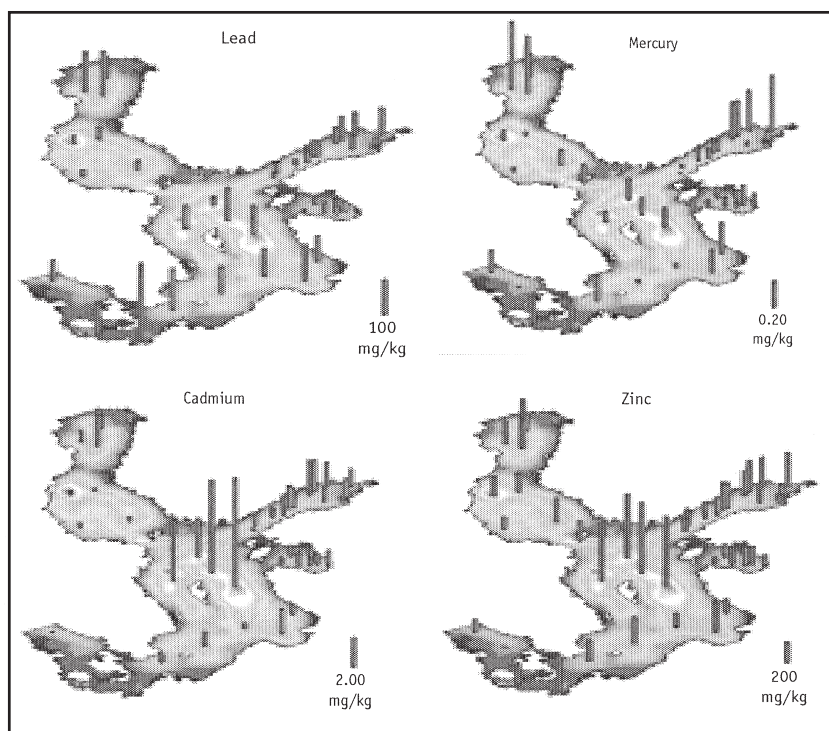


Figure 12.5. Levels of metal contamination in the upper sediment layers of the Baltic Sea. The sources are rivers, deposition on the surface, and effluents from municipalities and industry (values in mg/kg, dry mass of sediment). (Source: Helsinki Commission, 2001.)

discharges within the river catchment areas are probably the main sources of the riverine load. The cadmium load data from Russia from municipalities and industrial plants discharging directly into the Gulf of Finland are very high. A compilation of the data from 1995 is presented in the Table 12.5.

The most affected area of the Baltic Sea is the Gulf of Finland, where the eastern part is receiving poorly purified waste water from the Neva river. The other heavily polluted area is located in the Bay of Gdansk. In 1995 the Wisła river, which is draining 40% of Poland, deposited 1,455 tonnes of zinc, 173 tonnes of lead, 177 tonnes of copper, 13 tonnes of cadmium, and 67 tonnes of mercury. In the Baltic Sea the levels of metals are always higher near the shores, with smaller differences for cadmium (about 30 ng/l) but very high for mercury (2 – 630 ng/l). Data from around 1995 suggest that about 20 % of cadmium and mercury and about 35 % of lead comes from deposition of air pollutants and slightly more than 50 % from the river outflows. Other sources are urban centres and industries on the shores (Table 12.5 and Figure 12.8).

It is more convenient to analyse metals in sediments than in the water phase itself, because the concentrations are usually higher in the sediments. Sediment analyses can also provide information on metal levels in the past, discovering the history of metal pollution several hundred years ago. Pre-industrial levels of metals can also be detected through analyses of specimens stored at biological museums. Also, samples from recently taken samples are specially preserved in so-called specimen banks. They will be used for future comparisons. It is expected that improved technology will result in a strong reduction in the levels of metal contamination.

METAL	Rivers	Municipalities	Industries	TOTAL
Mercury	11,580	1,140	610	13,330
Cadmium	16,410	6,590	610	23,610
Zinc	3,584,180	360,660	87,930	4,032,770
Copper	1,469,200	75,880	49,630	1,594,710
Lead	300,500	32,940	3,960	337,400

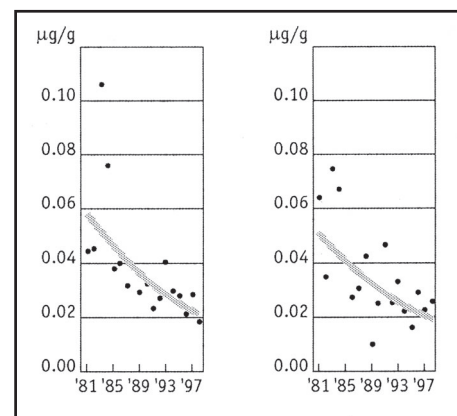


Figure 12.6. Lead concentration in fish liver. Left image shows concentration of lead in cod of the Baltic proper and the right shows lead concentrations in cod of the Kattegat. (Source: Helsinki Commission, 2001.)

Table 12.5. Heavy metal loads to the Baltic Sea (kg per year 1995). (Source: Helsinki Commission, 1998.)

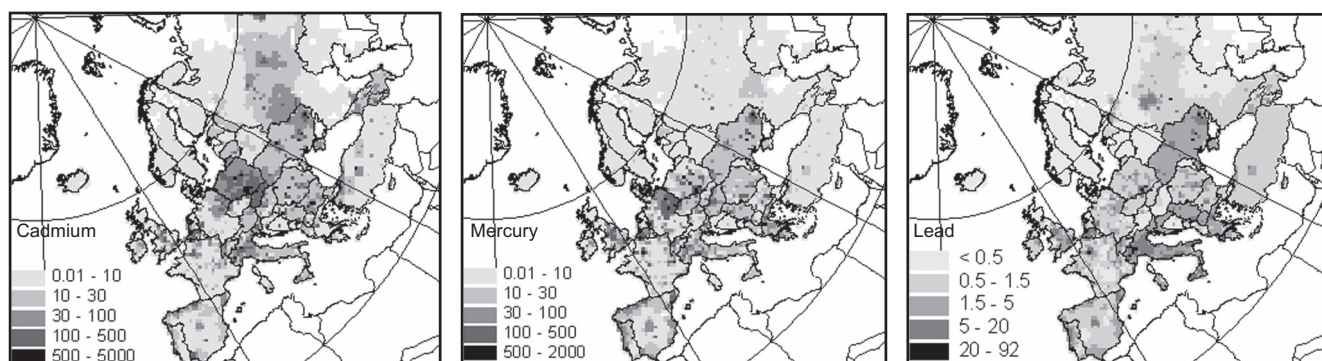
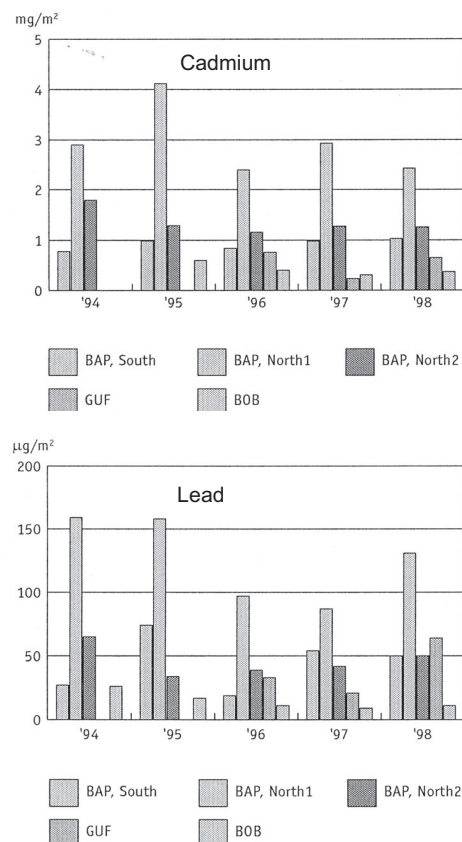


Figure 12.7. Anthropogenic emissions of cadmium, mercury, and lead in Europe in 1999. Values are given for cadmium (left), mercury (middle), and lead (right). The spatial resolution is 50x50 km and values are given in g/km² per year (cadmium and mercury), and kg/km² per year (lead). (Source: Meteorological Synthesizing Centre-East; EMEP. <http://www.msceast.org/hms/emission.html#Spatial>.)

Figure 12.8. Deposition of cadmium and lead on the Baltic Sea. Monitoring was done at five stations: 1) southern Baltic proper, 2) northern Baltic proper 1, 3) northern Baltic proper 2, 4) Gulf of Finland and 5) Bothnian Bay. Values are given in µg/m² per year, which is also g/km² per year, for cadmium and mg/m² per year, which is also kg/km² per year for lead. One-third of the lead, and one-fifth of cadmium and mercury, in the Baltic Sea comes from atmospheric deposition. It is assumed that Germany and Poland are the major sources for this fallout (see Figure 12.6). No clear trends between years were obvious during the assessment period 1994-98 (Helsinki Commission, 2001).



The upper sediment layers in the Baltic Sea have been found to contain over 10 times higher concentrations of cadmium and mercury than the deeper sediment layers, demonstrating a continuously increased anthropogenic load of these metals. For lead and zinc the levels are three to five times higher. Concentrations of arsenic, copper, and cobalt have been 1.5 to two times higher. In addition to the large-scale trends towards higher metal concentrations in the sediments, attention should be drawn to the high load of metals in several limited near-shore regions in the Baltic Sea (e.g., the Gdansk Bay and the Bothnian Bay) caused by large local, mostly point-source discharges (Figure 12.8).

Metals in atmospheric deposition

Eventually, most of the heavy metals that are emitted from urban and industrial areas and spread through the atmosphere end up in vegetation, whether they are dissolved in precipitation or carried by particles. The dense carpets usually formed on the ground by *Hylocomium splendens* (stair-step moss), *Pleurozium shreberi* and other mosses have been found to be particularly efficient at trapping deposited metals. They act almost like a filter (Rühling and Tyler, 1970; Rühling and Steinnes, 1987). One of the reasons for this is that mosses lack the outer protective layer of cells found in higher plants. They are thus in more direct contact with the surrounding atmosphere and successfully collect nutrients arriving with air and precipitation. Heavy metals can take the same route and end up being stored in moss tissues. By contrast, mosses take up insignificant amounts of metals and other substances from the soil. Concentrations of metals in the moss cover can thus be used as a gauge of the atmospheric deposition. With the moss method a great advantage also lies in the fact that it is possible to measure the accumulated metal deposition over a period e.g. in mg per m² and year.

Following an initial survey of heavy metal levels in mosses in Scandinavia in 1968-71, more detailed studies have been carried out in Sweden every five years since 1975. In 1980 a moss inventory was performed in Denmark in parallel with the Swedish survey, and since 1985 metal concentrations in mosses have been surveyed on a Nordic basis, bringing in Norway and Finland as well. Some pilot studies have now also been carried out in North America. Other European countries were invited to participate in the 1990 inventory. As a consequence the latest results, 1995-96, have recently been presented for 21 countries in Europe (Rühling and Steinnes, 1998).

In the Nordic countries the atmospheric background deposition levels decrease towards the north. This pattern is especially pronounced in the case of cadmium, lead, and vanadium, which points to the conclusion that a major part of this metal deposition is still due to long-range transport from the more densely populated areas of Europe. The concentrations of chromium, nickel, and to some extent zinc also show weak south-north gradients. The industrial and mining activity in the Kola Peninsula influences northern Norway and Finland with considerable deposition of nickel, copper, iron, and chromium. In southern

Finland the impact from the emissions across Gulf of Finland from the St. Petersburg area and the Isthmus of Karelia is also of importance. In the Baltic republics, the prevailing wind direction is from the south-west and west carrying with them pollutants from industrialised central Europe.

The monitoring shows a decrease of most metal depositions since 1970. For example the cadmium deposition in Denmark and Norway decreased by 35% only between 1985 and 1990. Most other metals have also decreased in the Nordic countries. For the countries outside the Nordic area there are no time series dating further back than 1990/91. However, there also seems to be a decrease in these countries.

Metals in soil

The Baltic Soil Survey (BSS) has established a directly comparable database of major and trace elements in agricultural soils within all countries surrounding the Baltic Sea. The project was carried out at the end of the 1990s by several of the Geological Surveys in the Baltic Sea region and show the elements in topsoils and

Methods

Box 12.2

Mosses for biomonitoring

While in many circumstances a correlation between metal concentration in living organisms and in their environment does not exist, mosses offer an unusually safe method for biomonitoring metal pollution. It is the "stem" called the *thallus* (plural *thalli*) of the mosses that are used when analysing metal content (Figure 12.9.).

Thalli of mosses are very useful for biomonitoring of pollution because:

- they have no roots and transport tissues,
- get minerals necessary for life from wet and dry deposits,
- have thin cellular walls of epithelial cells, and cells are permeable for water and minerals,
- constituents of their cell walls are rich in anion groups ready to bind heavy metals, and



Figure 12.9. Mosses used as biomonitors of metal pollution. Mosses are efficiently used to monitor deposition since they absorb substances from the air directly. They thus accumulate substances absorbed over a period of time. As metals are not degraded they can be measured precisely. (Photo: Pawel Migula.)

- in some mosses (i.e. *Hylocomium splendens*) it is easy to separate yearly increases of thallus, a convenient feature for time related analysis of exposure.

One of the cheapest and a quite effective methods used for biomonitoring is a distribution of plastic bags with thalli of mosses (often *Fontinalis antipuretica*) on target areas for a given period of time (e.g. for 2 months). After this time, the bags are collected and metal content is determined to obtain a picture of deposition of pollution (Figure 12.10.).

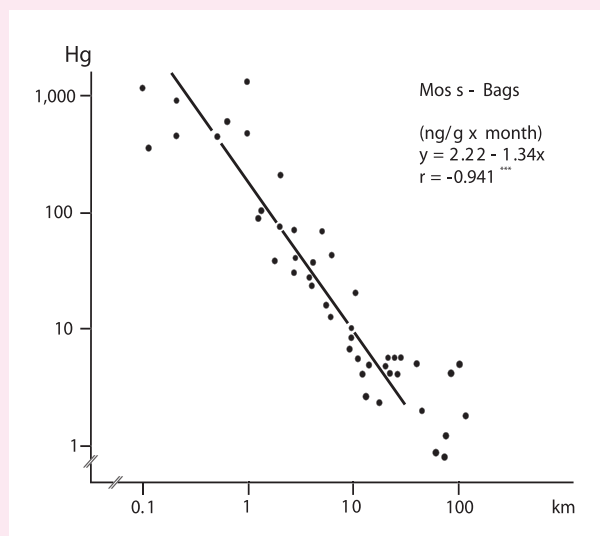


Figure 12.10. Mercury monitoring using moss bags. The role of distance for mercury pollution was studied in this experiment. The distance from the source of emission is directly related to the amount taken up by the moss bag. (After Lodenius, 1990.)

Case

Box 12.3

Regional geochemical mapping in the Baltic Sea region

In most countries in the Baltic Sea region, geochemical mapping is mainly carried out by the national geological survey. These maps are of immense value in environmental work as they show for example the heavy metal content in different media such as soils, waters, bedrock, and plants. They give information not only on the natural background values of the heavy metals but also the anthropogenic impact.

The Geological Survey of Sweden started a monitoring/mapping programme in 1980. A biogeochemical method is used that reflects the metal concentrations in streaming water. The roots and mosses used for the programme respond closely to chemical variations in background levels related to different bedrock types as well as effects of pollution. The biogeochemical samples provide information on the time-related *bioavailable* metal content in the environment. The biogeochemical mapping programme now comprises about 50% of the land area of Sweden (40,000 sample points), where about 80% of the population of Sweden is living. Parallel to this programme there is also an ongoing extensive soil geochemical mapping programme. This means that the Geological Survey of Sweden now has an extensive data base of

analyses for use in environmental and geomedical research (Geology, 1994).

In Finland, geochemical maps of the whole country have been published showing the element contents, including heavy metals, in soils, stream sediments, and waters.

In the Baltic states and Poland, extensive mapping of heavy metals has also been carried out. Geochemical atlases have been published covering the whole of Estonia and Lithuania as well as several regions in Poland, for example Silesia, which is an area of high pollution. In most cases, stream sediments, water, and soils are sampled and analysed (Geochem Atlas Polski, 1995; Jarzebski, 1997). Also Germany has been covered by geochemical maps showing the metals in the environment (Geochem. Atlas Bundesr. Deutschland, 1985).

In the Kola Peninsula, a large international multimedia mapping project has been carried out. Terrestrial moss, humus, topsoil, and B and C-horizons of podzol profiles have been sampled in an area of 188,000 km² (Reimann et al., 1997).

Olle Selinus

subsoils. The results show that element levels and variations are quite different from country to country and area to area. They mostly reflect differences in local geology. The results demonstrate that setting action levels for heavy metals in soils for a whole country or the whole of Europe may not be wise. It is not possible to use the very old Clark values (medium values of the Earth's crust) any longer to differentiate between "background" or natural concentrations and "pollution" as often attempted in environmental science. Levels of element in top and sub-layers of the soil are surprisingly comparable. The results suggest that local but widespread sources such as automobile traffic or agriculture may have a more important regional impact on element concentration in the top-layer than industrial emissions. Phosphorus is the one element showing a major build-up in the top-layer, which is due to landuse practices.

When the buffering capacity of the soil is insufficient, acid rain may cause trace element imbalance in plants and, via plants, in herbivorous animals. Certain essential trace elements, such as selenium and molybdenum, become less soluble in an acidic environment and their availability to the plants decreases. For grazing animals changes in the uptake via plants may result in changed metal concentrations as well as imbalance between metal concentrations in different organs, with severe consequences. Liming is used against acidification but recent investigations indicate that liming has serious side effects. The change of pH may cause negative health effects in plants and wild ruminants as the mobility of certain naturally occurring metals, micronutrients as well as toxic metals, can be altered.

THE HEAVY METALS

The forms – metallic, salts and organo-metallic compounds

In society we use, as has been mentioned, most metals in their metal, elemental, form. This is true for everything from golden rings to railways. In this form metals are easy to use, collect and are seldom toxic. A notable exception is mercury, since the pure metal is easily volatile and may be inhaled. Another is lead, e.g. from motor emissions and battery factories.

The elemental form of a metal is more or less easily turned into ionic form by oxidation. It may then form salts. When, for example, a new red copper roof turns black and green it is because of the reaction with oxygen and carbon dioxide in the air. Metal salts are soluble in water and as such they are absorbed by plants and taken up by animals and humans as components or contaminants in air and water. Metal salts are used in a number of technical applications, e.g. paint: ferrous oxide is a classical red paint, lead oxide and zinc oxide are white, cobalt oxide is deep blue, and so on. Metal salts are often toxic and even used for that reason. Copper sulphate is a beautiful blue copper salt used in large amounts in gardening and wine production as a fungicide.

Several metals may form very stable compounds with organic radicals such as methyl, benzyl, ethyl, etc. These have often very useful technical properties. They are also typically quite toxic and often persistent. The organo-metal compounds are typically soluble in organic solvents and thus also fat tissue, and for that reason accumulate in fat tissue when taken up in the body.

Mercury forms several different compounds with e.g. methyl and phenyl radicals. Methyl-mercury and phenyl-mercury were used already in the 1950s to treat seed as a protection against pests. Methyl-mercury in grains eaten by birds and rodents, however, accumulated in food chains and led to ecological disasters. The Minamata bay disaster in Japan in the 1950s, one of the pollution events that started the concern over the environment world-wide, was caused by methyl-mercury. The substance was released from a factory into the bay where it was eaten by fish which ended up on the dinner tables of the people living in the area. The people got sick from mercury poisoning and a total of 36 people died before anybody understood what was going on. Cats were also badly affected, a clue when finding out that the fish was the source of the



Figure 12.11. A hospital in Minamata Japan in 2001. The 40-year old man in the wheelchair was born paralyzed. He is one of the victims from the 1962 mercury poisoning disasters that killed over 100 in the village and harmed many more. The Minamata disaster was a turning point in history of concern for the environment. (Photo: Lars Hylander.)

Figure 12.12. The mercury cell hall in the Skoghall chlor-alkali industry. This hall houses 200 tonnes of metallic mercury. The production of chlorine from electrolysis of sodium chloride solution was changed from using mercury cells to the so-called membrane method in 1987. Still there are two factories using the mercury cell method in Sweden and some 60 in Europe, many of them in Russia, 40 in Germany and 2 in Poland. These factories were the largest mercury polluters as metallic mercury was lost from the cells, which were yearly receiving large refills of the metal. Today the refills are reduced to 100 tonnes/year in western Europe, of which at least 10 tonnes are lost to air, water and products. In Sweden, mercury cells will be outlawed in 2010. (Courtesy of AkzoNobel Industries.)

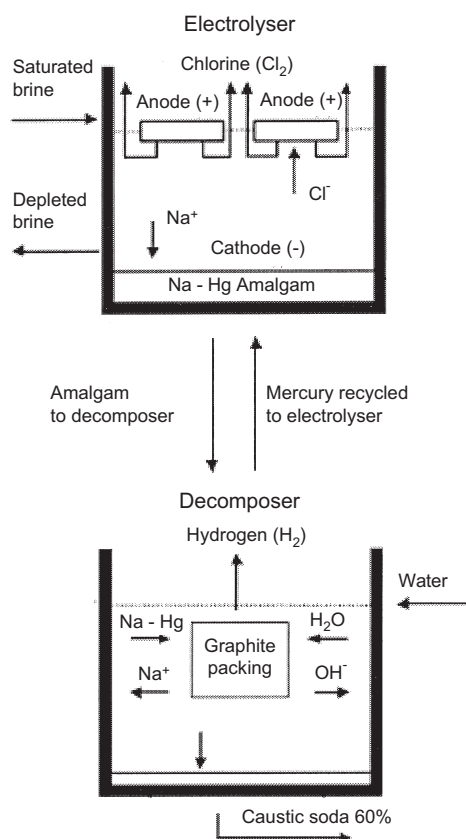


Figure 12.13. Mercury cell used in the chlor-alkali process. Mercury is used in the anode of the electrolyser. Sodium amalgam formed in the electrolysis is transferred to a decomposer cell. As water is added sodium hydroxide and metallic mercury is formed. The mercury is recycled to the electrolyser.

problem. Short-sighted economic interests dominated and emissions of mercury from the factory continued for nine more years after the cause of the disease was established. This resulted in up to 10,000 people getting the disease and more than 100 people died (Subaki and Takahashi, 1986) although the exact figures are very uncertain.

Organic lead compounds, tetraethyl-lead, are used as anti-knock additives in gasoline (nowadays prohibited in many countries). Lead gasoline caused diffuse pollution of large amounts of lead. As it is part of car exhausts it is breathed by pedestrians, not least children, and therefore a serious source of lead pollution.

Tetraethylated zinc is a very efficient component for treatment of small boats to protect them from unwanted growth of algae. The poison is slowly released into the water and kills certain molluscs efficiently, which has eradicated these from large parts of the Baltic Sea coasts.

Mercury pollution

Mercury (Hg) is the only naturally occurring liquid metal, although it turns solid during cold winters in the north of the Baltic Sea region. Pure (elemental) mercury has a relatively low boiling point (357°C) and is, consequently, easily spread through the atmosphere in vaporised form. There is therefore a growing concern about mercury exposure to humans, also in regions far away from the suspected pollution sources. In general, more than 95% of the total mercury content of the atmosphere is in the elemental form. Mercury vapours is quite hazardous, as it is inhaled and easily absorbed. Mercury is, however, easily transformed into the ionic form, and as such it will adsorb onto particles or water droplets in the air, and be deposited with precipitation. The transformation from elemental to ionic form is accelerated by the presence of other oxidising air pollutants, such as ozone. Some 20-60% of the mercury in untreated flue gases from incineration is emitted in the ionic form, bound to particles. The residence time of particle-bound mercury in the atmosphere ranges from a couple of days to weeks, which means that it can be transported several thousands of kilometres before it is deposited. Elemental mercury has a residence time of up to two years.

The distribution pathways for mercury in the environment are very complex. It is transported through the atmosphere, both in water-soluble and insoluble form, and appears often as amalgams, mixtures, with other metals. The many

Outlook

Box 12.4

Mercury and gold mining

Large amounts of mercury is used for gold mining in several developing countries. Mercury is used during gold mining to dissolve gold dust in sand, thereby forming amalgam. Pure gold is then produced by heating the amalgam so that mercury evaporates and is emitted to the air, leaving the pure gold behind. In the Amazon alone, some 2,000 tonnes of mercury has been emitted in this way during the two latest decades (Veiga and Meech, 1995). Most of this mercury has been imported from Europe. The fish in the gold mining areas have increased levels of mercury in their flesh, thereby poisoning the local population, whose staple food is fish. The gold miners are also exposed to mercury vapour, especially when amalgam is heated. The mercury emissions to the air contribute to the global burden of mercury. There is a law in Brazil against using mercury for gold mining. In spite of this, the gold miners are the main contributors to mercury emissions in Brazil. The export of mercury from Europe contributes to environmental crimes in Brazil.

LH

Figure 12.14. Extraction of gold by mercury. Goldiggers in South America often use the method of adding mercury to get a heavy amalgamate which sinks as the sand is washed. When the recovered heavy pieces are heated, mercury is vaporised and pure gold remains. The unprotected person in the photograph, from a gold mining area in Venezuela, was exposed to mercury vapours. (Photo: Lars Hylander, 2001.)



and various forms in which mercury appears are quite different with regards to distribution patterns, solubility, and toxicity.

Mercury present in ores and fuels is emitted to the environment through e.g. burning of fossil fuels. It is also emitted from solid waste incinerators, coming from e.g. electrical batteries and thermometers in the waste, and from mining and dental clinics. Mercury is also used in production of electric equipment, such as smoke detectors, fluorescent and mercury lamps, and in paints. In Sweden smoke from crematoria is today a dominating source of mercury, where it comes from teeth repaired with amalgam.

One very important source of mercury contamination of the Baltic Sea region has been the production of chlorine and caustic soda, in which chlorine and sodium hydroxide are produced from water and sodium chloride by electrolysis. In one old process, the so-called mercury-cell method, the separation of chlorine and sodium hydroxide is performed by a mercury electrode, forming sodium amalgam, which then is transformed to sodium hydroxide. Diffuse leakage of mercury from the cells and a leakage in connection with the handling of mercury in the manufacturing stage have seriously contaminated the surroundings of such plants. Enhanced levels of chlorinated organic pollutants have also been found in the vicinity of chlor-alkali industries.

Today, alternative methods for the production of chlorine and sodium hydroxide have found increased application. The most obvious advantage of these alternative methods, known as the diaphragm method and the membrane method, is the fact that they are mercury-free. In addition, the membrane method uses less energy. The drawback of both methods is, however, more diluted sodium hydroxide.

Mercury compounds were the causes of several serious early environmental hazards. Over a period in the 1960s the concentrations of mercury in fish in Swedish lakes increased markedly and fishing in many lakes was banned. Regrettably, the mercury contents in the environment today is still increasing and poses a problem. The reason is that during the period when there was a larger deposition of mercury than today, large pools of mercury were built up in the soils. Partly because of present acidification, mercury from these pools

Hundreds of tonnes of virgin mercury is produced yearly in Almadén, south-west of Madrid, where the worlds most important mercury mine is situated. The production was 673 tonnes of mercury in 1998 and 433 ton in 1999. About 85% of the production is exported, primarily to China, the Philippines, Brazil and other developing countries. The emissions to the air are estimated to be around one kilogram mercury per hour during the production of mercury in Almadén. This resulted in more than four tonnes mercury being emitted to the air during 1995, when 1,500 tonnes of mercury was produced (Gobi International, 1999).

Gilders in St Petersburg

When the Isaac Cathedral in St Petersburg was built in mid 19th century the huge copper roof and many other details were covered with gold. Some 100 kg of gold was used for gold plating. The gold was mixed with mercury and the liquid amalgam was painted on the copper plates. Thereafter the plates were heated in special workshops to evaporate the mercury and leave the pure gold behind in a thin layer. This was the most dangerous part since mercury was inhaled by the workers. It is reported that some 60 workers died of mercury poisoning.

This is only one case of gilding work at the time. Many other buildings and sculptures were gilded both in St Petersburg and other cities.

Mercury in lakes

Many thousands of lakes in Sweden and Finland were polluted by increased levels of mercury. As a result these lakes were blacklisted, meaning that commercial fishing was not allowed. Black-listing has today been replaced by a recommendation that pregnant and breast-feeding women should not eat fish from Swedish lakes, and other persons not more than once a week.

Mercury measured in fecalia of Finns who had mercury dental fillings showed 17 times higher levels than in fecalia from others who never had had this type of filling.

becomes mobile and once more affects living organisms. In 40% of the Swedish lakes (40,000 lakes) pike have mercury contents exceeding 0.5 mg/kg wet weight (w.w.), which is the limit for human consumption recommended by Codex Alimentarius (United Nations).

The average concentrations of mercury from different sites in the Baltic Sea does not significantly differ from that in the north-eastern Atlantic. The main pathways through which mercury enters the Baltic Sea are river discharges (8-44 tonnes/year), atmospheric deposits (4-29 tonnes/year), and direct discharges from cities and industrial plants.

In fish mercury is bound as methyl mercury. The highest levels of mercury is reached at the top of both salt and fresh water food chains, so that predatory fish and predatory birds eating fish have the highest Hg concentrations. In Finland up to 6.9 mg/kg w.w. were found in pike from Lake Kirkkojärvi, and the mink from Finnish archipelago had nearly 6 mg/kg in their liver. Grey seals had the highest concentrations of Hg in liver (Table 12.6).

Also inorganic Hg compounds used in paints or batteries are toxic, and the toxicity increases more than an order of magnitude when they are converted into more hazardous organic forms such as methyl mercury by bacteria. Biological processes in bottom sediments and water transform deposited mercury into the more toxic and more mobile forms, mono and dimethyl mercury. Bacteria in the aquatic system is responsible for methylation of mercury. The methylated forms of mercury are more fat-soluble than metallic mercury, which means that the methylated forms penetrate the blood/brain barrier to the brain and the placental barrier of pregnant mammals and humans. Methyl mercury binds firmly to sulphur compounds, making it persistent, with a biological half-life of approximately two years, and thus bioaccumulating in living organisms. It is easily taken up and transferred in the trophic chains, which leads to biomagnification.

Ultimately methylated mercury reaches humans through fish consumption. Seafood is the largest source of present day Hg exposure in the Baltic Sea region, while consumption of rice is the main source in some areas of China and dental amalgam for many inhabitants in the US. The levels of methyl mercury in offshore areas of the Baltic Sea are normally low, but in stationary predatory fish in some local near-shore regions, the levels are above 0.5 mg/kg w.w. People eating much fish absorb amounts of methyl-mercury, which are harmful to their health. Prenatal and growing children are most sensitive. Their brains are developing rapidly and Hg may lead to various irreversible mental abnormalities such as blindness, deafness, and paralysis, due to destroyed brain



Figure 12.15. Pike in blacklisted lakes. Pike is one of the fish which accumulates mercury in blacklisted lakes, to the despair of the young fisherman in the photo. In Sweden in the 1960s, large pikes had 5-8 mg Hg/kg w.w. (a few even more than 10 mg/kg in the 1950s. (Photo: Lars Rydén.)

Species and area	Cadmium		Mercury	
	median	range	median	range
Harbor seal - Skagerrak				
young healthy	0.21	0.07 - 0.44	3.56	0.72 - 7.69
young epizootic	0.32	0.16 - 0.78	2.84	1.24 - 7.30
adult	0.46	0.23 - 0.74	26	1.31 - 66
Ringed seal - Baltic				
young healthy	0.2	0.02 - 0.24	0.44	0.20 - 0.85
adult	2.12	1.36 - 5.41	44.0	4.77 - 87
Grey seal - Baltic				
young healthy	0.93	0.25 - 1.93	15	7.03 - 37
adult	1.26	0.59 - 12.72	26	23.0 - 92

Table 12.6. Mercury and cadmium in Baltic Sea Seals. Concentrations of Cd in kidneys and Hg in livers of harbour, grey, and ringed seals from the Baltic Sea. Values given are mg/kg wet weight. (After Frank et al., 1992.)

cells. Lower exposure to methyl Hg leads to restricted visual field, and retarded mental development, manifested among school children by learning problems. Accumulation of Hg in seawater organisms is similar to accumulation of selenium. This means that freshwater organisms are more endangered, because selenium is known as a partial protective agent against Hg toxicity.

Cadmium – increased levels in biota

The overall cadmium (Cd) concentrations in the Northern Hemisphere have increased tenfold since the last century. The accepted daily human intake level of cadmium, recommended by WHO, is 64 mg.

Cadmium is emitted from various industrial processes, such as metal production, galvanising, production of plastic and oils for electrical transformers, mining of zinc ores with accompanying Cd, combustion of fossil fuels (especially coal), and the burning of unsorted waste containing, e.g., electrical batteries. It is also a common contaminant in chemical phosphate fertilisers, in sulphuric acid (produced from cadmium-containing sulphur dioxide), in red and yellow pigments, and in stabilisers. Relatively much Cd is also present in tobacco smoke.

Cadmium is the most mobile of the ordinary heavy metals. Cadmium accumulates in the renal cortex in the kidney, causing lesions. It is an element that leaves the body very slowly and is continuously accumulated throughout life as it is bound to low-weight proteins known as metallothioneins present in our liver and kidney. In many plant species, polysaccharides called phytochelatins play a similar role. In both cases, cadmium, as well as some other heavy metals, are withdrawn from the circulation and the cells are protected.

Cadmium acts as a probable carcinogen and causes fragile and malformed skeleton, so-called Itai-itai disease in Japan in the 1960s. In chronic exposure it may lead to lung and kidney diseases and deprives our immune system. That is one reason why it is important to reduce the use of this metal and handle it properly.

In Scandinavia, the amount of cadmium in soil that is available to plants is rising. This is due partly to acidification, but, in the case of farmland, mostly due to

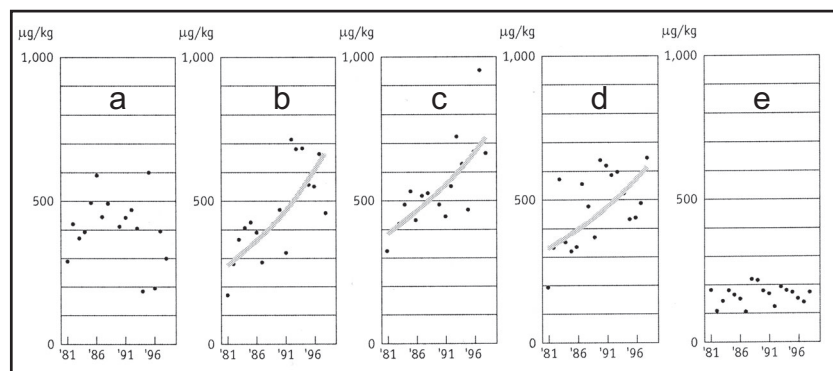


Figure 12.16. Cadmium concentration in herring liver collected along the Swedish coast during the 1980s and 1990s: a) the Bothnian Bay, b) the southern Bothnian Sea, c) the northern Baltic Proper, d) the southern Baltic proper and e) the Kattegat. If statistically significant a solid line shows the trend (Source: Modified from Helsinki Commission, 2001.)

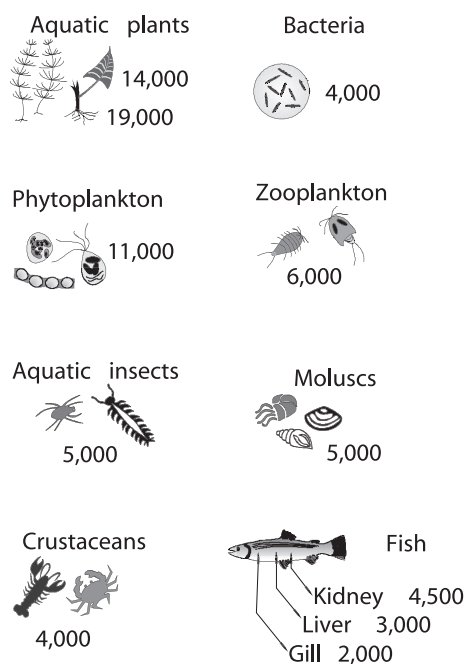


Figure 12.17. Bio-accumulation of cadmium. Organisms in an aquatic ecosystem polluted by cadmium bio-accumulate the metal along the trophic chain with concentration factors as indicated. (Compiled by Pawel Migula.)

the rather high concentration of cadmium in artificial fertilizers. The levels in many plants, including farm crops, have consequently increased. The uptake by plants increases still further when the groundwater becomes acidified. At the same time, people who are already ingesting dangerous amounts of cadmium, for instance by smoking, will be at grave risk if more cadmium gets into the drinking water.

Cadmium levels in biogeochemical samples (roots and aquatic mosses) are increased in the southernmost counties (Skåne) of Sweden and along the west coast of Sweden. Transboundary atmospheric transport and deposition of anthropogenic origin is the main reason in west Sweden. Parts of Skåne have in addition a high natural background level of Cd due to its geology. The Cd burden has been further engraved by intense use of fertilisers and waste water sludge containing Cd. This region is a densely populated farming region from which crops are distributed to the rest of Sweden. Samples of winter wheat from Skåne had an average of 73 $\mu\text{g Cd/kg d.w.}$ (dry weight), and several values exceeding 100 $\mu\text{g Cd/kg d.w.}$ In comparison, an area in central Sweden yielded on analysis only 29 $\mu\text{g Cd/kg d.w.}$ on average in autumn wheat. The Cd contents in wheat from Skåne is therefore a matter of concern. However, wheat from abroad may contain even higher levels of Cd, since most countries have still not realised the risk of Cd. In addition, durum wheat, the wheat sort generally used for pasta and spaghetti take up more Cd than the Swedish wheat sorts. In Skåne, drinking water from wells had an almost identical distribution of high Cd contents as depicted in the biogeochemical map. For drinking water, the WHO has set a limit of 5 $\mu\text{g Cd/L.}$ In comparison, some wells in Skåne, within the region with a high Cd burden, have average levels of about 400 $\mu\text{g Cd/L.}$ In this area, moose also accumulate elevated contents of cadmium.

Several interacting factors contribute to the high Cd concentrations in this region, including deposition of airborne Cd, acid rain from Eastern, Western and Central Europe, and cadmium from local sources, not the least phosphate fertilizers used in agriculture. However, recent studies have shown that the high contents of Cd are probably derived from the sedimentary bedrock (sandstones with disseminated Cd). Therefore we have a reason to believe that we have a connection between geology, acidification, and possible health effects caused by cadmium.

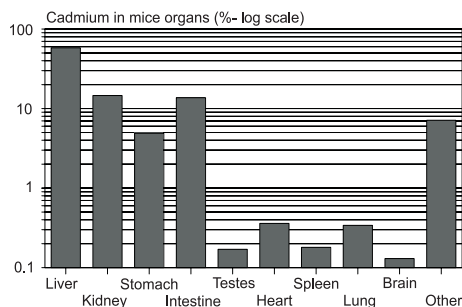
In the same region the selenium contents are also high, derived from sedimentary bedrock. This could be lucky because selenium and cadmium are antagonistic elements. Elevated selenium contents may decrease the harmful effects of cadmium.

Cadmium reaches the Baltic Sea mainly through the atmosphere, via rivers, and by means of direct discharges from point sources along the coast. The regional variations in the cadmium content of water are fairly small with mean concentrations of approximately 30 ng/L , with some higher values reported from the near-shore regions, e.g., in Poland (260-270 ng/L).

The concentrations of cadmium in fish (cod and herring) and in mussels have been reported to range from 2 to 200 $\text{mg/kg fresh weight (fish)}$ and 1,300-10,800 $\text{mg/kg fresh weight (mussels)}$, respectively. Humans receive most of the cadmium (80-90%) with food. The exposure of humans to cadmium today has dramatically increased and might be even more than a 1,000 times that of our ancestors.

There is a tendency towards a more restricted use of cadmium in a number of countries in the Baltic Sea region today, and substitutes for cadmium in many applications already exist or are being developed. In Sweden, cadmium is outlawed and its use will eventually be phased out totally. Collection systems for nickel-cadmium batteries for recycling purposes have been established in many countries, which is a typical example of a way by which the general consumer can participate in the efforts to lower the emissions of toxic substances into the environment.

Figure 12.18. Relative distribution of cadmium in organs of mice. Cadmium accumulates in kidney and liver as it is bound by special cadmium binding proteins. (Source: Migula, 1993.)



The main analytical methods used for analysis of elements are:

- Atomic Absorption Spectroscopy (AAS),
- Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES), and
- Inductively Coupled Plasma- Mass Spectroscopy (ICP-MS).

Atomic Absorption Spectroscopy (AAS)

This method is used for analysis of a broad range of metal ions. A solution of a sample containing the metals is heated to vapour using *flame or electrical heating*. Radiation from a hollow cathode lamp is passed through the flame with the vaporized sample where the metals are atomised, and absorb a part of the radiation proportional to their amount in the sample. The cathode lamp is coated with the element to be analysed to provide the appropriate wavelength.

The beam goes onto a monochromator and then to an amplifying detector. A computer fed with the detector signal recalculates the results compared with calibration curves, which show straight line relationships in narrow concentration ranges. The wavelength and amount of radiation absorbed allow measurement of the kind of element present and at what concentration.

The basic parts of the AAS system are presented in (Figure 12.19). The flame is generally a mixture of air-acetylene or nitrate oxide-acetylene (for higher temperatures).

For mercury determinations a *cold vapour* method is applied where this element is reduced to the elemental state by a solution of tin at room temperature.

An up to 1,000 times higher sensitivity is achieved when the sample is treated in a carbon furnaces equipped with electrothermal heating. A very small sample is injected into a hollow graphite cylinder which is electrically heated so that the sample is rapidly vaporised. The light beam is then passed through it and the spiked absorption signal is measured as before (Figure 12.20).

Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES)

ICP-AES is another commonly used technique, and is very convenient for measurement of several elements simultaneously in the same extract. The excitation of metal atoms to be analysed takes place in argon gas, inductively heated by electromagnetic waves in the radio frequency range. Atoms in the sample are heated to much higher temperatures than in flames, about 8,000°C, which turns the sample into a plasma. The emission of light is increased exponentially with temperature allowing the detection limits to be dramatically extended. The frequency and intensity of the emitted light is used to identify and quantify the elements. (Manahan, 1994) (Figure 12.21).

Inductively Coupled Plasma Mass Spectroscopy (ICP-MS)

ICP-MS is a method where the atoms in the sample, excited into a plasma through application of a radio frequency, is accelerated in an electric field. The atom beam is deviated in a system of magnetic lenses and finally registered as it hits the detector. Extreme sensitivity is achieved as each atom produces an impulse. As the mass number of the atom is registered all metals are resolved into their component isotopes. The instruments used are advanced, but can certainly not distinguish between an atom and a radical of the same mass but originating from different elements. Hence, a major difficulty is to prepare samples without elements (e.g. from the extractant) disturbing the analyses of studied elements. Another is to avoid background contamination. A range of new applications has become possible, since the ICP-MS method can be used to measure various isotope ratios of studied elements in biological samples.

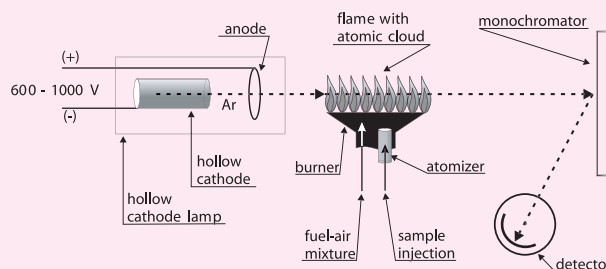


Figure 12.19. Atomic absorption spectrophotometer. (After Manahan, 1994.)

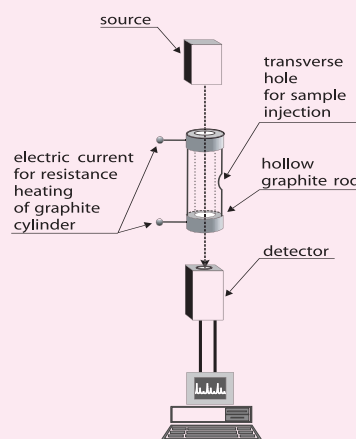


Figure 12.20. Atomic absorption spectrophotometer with graphite furnace. (After Manahan, 1994.)

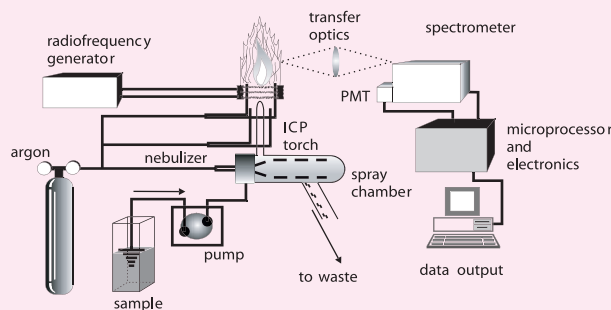


Figure 12.21. Inductively coupled plasma-atomic emission spectrometer, ICP-AES. (After Fifield and Haines, 1996.)

Table 12.7. Sensitivity of methods for metal analysis. Values are given as detection limits in µg/g of sample for some metals for the different analytical techniques (Perkin Elmer, 1988.)

Metal	Flame AA	Hg/hydride	GFAA	ICP -emission	ICP-MS
Cd	0.5		0.003	1	0.02
Cu	1		0.02	0.9	0.03
Hg	200	0.008	1	20	0.03
Ni	4		0.1	4	0.03
Pb	10		0.05	20	0.02
Se	70	0.02	0.2	60	0.5
Zn	0.8		0.01	1	0.08

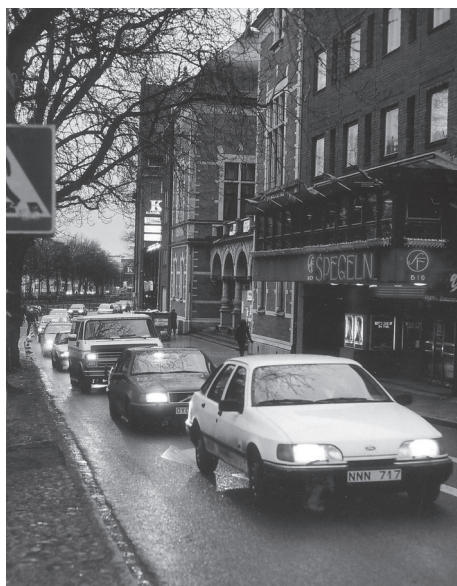
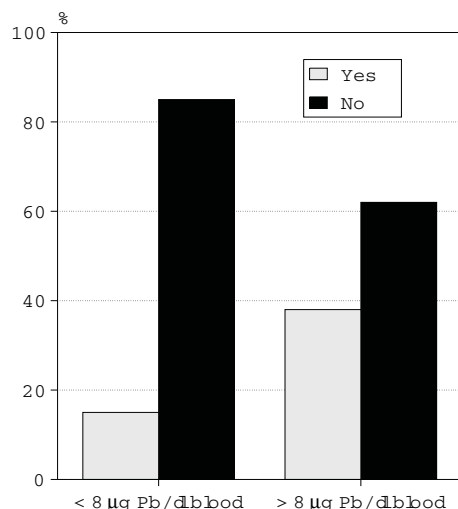


Figure 12.22. Lead in petrol. Tetra-ethyl lead in car fuel was for a long time the major cause of lead pollution. Since 1996, only unleaded fuel is used cars in the Scandinavian countries and mostly in the other countries in the Baltic Sea region. (Photo: Lars Rydén.)

Screening analysis of blood lead levels is very important for occupational health in areas at risk of Pb contamination. A good example is the small town Miasteczko Slaskie in southern Poland where emissions from a large non-ferrous plant significantly polluted the surrounding environment in a very short time. The correlation between blood Pb level and learning difficulties in 10-11 years old children was obvious. The critical Pb level is about 8 µg Pb/100 ml blood.

Figure 12.23. Effects of lead poisoning. Percent of children 10-11 years of age with some learning difficulties that live in a Pb polluted area. (Source: Norska-Borowka, 1999.)



Lead – declined levels but hazards still exist

Lead (Pb) is also a common heavy metal causing severe irreversible alterations of health, especially in young growing organisms. As compared to other toxic metals humans use vast quantities of this metal. Global use was in the late 1980s 5.5 million tonnes yearly of which 60%, that is 3.3 million tonnes, came from newly extracted metal. In the Baltic Sea region, Sweden and Poland were big producers with, respectively, 2.4% and 1.4% of global mining. The use of lead has a several thousand years long history. Lead poisoning seems to have been a common problem already in the Roman Empire.

Lead is widely dispersed throughout the environment. It is estimated that 80-90% of lead in the air is released from vehicles utilising alkyl-lead gasoline. The introduction of un-leaded gasoline during the period 1990-96 has been 100% for all Nordic countries, and 40-80% for the other countries in the region (European Environmental Agency, 1998), however lead is still added to aircraft fuel. Another important but more locally distributed source arises from industrial and technological handling of lead, e.g. in mining of lead containing ores, zinc/lead melting plants, incineration plants, production of paints, car batteries, and other materials containing lead. Although lead is easily transported over long distances through the atmosphere, it seems to have a high tendency to concentrate in the vicinity of the point of discharge. Hence, increased levels of lead are found especially in areas close to highly industrialised centres with dense traffic. In rural areas air concentration of Pb is about 0.1 – 0.3 µg/m³ but in suburban areas it is about 3 µg/m³.

Fortunately, lead in the environment has strongly declined in recent years. This has been observed also in marine species. The concentration of lead in fish and blue mussels in the Baltic Sea has shown a decreasing trend since the early 1980s. The main reason is obviously to be found in the successful measures, which have been taken in order to lower emissions from industries. Another important reason is the increasingly restricted legislation regarding lead, which has resulted in an increased share in the use of unleaded gasoline to cars. The decreasing average levels of lead in blood of both children and adults fit very well to the decreasing trend of lead used. Both correlations have shown a significant decline from the late 1970s. By a simple calculation we can predict that 2-3 µg of Pb/m³ air will give 0.04-0.06 µg Pb/ml blood. We know that in a concentration exceeding 0.1 µg/ml blood, lead negatively influences processes of heme synthesis. In slightly higher amounts, Pb may cause alterations in the central nervous system. Monitoring of Pb levels in children at risk is thus very important. In areas close to zinc or lead smelters, the levels of lead are still much higher than the accepted 10 µg/100 ml of blood, reaching up to 50 µg/100 ml, a level indicating acute lead toxicity.

Zinc – no great problem

Zinc (Zn) is an essential trace metal which is necessary for the function of various enzymes. Zinc is as well one of the less toxic of the heavy metals (although it can be of a problem for e.g. aqueous organisms), but also one with the most wide occurrence.

If the zinc uptake of an organism is very large, the normal mechanisms for transport and excretion cannot balance the uptake. The levels in the tissues may then increase so much that the zinc becomes toxic. This can manifest itself when the zinc affects various biochemical processes in which it is not really supposed to participate. The toxic effect of zinc in living organisms seems mainly to be associated with the fact that it competes with other metals, mainly copper and iron, for their binding sites. The usual result is that the organism shows symptoms of a deficiency of the displaced metals. There are few or no examples of adverse effects in terrestrial plants and animals, including man, of a moderately elevated zinc exposure. Zinc is displaced from many of its sites when the stronger binding cadmium is present.

Case

Box 12.6

Heavy metal pollution in southern Poland

The first official Polish document of the Central Statistical Office (GUS) on the *State of the Environment in 27 Areas of Ecological Hazards in Poland* was published in 1984. Political and economical transition after 1989 changed significantly the levels of emissions of most environmental pollutants. The methods used by the Central Statistical Office to collect and report data have, however, underestimated the levels, as they did not include emissions from small enterprises, which since this year markedly increased in number.

Upper Silesia in southern Poland with a high industrial concentration, has been highly exposed to metal pollution. Even if emissions have decreased markedly during the last decade,

Table 12.8. Metal pollution in the Katowice area in southern Poland.

A comparison of yearly average concentrations of metals as air pollutants for the years 1990 and 1996. (From Jarzebski, 1997.)

Pollutant	1990	1996	Permitted level
Pb; ng/m ³	100-3,200	87-533	200
Cd; ng/m ³	2-119	2-104	10
Pb deposition; mg/m ² /yr	2-2,822	8-491	100
Cd deposition; mg/m ² /yr	0-87	0-110.6	10
Mn; ng/m ³	-	88 (max)	1,000
Cr; ng/m ³	-	15 (max)	400
Ni; ng/m ³	5-15	16 (max)	25

Table 12.9. Metal pollution in the Katowice area in southern Poland.

Concentration of Cd, Pb, and Zn in arable soil (0-20 cm). (Modified after Terelak et al., 1997.)

Metal	Area	Geom. mean (mg/kg)	Conc. range (mg/kg)
Cd	Katowice	1.1	0.10 - 49.7
	Poland	0.2	0.01 - 49.7
Pb	Katowice	50.9	10.0 - 1,723
	Poland	13.8	0.10 - 1,723
Zn	Katowice	116.2	5.0 - 2,837
	Poland	32.7	0.5 - 2,837

unhealthy levels of metals as well as persistent xenobiotics still exist, both in the air and in the soils (Tables 12.8 and 12.9).

The concentrations of heavy metals in soils are especially high around the smelters. Karweta (1980) studied the levels of zinc for ten consecutive years around a zinc smelter before smelting started. The level of Zn increased from 162 mg/kg in 1966 to 1,240 mg/kg of soil in 1976, Pb from 91 to 850 mg/kg, and Cd from 1.6 to 4.0 mg/kg. Concentration of Zn in 1976 in litter from the same area were about 10 times higher than in arable land. More recently the level of lead was found to be higher than 3,600 mg/kg (Godzik et al., 1998). The highest concentrations found close to the smelter in Szopienice were the extreme 34,000 mg/kg for Zn, 3,800 mg/kg for Pb and 290 mg/kg for Cd. Fortunately, all these smelters have been modernized or closed.

The total transport of zinc with Swedish watercourses to adjoining marine areas amounts to around 1,500 tonnes/year (mean value for 1992-94). Atmospheric deposition of zinc on the sea is about 1,000 tonnes/year (data from half of the surface area of marine areas bordering the Swedish coastline), while the direct zinc input to the sea from point sources and diffuse sources in Sweden can roughly be estimated as 400 tonnes/year.

The zinc concentration in seawater is lower than in fresh water, and consequently it is higher in the more fresh-water influenced waters of the Bothnian Bay than in the southern parts of the Baltic Sea. Compared with deeper sediment layers, which represent conditions 100-200 years ago, the zinc concentration in the superficial sediment layers in various parts of the Baltic Sea is on an average 1-2 times higher. Greater concentration differences are found outside the Rönnskär smelter for example.

Significantly elevated zinc concentrations have been measured in some parts of the Stockholm harbour area, something which may be related to an elevated organic content and oxygen deficiency, factors which both raise the zinc concentration. The average zinc concentration in the surface sediments in the inner and outer archipelagos is, however, only slightly higher than in both the deep, oxygenated bottoms of the central Baltic Sea, and in pre-industrial Swedish lake sediments, despite the nearness to greater Stockholm.

Chromium

Chromium (Cr) is essential for some organisms. Three-valued chromium, Cr³⁺, is considered to be relatively harmless, while six-valued chromium, Cr⁶⁺, is highly toxic. Some Cr⁶⁺ compounds are known to be carcinogenic. The main

uses of chromium is for stainless steel and other alloys, chrome plating, pigments, tanning, wood impregnation, and refractory bricks. In Scandinavia, there are several examples of tanning factories with chromium pollution.

The anthropogenic sources of chromium in the environment are mainly derived from leakage from waste deposits, corrosion of stainless steel and other alloys, from traffic (e.g. the studs in winter tyres), impregnated wood and leakage from agriculture. The main point source of chromium pollution in Sweden is the alloy plant Vargön in western Sweden.

According to the moss monitoring programme described earlier the deposition of chromium and nickel has decreased in Sweden with 60-80% between 1970-1995. The deposition in Sweden is now almost on a level which can be characterized as natural deposition. Metal contents in sediments in profiles in the different basins of the Baltic Sea have been compiled (Borg and Jonsson, 1996). Relatively small differences can be seen between the different basins and between the surface sediments and the pre-industrial sediments. Increased chromium levels can normally be seen in the Baltic Sea proper.

Arsenic

Arsenic (As) is not a heavy metal, however, it is often discussed in connection with metals because it is a toxic element, released together with several heavy metals. The toxicity depends on valency: As^{5+} , arsenate, compounds are less toxic than As^{3+} , arsenite, compounds.

Long term exposure to inorganic arsenic can give rise to health effects in a large number of organs, for example skin, lungs, liver, cardiovascular system, nervous system and reproductive system. There is evidence that arsenic also has a physiological role affecting methionine metabolism in animals. Toxicity is inhibited when ingested with selenium. Arsenic is a constituent of most plants. The uptake of arsenic into crop plants is of concern, since this provides an entry of the toxic element into the food chain.

Worldwide natural emissions of arsenic into the atmosphere in the 1980s totalled 1.1 to 23.5 tonnes per year, derived mostly from volcanoes, wind born soil particles, sea spray and biogenic processes. The thousand fold larger values for anthropogenic emissions are mostly attributed to pyrometallurgical non-ferrous mining and production, iron and steel manufacturing and coal combustion. Coal combustion alone accounts for 20% of the atmospheric emissions, and arsenic from coal ash may be leached into soils and waters. Atmospheric emissions of arsenic in Europe, peaking in the period 1960-65 at around 11,500 t per year fell to 4,570 t per year by 1985. At this later date, over half of the emission was from USSR. Forward projections estimate emissions for Europe to fall to about 1,900 tonnes As in the year 2000 and about 1,600 t in 2010, with Russia accounting for around 30% of the total.

A considerable portion of the arsenic dissemination comes from wood preservation practices. The volume of wood preserved in Sweden for example was in 1995 about 280,000 m³, out of which 78,000 m³ went to the home market. This is a large volume to put into waste deposits and problems will be seen in the future in water contamination at saw waste deposits at impregnation sites and at waste deposits on the municipal level.

Contamination of the environment with arsenic, both from natural, for example in northern Sweden, and anthropogenic sources, is wide spread and may be regarded as a global issue. We will continue to find many more situations where contamination of surface and sub-surface waters and soils will increase. New occurrences will be found particularly in Central and Eastern Europe and the developing world. A very serious case of arsenic poisoning occurred during the 1990s in Bangladesh, and West Bengal in India, where a large number of newly drilled wells contained high levels of arsenic in the water, affecting more than 40 million people.

GOOD MANAGEMENT OF METALS

Stop dissipative uses

During their use metals are dissipated in society, the techno-sphere. This dissipation might be accidental such as when metal is left in infrastructure no longer in use, e.g. wires in the ground, various technical equipment or scrap metal left in the environment. It may also be intentional as when lead in ammunition or lead in leaded gasoline is dissipated. As an example we may look at 1989 data for Sweden for lead. The total turnover of lead in 1989 was 35,000 tonnes. Of this, 20,000 tonnes were recycled metal, that is about 60%, while the global average was 40% recycled metal. Thus 20,000 tonnes went back to products, mostly accumulators; 500 tonnes of lead was emitted to air and water while 3,000 tonnes ended in landfills the same year. A total of 11,500 tonnes were incorporated in built infrastructure that in time will leak into the environment, if not collected and recycled. It is estimated that Swedish society contains a total of about two million tonnes of dissipated lead since earliest times.

Metals, as has been mentioned several times, never disappear. They are elements and thus are always present. This property makes metals a special case in environmental management. If we want to get rid of them we have to find them and collect them. This can be difficult since metals are often dissipated with wind and water. Collection is much easier if the metal is used in a technical context. To make collection of metal possible, the dissipative uses have to stop.

Technical cycles of metals

Metals have possibilities to enter into a system of strict recycling, that is *technical cycles* rather than biogeochemical cycles. To keep dissipation in society on an acceptable level one would need to achieve more than 99.5% efficiency in such a system (Karlsson, 1997). This is technically possible, assuming that dissipated uses are discontinued. This would also lead to a situation where mining of virgin metal from ore could be reduced substantially, which is required by sustainability principles.

There are two reasons for introducing a system of technical recycling: to avoid environmental impact of toxic metals, and to reduce economic costs. Production from recycled metals is considerably cheaper than extracting metals from virgin ore. For example, when counting only on the use of energy and other material resources, the gain for copper is about 30 times. For aluminium it is even more. For iron, for which mining is comparatively cheap, the gain is about five times. It is clear that the profit would be considerable if one is able to organise an efficient system for collecting scrap metal. However, many metallurgic industries are set up to process virgin metal rather than recycled. Recycling of iron and aluminium, however, as well as copper, is today well developed in many countries.

Discontinue the use of toxic metals

The use of toxic metals has reduced markedly in Europe the last decade. The Swedish parliament decided in 1991 to limit the use of, and in the long term outlaw, mercury, lead, and cadmium. This decision is now in the implementation stage. Mercury is not used any longer except for fluorescent tubes and amalgam for tooth fillings. Thus, thermometers with mercury have not been sold since 1993. Toxic metals are never broken down to harmless products and thus everything ever used has to be collected. Collection of mercury dispersed in society is an important part of the Swedish policy to reduce the Hg stock, which otherwise is at risk of entering the biological cycle. Specially trained dogs have been used to sniff out mercury in

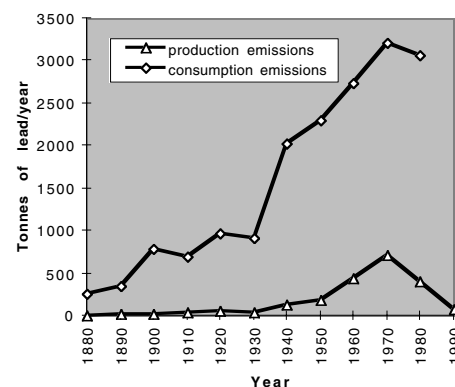


Figure 12.24. Production and consumption emission of lead to the environment in Sweden since 1880. Consumption emissions are large over the entire period. Production emissions, representing point sources, were well controlled around 1990. The beginning decline of consumption emissions in the late 1980s is due to introduction of unleaded gasoline. (Source: Karlsson, 1997.)



Figure 12.25. Refund methods. A refund on returned beer cans has turned out to be up to 90% efficient for recycling aluminium. It is legally required in Sweden, but not used in e.g. Denmark or Poland. (Photo: Inga-May Lehman Nâdin.)

Figure 12.26. Legally required recycling. Lead-containing accumulators are legally required to be recycled. They may be turned in at e.g. gas stations. This has established an almost 99% efficient recycling scheme in Sweden. (Photo: Inga-May Lehman Nâdin.)





Figure 12.27. Changing technology. The chlor-alkali factory outside Skoghall in west Sweden once used the mercury electrode method to produce chlorine. In 1987 the new membrane based technology was introduced, replacing all use of mercury. There has been a 100% change to this new technology in Japan, a partial change in Western Europe and USA, but no change has yet taken place in eastern and central Europe. (Courtesy of AkzoNobel Industries.)

schools and hospitals, etc. So far more than six tonnes of mercury have been collected at a cost varying between 70 and 1,300 US\$ per kg (Rein and Hylander, 2000). As a comparison the world market price of mercury has been around 4 US\$ per kg for the last years. Collected mercury will be disposed off in a deep rock storage with safety precautions resembling those for nuclear waste.

The use of mercury has also been markedly reduced in other EU countries. Sweden has a ban on the export of mercury, to avoid Swedish mercury becoming a burden to the environment in other countries. In contrast, the mercury mine in Almadén in Spain, the largest still active producer in Europe, sells its mercury to developing countries.

A major concern of phasing out mercury are the chlor-alkali industries. More than half the quantities of chlorine gas and sodium hydroxide in Western Europe is produced with mercury cells. In the USA, only 20% of this industry uses this old technology, while Japan substituted their mercury cells already 15 years ago (Harris, 2000). Converting from mercury cells to the membrane technology results in several advantages such as eliminated emissions of mercury and lower energy consumption. The chlor-alkali factories in all Europe emitted 41 tonnes of mercury in 1995, which is 12% of 342 tonnes, the estimated total anthropogenic mercury emissions in Europe. Within the European Union there are today 12,000 tonnes of mercury in chlor-alkali factories. It is socially as well as economically feasible to convert all chlor-alkali factories in the EU to mercury free technology by the year 2007. What then should be done with the mercury? Export of surplus mercury to developing countries is unsuitable for environmental and health reasons. In addition it is unethical. The policy of keeping the metal in long term storage in mountain rooms is preferable (Hylander, 2001).

REVIEW QUESTIONS

1. Enumerate the six most important metals used in society and order them according to the amounts used.
2. Define and describe *heavy metals* according to various definitions and give some examples.
3. Enumerate the most important biologically *essential* metals and give a few examples on their function in living cells.
4. Briefly describe the toxic effects of the biologically *toxic* metals mercury, lead, cadmium, and the semimetal arsenic.
5. Describe the three stages in *metal flows* – extraction, processing, and use – and indicate the possible or actual environmental impact at each stage.
6. Give at least six examples of usage of metals in their *metallic form*, in *ionic form*, and as *organo-metallic* compounds, and the environmental problems associated with each type of use.
7. Give a brief indication on the role of the *chlorine-alkali industry* in mercury poisoning and possible options for an improvement.
8. Describe the information that can be obtained when *analysing metals* on mosses, in the air, and in sediments in the Baltic Sea.
9. List three important *methods* of metal analysis.
10. Describe the usage of *mercury* in society and how it should be changed to make it environmentally acceptable.
11. Describe the usage of *lead* in society and how it should be changed to make it environmentally acceptable.
12. Describe the usage of *cadmium* in society and the most important sources for cadmium accumulation in humans.

LITERATURE AND REFERENCES

- Atlas Geochemiczny Polski* (1995). Warszawa: Polish Geological Institute.
- Borg, H. and P. Jonsson (1996). Large Scale Metal Distribution in Baltic Sea Sediments. *Marine Pollution Bulletin*, Vol. 32, No. 1, pp. 8-21.
- European Environment Agency (1998). *Europe's Environment. The Second Assessment*. Copenhagen: Elsevier Science Ltd.
- Fifield, F.W. and P.J. Haynes (1996). *Environmental Analytical Chemistry*. Blackie Acad. and Professional. London.
- Frank A, V. Galgan Roos., M. Olsson, L.R. Petersson and A. Bignert (1992). Metal Concentrations in Seals from Swedish Waters. *Ambio* 21, 8, pp. 529-538.
- Geology. (1994). *The Swedish National Atlas*. Ed Freden.
- Geochemical Atlas of the Humus Horizon of Estonian Soils (1997). *The Geological Survey of Estonia*. Tallinn and Uppsala.
- Geochemischer Atlas Bundesrepublik Deutschland* (1985). Bundesantalt für Geowissenschaften und Rohstoffe. Hannover.
- Gobi International (1999). *Mercury - a Gobi International Market Research Report on the World Mercury Industry*. London, United Kingdom. Website: <http://www.gobi.co.uk>
- Godzik S., P. Kubiesa, T. Staszewski and J. Szdzuj (1998). Ecological Problems of the Katowice Administrative District. In: D. Peakall, C. Walker and P. Migula (eds.). *Biomarkers*. Dordrecht, the Netherlands: Kluwer Academic Publishers.
- Harffy, J. (1997). Mercury Mining: Profit or Loss? *Nature* 390, pp. 112-113.
- Harris, M. (2000). Phase-out Issues for Mercury Cell Technology in the Chlor-Alkali Industry. Proceedings of the 2000 London Chlorine Symposium, Manuscript CL8 2/1999.
- Helsinki Commission (1987). *Baltic Marine Environment Protection Commission Report*.
- Helsinki Commission (1998). *Baltic Sea Environment Proceedings No. 70. The Third Baltic Sea Pollution Load Compilation (PLC3)*.
- Helsinki Commission (2001). *Baltic Sea Environment Proceedings No. 82. Fourth periodic assessment of the state of the environment of the Baltic marine area 1994-1998*.
- Hylander, L. (2001). Global mercury pollution and its expected decrease after a mercury trade ban. In: *Water, Air Soil Pollution* 125 (1/4):331-344.
- Jarzebski, L. (ed.) (1997). *Report on the State of the Environment in the KAD for the Years 1995-1996*. Katowice: Biblioteka Monitoringu Srodowiska. (in Polish)
- Karlsson, S. (1997). Man and Material Flows – towards Sustainable Materials Management. *A Sustainable Baltic Region. Session 3*. Baltic University Programme, Uppsala University, Sweden.
- Karweta, S. (1980). Effects of Industrial Air Pollution on Soil and Plants Contamination by Heavy Metals in the Upper Silesia Industrial Region. In: H. Janczewski (ed.). *Proceedings of the Conference on Effects of Air Pollution on the Environment*. pp. 314-324. Warszawa: NOT.

- Kirshner, R.P. (1994). The Earth's Elements. *Scientific American* 271 (October), pp. 58-65.
- Lodenius, M. (1990). *Environmental Mobilization of Mercury and Cadmium*. Department for Environmental Conservation, Helsinki University, Helsinki.
- Manahan, S.E. (1994). *Environmental Chemistry. Sixth Edition*. Boca Raton and London: Lewis Publishers.
- Migula, P. (1993). *Functioning of Animals in Areas Degraded by Industry*. Friedrich-Nauman Stft. V Polish German Ecological Forum, DiG Publ. pp.101-113.
- National Environmental Protection Agency (1990a). *Marine Pollution 1990*. Solna, Sweden.
- National Environmental Protection Agency (1990b). *Large Scale Environmental Effects and Ecological Processes in the Baltic Sea*. Report 3849. Solna, Sweden
- Naturvårdsverket (1997). *Terminal Storage of Mercury - an Important Step on the Road to a Sustainable Society* Rep 4752, Stockholm: Naturvårdsverket. (in Swedish and English)
- Nieboer E. and D. Richardson (1980). The Replacement of the Nondescript Term 'Heavy Metals' by a Biologically and Chemically Significant Classification of Metal Ions. *Environmental Pollution*, 1B, pp. 3-26.
- Norska-Borowska, I. (1999). The Influence of Environmental Pollution on the Health Status of Children in Upper Silesia. In: M. Nakonieczny and P. Migula (eds.) *Problems of Environment and its Protection*, Vol. 7, WNT EkoEdycja, Katowice, pp.103-112. (in Polish)
- Nriagu, J. O. (1990). Global Metal Pollution. *Environment* 32, pp. 7-32.
- Perkin Elmer (1988). Guide to Techniques and Applications of Atomic Spectroscopy.
- Reimann, C., M., Åyräs, V. Chekushin, I. Bogaturov, R. Boyd, P. Caritat, R. Dutter, T. Finne, J. Halleraker, Ö. Jaeger, K. Kashulin., O. Lehto, H. Niskavaara, V. Pavlov, M. Räisänen, T. Strand and T. Volden (1997). *Environmental Geochemical Atlas of the Central Barents Region*. NGU-GTK-CKE special publication.
- Rein, K. v. and L.D. Hylander (2000). Experiences from Phasing Out the Use of Mercury in Sweden. *J. of Regional Environmental Change* 1. pp 126-134. Springer-Verlag (See also the Website address below).
- Rühling, Å. and G. Tyler (1970). An Ecological Approach to the Lead Problem. *Botaniska Notiser*, 122, pp. 248-342.
- Rühling, Å. and E. Steinnes (eds.) (1998). *Atmospheric Heavy Metal Deposition in Europe 1995-1996*. NORD 1998: 15, 66 p.
- Stanners, D. and P. Bourdeau (eds.) (1995). *Europe's Environment. The Dobris Assessment*. Copenhagen: European Environment Agency, 676 p.
- Subaki, T. and H. Takahasi (1986). *Recent advances in Minamata disease studies. Methylmercury poisoning in Minamata and Niigata, Japan*. Tokyo: Kodansha. 214 pp.
- Thornton, I. (ed.) (1983). *Applied Environmental Geochemistry*. London: Academic Press. 501 pp.
- Trelak, T., T. Stuczyński, T. Motowocka and M. Trelak (1997). Content of Cd, Cu, Ni, Pb, Zn and S in Soils of Katowice Voivodship as Compared to Soils of Poland. *Archiv. Environ. Protection* 23, 3-4, pp. 167-180. (in Polish, summary in English)
- Tyler, G. (1970). Moss Analysis - a Method for Surveying Heavy Metal Deposition. In: H.M. Englund and W.T. Berry (eds). *Proc. Sec. Int. Clean Air Congress*. New York: Academic Press.
- Veiga, M.M. and J.A. Meech (1995). Gold Mining Activities in the Amazon: Clean-up Techniques and Remedial Procedures for Mercury Pollution. *Ambio* 24, pp. 216-220.
- World Mineral Statistics 1995-99 (2000). *British Geological Survey*, London, UK.

INTERNET RESOURCES

- American Metal Market, the daily newspaper of the metals and recycling industries
<http://www.amm.com/index2.htm>
- Arsenic and CCA Pressure Treated Wood
<http://www.origen.net/arsenic.html>
- Chronic Arsenic Poisoning: History, Study and Remediation
http://phys4.harvard.edu/~wilson/arsenic_project_introduction.html
- Coalition Clean Baltic
<http://www.lanet.lv/org/ccb/>
- EMEP on Heavy metals (HMs)
<http://www.msceast.org/hms/index.html>
- Environmental Working Group
<http://www.ewg.org/>
- Experiences from phasing out the use of mercury in Sweden.
<http://link.springer.de/link/service/journals/10113/contents/00/00016/paper/s101130000016ch110.html>
- Heavy Metal Toxicity
<http://www.ephca.com/metals.htm>
- International Minerals Statistics and Information
<http://minerals.usgs.gov/minerals/pubs/country/>
- Ken Friedman's homepage, Chemical backgrounder - heavy metals
<http://www.lehigh.edu/kaf3/public/www-data/background/hvymtl2.html>
- Medical Geology
<http://home.swipnet.se/medicalgeology>
- Mercury - a Gobi International Market Research Report on the World Mercury Industry. London, United Kingdom.
<http://www.gobi.co.uk>
- The National Network of Observation of the quality of the marine medium (RNO)
<http://www.ifremer.fr/delao/monitoring/network/rno/general.html>
- The new Protocol on Heavy Metals to the Convention on Long-range Transboundary Air Pollution, UN/ECE Release 24 June 1998.
http://www.unece.org/env_h.htm
- Present Conditions in the Baltic Marine Habitat
<http://www.envir.ee/baltics/frame1.htm>
- Reference document on Best Available Techniques (BAT) in the Chlor-Alkali Manufacturing Industry (BREF) 2000. Institute for Prospective Technological Studies, Seville, Spain.
http://www.eippcb.jrc.es/cgi-bin/locate?cak_final_5-12-00.pdf
- Trends in Pollution of Scottish Soils
<http://www.macaulay.ac.uk/tipss/index.html>
- UNEP. Global mercury assessment homepage.
<http://www.chem.unep.ch/mercury/>
- WebElements - The Periodic Table on the WWW
<http://www.webelements.com/>

382 METAL FLOWS AND ENVIRONMENTAL IMPACT

GLOSSARY

alloys

mixture of elemental metals; iron is often used in alloys with the so-called ferro-alloy metals, titanium, chrome, nickel, vanadium, and magnesium

arsenic (As)

a semimetal often discussed in connection with heavy metals because it is toxic and released together with several heavy metals

Atomic Absorption Spectrometry (AAS)

a method used for analysis of a broad range of metal ions, in which a solution of a sample containing the metals is heated to vapour using a *flame* or *electrical heating* and the radiation measured from a cathode lamp is absorbed by the atoms in proportion to their amounts in the sample

bioavailability

the extent to which a metal is available for uptake by living cells

chlor-alkali process

the production of chlorine and caustic soda, by sending electricity through a solution of sodium chloride in water; in the so-called mercury-cell method, the separation of chlorine and sodium hydroxide is performed by mercury in one of the electrodes

chromium (Cr)

is essential for some organisms; three-valued chromium, Cr^{3+} , is considered to be relatively harmless, while six-valued chromium, Cr^{6+} , is highly toxic; some Cr^{6+} compounds are known to be carcinogenic

deficiency

disease caused by lack of an element, such as iron deficiency causing anaemia and cobalt deficiency causing another form of anaemia, called “white liver disease”

discontinued metal use

the long term phase out and finally outlawing of metals; the use of mercury, lead and cadmium is being discontinued in Sweden after a 1991 decision in parliament; the decision is now in the implementation stage as mercury is hardly used in products any longer, and is being collected and to be stored in mountain rooms

dissipative uses

use of metals that lead to their dissipation, dispersion and loss in society, either accidentally such as when metal is left in infrastructure no longer in use, or intentional as when lead in ammunition or lead in leaded gasoline is dissipated

essential metal

an element, e.g. a metal, which is necessary in some amounts for biological functions of organisms, e.g., cobalt, copper, manganese, molybdenum, zinc, nickel, and vanadium

forms of metals

the elemental form of a metal, the *metallic form*, is more or less easily turned into *ionic form* by oxidation to produce salts, which may react with organic radicals such as methyl, benzyl, ethyl, etc., to produce very stable *organo-metal compounds*, often with very useful technical properties, but also typically quite toxic and often persistent

heavy metals

formerly defined as metals with a density greater than five, which explains their name, but their chemical properties expressed in the periodic system, are more essential for the classification; heavy metals form compounds with oxygen, nitrogen, and sulphur atoms, and thereby give rise to oxides,

sulphides, etc.; today the term is often used for metals which are toxic in the environment

inductively coupled plasma atomic emission spectroscopy (ICP-AES)

a commonly used sensitive technique for measurements of metals as well as As and Se in which the atoms in the sample, excited into a plasma through application of a radio frequency, is radiating at characteristic frequencies, and intensities proportional to their amounts

inductively coupled plasma-mass spectroscopy (ICP-MS)

a method where the atoms in the sample, excited into a plasma through application of a radio frequency, is accelerated in an electric field, where the atom beam is deviated in a system of magnetic lenses and finally registered according to their mass as it hits a detector

mercury (Hg)

the only naturally occurring liquid metal; mercury vapours are quite hazardous, as they can be inhaled and are easily absorbed

metal

an element which in elemental form is a good conductor of electric current and heat, and with a reflecting surface

metallothioneins

low-weight proteins present in our liver and kidneys, binding cadmium, which is continuously accumulated throughout human life

micronutrients

elements that are essential in very small amounts

monitoring metal deposition using mosses

using concentrations of metals in the moss cover as a gauge of the atmospheric deposition of metals; with the moss method it is possible to measure the metal deposition in mg per m^2 and year

mono and dimethyl mercury

microbiological processes in bottom sediments transform deposited mercury into the more toxic and more mobile forms, mono and dimethyl mercury; the methylated forms of mercury are more fat-soluble than is metallic mercury and therefore more toxic

regional geochemical mapping

geochemical mapping carried out mainly by the national geological surveys in each country, giving information on the natural background values of heavy metals and their anthropogenic impact

strip mining

mining from a comparatively thin layer close to the surface, which leads to the destruction of large land areas; strip mining of copper and lignite in some sites in Poland, and of oil shale in Estonia, have destroyed large areas

technical cycles of metals

when metals enter into a system of strict recycling, in *technical cycles* rather than biogeochemical cycles; to keep dissipation in society on an acceptable level one would need to achieve at least 99.5 % efficiency in such a system, which is technically possible

toxic metals

metals that are poisonous at low concentrations and give rise to toxic effects; mercury, lead, cadmium, copper, and some other metals have all been connected to various toxic effects in living organisms