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The Elements in the Second Rank

- an Environmental Problem Now or in the Future?

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Summary and Conclusions

For many years, heavy metals such as cadmium, lead and mercury have been known for their potential to cause serious negative effects on humans and the environment. Therefore, gradually, certain restrictions on the use of these metals have been imposed nationally and internationally, and limit values and quality criteria have been established to reduce emissions and discharges into the environment.

A result of restrictions on use can be that the most critical heavy metals become substituted by other elements that are assessed to be less toxic to humans or harmful to the environment. The substitution of cadmium with lithium in batteries can be mentioned as an example of this. Also a number of more exotic metals and metalloids, e.g. gallium and indium, are being introduced for a variety of applications and used in increasing quantities, often without any detailed beforehand knowledge or assessment of their possible adverse effect on health or environmental.

These "new" elements are within the framework of this project termed the "elements in the second rank" (whereas the traditional heavy metals are the "elements in the front rank").

The objective of the study was to collect, analyse and present the present knowledge of 11 selected "second rank" elements with regard to use pattern and consumption in Denmark, dispersal into and behaviour in the environment, hazards to human health and potential effects in the environment, primarily aquatic systems. The 11 elements were antimony, beryllium, bismuth, boron, gallium, indium, lithium, molybdenum, palladium, platinum and vanadium.

Due to the scarcity of data on the occurrence of the selected elements in environmental matrices, not least the waste streams of modern society, a limited programme of chemical analyses was conducted, which comprised municipal wastewater and sewage sludge, stack gas from municipal waste incineration (MSW), leachate from sanitary landfills and from depots for residual products from MSW incineration, and compost from household and garden biowaste.

The outcome of the study can briefly be summarised as follows:

Use pattern and consumption

The application areas of the second rank elements span over a wide range of functionalities and products. Many of the elements are used in modern electronic products including computers and telecommunication equipment and in alloys where the content can be limited to a few percent or even less.

Fossil fuels, in particular coal, contain low concentrations of most of the elements. The total quantity can, however, for some elements be considerable (depending on origin and quality of the coal) or even dominating; i.e. for vanadium up to about 400 tonnes out of a total of approx. 500 tonnes based on the present annual consumption of coal in Denmark.

The consumption of the second rank elements for other purposes than fossil fuel based energy production is estimated to be higher than 10 tonnes per year for antimony, bismuth, boron, lithium, molybdenum and vanadium, whereas the consumption of gallium and indium is less than 1 tonne per year. The yearly consumption of beryllium, palladium and platinum is estimated to be in the range 1-10 tonnes.

Effects on human health and the environment

Based on the available data, the following conclusions are drawn:

- Antimony, beryllium, boron, molybdenum, platinum and vanadium are classified as dangerous to humans and/or the environment, primarily based on experience related to occupational exposure;
- Antimony, beryllium and vanadium can have serious long term effects (carcinogenicity, mutagenicity or effects on reproduction);
- Antimony, bismuth, boron, palladium and platinum can cause sensitization;
- A number of compounds of antimony, beryllium, bismuth, palladium and platinum are highly toxic to aquatic organisms;
- The consumption and use of most of the second rank elements are increasing, but for the elements beryllium, gallium, indium, palladium and platinum the present use is still very limited and, consequently, the general risk of exposure is considered low at present;
- Boron and lithium are, at the present level and pattern of use, not believed to cause significant effects on human health or the environment;
- If the inherent toxicity and environmental toxicity of the elements are combined with consumption, use pattern and risk of dispersal into the environment, antimony and vanadium are assessed to be the most critical among the second rank elements at present.

Available data

The available data on the properties and use of the second rank elements are generally limited and insufficient to draw firm conclusions regarding possible impacts on humans or the environment. In particular, the data on long term health effects of beryllium, boron, gallium, indium, lithium, molybdenum, platinum and vanadium are rather sparse. The data on environmental properties of gallium, indium, palladium, platinum and vanadium are very incomplete.

1 Introduction

1.1 Background

When new products are developed or the requirements to quality and performance of existing products and production change, new materials and production processes are often introduced. Similar consequences can result when chemicals on the Danish Environmental Protection Agency's (DEPA) ”List of undesired compounds” are phased out or more strict limits are imposed for the working environment or for emissions to the environment.

Thus, substitution of e.g. mercury, lead, cadmium and chromium will increase the consumption and change the use patterns of metals, metaaloids and non-metallic elements, which previously were less used. Examples of this are the increased use of battery-powered electronics (lithium batteries), the dramatic increase in the number of personal computers during the last decade (a large number of "exotic" metals such as antimony in displays and printed circuit boards), and the introduction of catalytic converters containing platinum and palladium in the automobile industry.

Concurrently with this development, the demand for data on the use and flow of these "new" elements increases as well as the need of knowledge on their fate and effect in the environment. Until now, the focus has been on just a few metals from the classical industrial environment. These metals are the heavy metals lead, cadmium, chromium, copper, mercury, nickel, zinc, and to a certain extent arsenic.

It is beyond doubt still very important to be observant of these classical metals and work on their substitution with less problematic alternatives, but those efforts should not be an obstacle to considering the possible environmental consequences of the increasing use of “new” metals in our dynamic society. Therefore, the DEPA decided to support this study on the health and environmental aspects of a number of elements, which today are regulated very little, but which potentially can turn into environmental problems due to their inherent properties if the emissions into the environment increase.

1.2 Scope

The scope of the project was to collect and systematize existing data on health and environmental effects of a selection of the "new" elements. The data include use and consumption, dispersal and fate in the environment, and their adverse effects on humans and other organisms.

The report summarizes and evaluates the data of the selected elements. The data regarding use, consumption, health and environmental effects are presented in a short handbook format.

1.3 Project team

The project was carried out by the following project team from COWI A/S: Jesper Kjølholt (project manager), Frank Stuer-Lauridsen, Anders Skibsted Mogensen, and Sven Havelund.

The project steering group consisted of: Henri Heron, Chemicals Division of DEPA (chairman), Professor Finn Bro-Rasmussen, (Technical University of Denmark, DTU), docent Jens Christian Tjell, DTU, Jesper Kjølholt, COWI and Frank Stuer-Lauridsen, COWI.

Analysis of a number of selected emissions sources and waste products were included in this study. The measurements were conducted in the autumn of 2001. The major part was analyzed by Teknologisk Institut, Tåstrup, Denmark. The samples of stack gas from MSW incineration were analyzed by the laboratories that are in charge of the routine sampling program (dk-Teknik, Søborg, Denmark and Miljölaboratoriet AB, Trelleborg, Sweden, respectively).

We thank the following waste and waste waster companies and plants for kind assistance with the collection of samples: I/S Amagerforbrænding and I/S Vestforbrænding (MSW incineration plants, stack gas samples), AV-Miljø (landfill for gas cleaning residuals), DTU - Miljø & Ressourcer (sediment from road runoff retention basins), Lundtofte waste water treatment plant and Spildevandscenter Avedøre (treated municipal waste water), Noveren I/S (landfill leachate and compost) and Fakse Landfill (leachate).

1.4 Activities

During the project start-up, 11 elements were selected for the study. The selection was based on a screening of easily available information on the elements.

Data sheets with information from scientific literature, reports, databases, internet, and selected institutions have been prepared for each element. Each data sheet contains information on:

- uses and consumption
- dispersal and occurrence in the environment
- health effects
- environmental effects

Due to the scarcity of data on the presence of the selected elements in waste (and thereby the environmental burden), a limited analytical programme was conducted, which included treated waste water and sewage sludge, stack gas and gas cleaning residuals, landfill leachate, compost from municipal household waste and garden waste, and sediment from road runoff retention basins.

The elements were evaluated based on the information from the data sheets and compared to the corresponding features of the classical heavy metals.

2 Selecting Elements for this Study

2.1 The classical heavy metals

The project title "the elements in the second rank" indicates that there are also elements in the first rank. The first rank elements are those, which have been known for their adverse health and environmental effects for a number of years. Hence, they are regulated by limit concentrations, emission restrictions, ban, and out phasing programs exist on a national or international level. Furthermore, they are well examined regarding information on their use health and environmental effects.

From these criteria, the elements in the first rank are the classical heavy metals lead, cadmium, chromium, copper, mercury, nickel and zinc, and the metalloid arsenic.

The rare, but very toxic metal thallium could be included in this group. Today, its use has been restricted significantly. Also tin has received much attention in the last 10 to 15 years due to the toxicity of the organic tin compounds (especially butyl compounds) in the aquatic environment.

2.2 Selecting elements for this study

The elements in the second rank are more "exotic" than the elements mentioned above, and they have not received much attention. Therefore, the regulation on their presence and concentration in products, emissions or waste products is limited. To be regarded as a "second rank" element for this study, the element should have inherent properties, consumption pattern or disposal routes, which makes it a potential risk for the environment or human health.

In other words, the elements in the second rank are characterized by a potential for significant adverse health and environmental effects, including long-term effects. They are used in significant or increasing amounts in e.g. production of electronics, and the use or disposal pattern can result in dispersal in the environment.

Regarding health effects, the so-called CREAM effects (carcinogenicity, reprotoxicity, endocrine disruption effcts, allergenicity and mutagenicity) were considered. Regarding environmental effects, especially toxicity in long-term tests, persistency in the environment and potential for bioaccumulation were considered. It is noted that test of morphological, cellular and subcellular effects are relevant also, but these effects are generally little investigated. Therefore it was not expected to find data on these effects.

In the toxicological evaluation the organometalic compounds have not been considered, but inorganic compounds, e.g. salts, were included in the survey.

It was not possible to obtain data on all mentioned effects before selecting the second rank elements for this study. Hence, the selection was mainly based on data achieved from search in data compilations. This resulted in a gross list from which the elements for the final study were selected.

Compound	Notes
Aluminum	Large amounts, but well known metal. Evaluated recently.
Antimony	Large amounts. Flame retardants, electronics.
Barium	Large amounts. Possible substitute for lead in PVC.
Beryllium	Toxic. Electronics. Automobile industry. Telecommunications.
Bismuth	Possible substitute for lead. Glass. Electronics. Alloys.
Boron	Flame retardant. Wood preservative. Polymer additive.
Gallium	Electronics. Telecommunications. Environmental toxicity greater than for zinc.
Indium	Increasing use. Surface coating on glass/LCD
Cobalt	Large amounts. Thorough recent evaluation. Alloys.
Lithium	Large amounts. Batteries. Electronics. Ceramics.
Manganese	Batteries. Steel. Micronutrient.
Molybdenum	Large amounts. Alloys. Waste water/leachate.
Palladium	Catalysts (substitute for platinum). Electronics.
Platinum	Catalysts. More toxic than Pd.
Selenium	Medium amounts. Glass, pigments, alloys, electronics.
Silver	Medium amounts. Photo, soldering, catalysts. Toxic in the environment.
Tellurium	Iron/steel. Vulcanisation accelerator. Mutagenic and reprotoxic.
Titanium	Very large amounts. Pigment. Alloys. Low toxicity. Well known.
Vanadium	Large amounts. Alloys. Catalysts. Environmental toxicity not known.

From the list above, the following 11 elements were chosen for the study:

- antimony
- beryllium
- bismuth
- boron
- gallium
- indium
- lithium
- molybdenum
- palladium
- platinum
- vanadium

Among the elements on the gross list, aluminum, barium, cobalt, manganese, selenium and titanium were excluded due to recent, well documented evaluations and/or because they did not rise concern (e.g. titanium). Silver and tellurium were given low priority due to their stable consumption and lack of new application areas.

3 Elements in the Second Rank - an Overview

In this chapter the most important information on the 11 elements is summarized, while Appendix A contains more detailed data sheets for each element.

3.1 Uses and amounts

The metals are used in a wide spectrum of products, where the content can be as small as a few percent or less. Table 3.1 gives an overview of the main fields of use and the estimated yearly consumption of the metals in Denmark. The consumption estimates were in general calculated by multiplying the Danish population figure with the per capita consumption in USA. The expected consumption trend is reported as unknown, decreasing, constant or increasing. More information on the consumption can be found in the data sheets (Appendix A).

The data on use and consumption were obtained from a literature screening. The different usages are not prioritised with respect to the amount used. For some of the metals, the content in fossil fuels is very high compared to the other uses. Since the use of fossil fuels is not related with the content of trace metals, the amounts of the elements in the second rank resulting from energy production based on fossil fuels are given separately.

Table 3.1 Uses, yearly consumption and expected trend.

Element	Main uses	Amount (t/year, DK)	Trend in consumption
Antimony	Alloys, glass/ceramics, flame retardant, stabiliser in rubber, infrared detectors, cosmetics	840	Increasing
Beryllium	Metal- and electronic components, oil- and gas industry, dental alloy, sport equipment, X-ray equipment	5	Unknown
Bismuth	Alloys, electronics, pigment, plastic, pharmaceutical industry, cosmetic industry, lubricants, flame retardant	36	Unknown
Boron	Bleaching agent, metal alloys, plastic, biocide, flame retardant, Pyrex glass, dietary supplement	500*	Constant
Gallium	Electronics, photo diodes, solar cells, DVD's, CD's, metal alloys, UV-filters	0.24	Increasing
Indium	Electronics, LCD- displays, metal alloys, batteries	0.97	Increasing
Lithium	Perfume, pharmaceutical industry, lubricants, catalysts, batteries, metal alloys, plastic industry,	57	Increasing
Molybdenum	Metal alloys, pigments, plastic, catalysts, flame retardant, lubricants, dietary supplement	275	Constant
Palladium	Printed circuit board, catalysts, metal alloys	2.4	Increasing
Platinum	Printed circuit board, catalysts, displays, fuel cells	1.3	Constant
Vanadium	Metal alloys, catalysts, pigments, dietary supplement	96	Constant/ increasing

*only the consumption as bleaching agent

The majority of the metals are used in small or large scale in the metal industry in e.g. alloys. Many of the metals are used in electronics. As seen from Table 3.2, a relatively large part of the total amount of especially gallium, lithium and vanadium is found in coal. The Table shows minimum and maximum values for the content of the metals calculated from a yearly consumption of coal of 6.7×10^6 tonnes (Danmarks Statistik 2001). No data was found for ordinary heating oil.

Table 3.2 Estimated amounts of second rank metals in the total amount of coal consumed in Denmark. The amounts are based on the consumption of coal in Denmark in 2000 and the concentration of metals as given in Sternbeck and Östlund (1999).

Element	Amount in coal (t/year, DK)
Antimony	7-27
Beryllium	3-20
Bismuth	-
Boron	-
Gallium	7-235
Indium	0.2-1.3
Lithium	67-335
Molybdenum	-
Palladium	0-1.7
Platinum	0-11
Vanadium	67-400

Some details on the uses of the metals with the highest consumption, i.e. antimony, boron, molybdenum and vanadium are given below.

Antimony is used mainly as flame retardant, in lead alloys in batteries and infrared detectors. The consumption of antimony for lead alloys is decreasing due to their replacement with alloys that have a lower impact on the environment. Antimony is used along with e.g. polybrominated diphenyl ethers as flame retardant. Substitution of brominated flame retardants due to their adverse health and environmental effects will possibly result in decreased consumption of antimony. However, this drop in consumption will probably be counterbalanced by increasing use in the production of infrared detectors.

Boron is used for many purposes. The quantitatively most important use is in the form of sodium borate, which has the function of bleaching agent in detergents. Boron compounds are also used as e.g. flame retardant, biocide, dietary supplement and in the production of pyrex glass. The consumption is expected to be constant.

Molybdenum is used for alloys of steel - mainly specialty steel and stainless steel. Molybdenum is used as catalyst in the chemical and petrochemical industris, in colour pigments, as flame retardant and as dietary supplement. The consumption is expected to be relatively constant.

Vanadium is used mainly in the metal industry. It is used in titanium alloys, hard steel, and trade steel. Furthermore it is used as catalyst, pigments and dietary supplement. The consumption is expected to be constant.

3.2 Dispersal to and levels in the environment

When the metals are found in chemical combinations, e.g. as oxides or halides, the physico-chemical properties are significantly different from those of the pure metals. This applies for e.g. the aqueous solubility, which for most halides is very high. The character and extent of dispersal of an element into the environment varies according to the consumption, the specific chemical form and its physico-chemical properties. Table 3.3 reports the most important ways of dispersal of the metals to the environment with the different emissions and waste streams (as a sum of all metal compounds). The number of "x"s indicate the relative importance of the ways of dispersal for the individual metal. Thus, the number can not be compared within each way of dispersal.

Table 3.3 Qualitative overview of the most important ways of dispersal to the environment. The number of x's shows the relative importance of the ways of dispersal for the individual metal: "xxx" marks the main way of dispersal, "xx" marks an important way of dispersal and "x" marks a way of dispersal. No x's means that the way of dispersal is regarded as insignificant. The overview is based on an overall evaluation of the typical metal concentrations and the total mass flows of the different dispersal routes.

Element	waste water	sewage sludge	compost	waste (leachate)	gas cleaning waste (leachate)	stack gas
Antimony	xxx	xx	x	x		
Beryllium	x(x)	xx	xxx			
Bismuth	x	xxx	xx			
Boron	xxx	x	x	x		?
Gallium	xx	xxx	xx			
Indium	x(x)	xxx	x			
Lithium	xxx	x	x	x		
Molybdenum	xxx	xx	xx		x	x
Palladium	xxx	xx	xx	x		
Platinum	xxx	x				
Vanadium	xx	xx	xxx	x		(x)

Combustion of fossil fuels can result in emission of the trace metals found in the fuels. Data regarding metals in coal and oil shows that the level of the metals studied is highest in coal. However, certain oil types can contain relatively high levels of vanadium. Dependent on the physico-chemical properties of the metal, the applied technology in the incineration plant and the subsequent stack gas treatment, the metals will distribute differently between ash/cinder, stack gas cleaning residuals and stack gas.

Due to sparse literature data regarding the presence and concentration of the metals in the major waste streams in the Danish society, chemical analyses of a number of selected emission sources and waste products were included in this study.

Seven types of waste streams and waste products from which the metals can be dispersed into the environment were chosen: treated municipal waste water, sewage sludge, sediment from road runoff basins, compost from garden waste and municipal solid waste (MSW), leachate from controlled landfills, leachate from disposal sites containing residuals from waste incineration plants with semi-dry and wet gas cleaning technology, respectively, and cleaned stack gas from the same plants.

From each waste type, a representative sample was taken from two plants, except for garden compost, MSW compost, leachate from residuals from semidry and wet waste gas treatment, respectively. An overview of the results is given in Table 3.4, and more detailed results can be found in the data sheets.

Table 3.4. Concentration of metals in selected waste types. Each result is the average of samples from two plants. When individual values differ more than ±50% from the average value, both values are given.

Element	Treated waste water	Sewage sludge	Sediment, road runoff basin	Compost*	Leachate, landfill	Leachate, waste product**	Stack gas, waste incineration***
Unit	µg/L	µg/kg dw	µg/kg dw	µg/kg dw	µg/L	µg/L	µg/m3
Lead	0.33-1.9	110,000	210,000	39,000	2.6	320	18-280
Cadmium	0.12	3,000	2,200	440	0.35	13-670	1.3-24
Antimony	0.45-1.3	4,100	580-3,900	280	5.7	1.9-8.8	0.48-<5
Beryllium	<0.03	330	780	300	<0.03	<0.03	<2.6-<0.2
Bismuth	<0.03	1,500	500-1,900	140	<0.2	<0.2	<0.016-<5
Boron	800	76,000	44,000	33,000	1,700-9,400	1,100	-
Gallium	<0.02-0.12	2,200-6,400	4,700	1,800	0.24	0.23	<0.11-<0.2
Indium	<0.009	34-94	65	17	<0.04	<0.04	<0.045-<0.2
Lithium	16	5,500	16,000	4,700	49-200	330	<9.1-1.0
Molybdenum	4.3	11,000	3,700-11,000	1,500	0.5-9.0	27-1.100	120-1.5
Palladium	0.85	1,000	920	350	1.9	0.077-<0.03	0.22
Platinum	0.063	24	13	4.8	<0.03	<0.03-0.22	<0.041-<0.2
Vanadium	1.9	23,000	58,000	15,000	70	29-220	<39-<5.2

* Compost from garden and MSW waste.
** Leachate from disposal site with residuals from semi-dry and wet waste gas treatment
*** Stack gas from waste incineration after semi-dry and wet waste gas treatment, respectively

Data from Swedish measurements of the concentration in sewage sludge, sediment from road runoff basins and leachate is in general in the same range as the data presented in Table 3.4. However, there is tendency of the measured Danish concentrations to be somewhat higher, especially for palladium where the level is approximately a factor of 10 higher.

Considering the amounts consumed, it was not unexpected to find the highest concentrations in most waste types among antimony, boron, lithium, molybdenum and vanadium. It was, however, unexpected to find high concentration of gallium and palladium in e.g. sewage sludge and compost.

3.3 Health effects

The toxicological properties of the metals and their individual inorganic compounds vary greatly. An oxide of a metal can for example be more toxic than its chloride. It order to compare the toxicity of the metals, Table 3.5 gives a short summary of the information regarding the most toxic metal compounds.

It is underlined that the search and evaluation of data on environmental effects did focus on exposure of low concentration from ingestion or from exposure in the environment for prolonged periods of time. In other words, the focus was on the assessment of the possible impact on the general population more than assessment of the risk from exposure to high concentrations in the working environment.

Table 3.5 Inherent toxicological effects of the metals: Acute and local effects, carcinogenicity(C), mutagenicity (M), reprotoxicity (R) and sensitization. The effects are shown as identified danger (+), no identified danger (÷), and no available data (nd). There is no information on endocrine disrupting effects.

Element	Type of toxic effect Acute and local effect (A/L)	CMR	Sensitizing	Critical compound
Antimony	+/÷	+	+	antimony trioxide
Beryllium	+/+	+	+	beryllium and beryllium ions
Bismuth	nd/+	÷	nd	not stated
Boron	+/+	nd	+	boric acid and boron derivates
Gallium	nd/nd	nd	nd	-
Indium	nd/nd	nd	nd	not stated
Lithium	+/nd	÷	nd	lithium chloride
Molybdenum	+/+	÷	nd	molybdenum trioxide
Palladium	÷/nd	÷	+	metallic palladium and palladium alloys
Platinum	+/+	nd	+	chloro platinates
Vanadium	+/+	+	÷	vanadium pentaoxide

Most metals are not sufficiently investigated for the whole range of effects, as seen from Table 3.5 and only antimony has a complete dataset. No data was found on gallium, while beryllium, boron, indium, lithium, molybdenum, platinum and vanadium have a relatively poor dataset.

Antimony as antimony trioxide exhibit acute and local effects, and in experiments with animals, sensitization, reprotoxicity, and teratogenicity have been observed.

According to IARC, beryllium is regarded as carcinogenic. The critical exposures are mainly observed in the working environment. The divalent beryllium-ion can substitute Mg^{2+} in enzymes, and thereby inactivate them. At high doses, lung cancer has been observed.

Bismuth and bismuth compounds have resulted in adverse effects on humans from medical treatment more frequently than from exposure in the working environment [9]. Chronic exposure can result in poisoning symptoms which resemble the symptoms from lead and mercury exposure: Hyper salivation, stomatitis and greyish colouring of the gums. From prolonged exposure symptoms of damage on the central nervous system can be observed.

Exposure to boron, boric acid, and boron derivatives is related with exposure in the working and indoor environment. Ingestion, uptake from skin or mucous membrane result in loss of appetite, loss of weight, vomiting, mild diarrhea, skin eruption and anaemia.

Lithium is used therapeutically in treatment of manic-depression. It was shown that LiCl is moderately toxic in rats. Lithium resembles sodium chemically, but is more toxic: 5 g LiCl can result in mortal poisoning in humans. Brain weight of male offspring of rat was shown to decrease as a result of chronic exposure.

Molybdenum is a constituent of many enzymes and is regarded as an essential metal. No chronic effects seem to arise from exposure to low molybdenum concentrations.

Palladium has not been identified as acutely toxic or to cause CMR effects. Contact dermatitis has been reported from exposure to metallic palladium and palladium alloys.

Platinum in its metallic form is relatively harmless, but allergic dermatitis from especially complex salts is known. Platinum is, as the other noble metals, relatively toxic or ion form on soluble form.

The metallic form of vanadium does not seem to pose any essential risk to the human health. However, selected vanadium compounds are toxic with mutagenic and reprotoxic effects.

3.4 Environmental properties

Certain metal ions are essential micronutrients for both plants and animals and are assimilated by cells in trace concentrations. The metal ions are used in cell metabolism in e.g. redox reactions and many enzymatically catalyzed reactions. In high concentrations, the ions will have adverse effects on the cells. Some metal ions can be assimilated instead of the essential metal ions and thereby decrease or stop parts of the cell metabolism. This is the case for e.g. beryllium, which on ion form can be assimilated in cells instead of Mg^{2+} and replaces magnesium in certain magnesium-containing enzymes. Thereby, the reactions which are catalysed by these enzymes are deactivated.

Metals in the aquatic environment can, depending to their environmental behaviour and extent of assimilation in organisms be classified as either nutrient type, conservative or particle bound (Zenk, 1996 and Nozaki, 1997).

Metals of the nutrient type are essential for growth. They are assimilated naturally by e.g. algae and their function is related to for instance enzymatic processes. They are released into the environment with the eventual degradation of organic matter. The metals do not necessarily have a biological function. This applies to Be, B, Ga, In, Pd, Pt and V.

Conservative metals are not influenced by biologic assimilation or sorption and they have normally long retention times in aquatic environments. The consequence of a release of such a metal would be a long lasting presence in the environment. This is especially the case for alkali metals. Of the metals included in this study, lithium is the only conservative metal.

Metals strongly influenced by sorption will bind to particulate matter. This applies to a various degree to Sb, Bi, Ga, In, Mo, Pd and V.

3.4.1 Environmental chemistry

The environmental properties of the metals depend among others on their form (speciation), redox state and distribution into highly and low soluble compounds. In aquatic ecosystems, the metals are found as ions, as halogenated compounds and as oxo- and hydroxylated compounds.

3.4.1.1 Ion form

Beryllium and lithium are found as ions. Their concentration is regulated by the solubility of their salts, which depends on e.g. pH. The concentration of beryllium ions is normally low in aquatic ecosystems because of the low solubility of the salts at the pH-values typically found in these environments.

3.4.1.2 Halogenated compounds

Most of the metals in the second rank can be found as halogenated compounds. In the aquatic environment it is primarily palladium and platinum that are found in this form. In sea water, $PdCl_4^{2-}$ and $PtCl_4^{2-}$ are the most common forms of these two elements.

3.4.1.3 Oxo compounds

Nearly all elements form compounds with oxygen. Molybdenum and vanadium are in the aquatic environment found as $MoO_4^{2-}$and HVO_4^{-2}. In oxygen limited environments, molybdenum is reduced and forms low-soluble compounds with e.g. iron monosulfides, which subsequently precipitate.

3.4.1.4 Hydroxylated compounds

Many of the metals in the second rank form hydroxylated compounds, and in the aquatic environment the following compounds are found: $BeOH^+$, $Bi(OH)_2^+$, $B(OH)_4^-$, $Ga(OH)_4^-$, $In(OH)_2^+$, $In(OH)_3^0$, $Pd(OH)_2^0$, $Pd(OH)_2^0$, $Sb(OH)_3$ and $Sb(OH)_6^-$. Their chemistry varies a lot and the pH has for example very different effect on the solubility. Some metals also form complexes with other metal ions.

3.4.1.5 Persistency

Metals and other elements are conservative. Some elements are changed by radioactive decay, but none of the metals included in this study do so. The metals can form numerous inorganic compounds and certain among them can also be methylated. The latter is, however, a phenomenon that is relatively poorly investigated among the second rank metals.

3.4.2 Aquatic toxicity

The aquatic toxicity of the metals depends greatly on which metal compound is used for the toxicity testing. This is partly due to the different solubility of the inorganic compounds, but also the susceptibility for formation of complexes is important. In Table 3.6, the highest aquatic toxicity reported of the metals (the specific compounds are shown in the table) is given. It can be seen that antimony, beryllium, bismuth, palladium and platinum are very toxic to aquatic organisms.

3.4.3 Bioaccumulation

Some metals can accumulate in organisms because of their lipophilic character, and biomagnification can be observed in the food web. The ion forms of the metals are non-lipophilic, but organo-metallic forms can often bioaccumulate. In Table 3.6, bioconcentration factors (BCF) or expected ability to bioaccumulate are shown.

The biochemical regulation of certain metals in cells depends on proteins, which are induced by the presence of certain metals. Induction depends upon the metal - the classic heavy metals have highest effect - but also indium, bismuth and gallium have this property.

Table 3.6 Overview of second rank metal compounds with highest aquatic toxicity and their potential for bioaccumulation (as BCF)

Element	Aquatic toxicity LC_{50}/EC_{50} (mg/L)	Compound	BCF
Antimony	0.07-1.0 (algae)	Sb_2O_3	7-17
Beryllium	0.05-0.9 (daphnia)	$BeCl_2$	-
Bismuth	0.66-1.48 (worm)	BiN_3O_9	b
Boron	21.3 (daphnia)	BF_3	b*
Gallium	3.5 (fish)	$GaCl_3$	-
Indium	-		-
Lithium	1-6.4 (fish)	LiCl	b-
Molybdenum	4.5-100 (algae)	Mo	b*
Palladium	0.142-0.237 (worm)	$PdCl_2$	-
Platinum	0.061-0.095 (worm)	$PtCl_6H_2$	b-
Vanadium	2-6.4 (fish)	V_2O_5	400-1,900

- no data.
b indications of ability to bioaccumulate.
b- not expected to bioaccumulate.
b* bioaccumulation due to essential micro-nutrient.

3.5 Existing regulation

There are only few limit values and quality criteria for the metals in the second rank in air, soil and water. This is possibly a result of the general lack of information on their effects on health and environment and their lower priority compared to the traditional heavy metals.

There are limit values in drinking water for boron, lithium and molybdenum. Limit values exist for antimony, beryllium, boron, lithium, molybdenum, palladium, platinum and vanadium on national or EU-level, see Table 3.7.

Table 3.7 overview of existing Danish/EU regulation of the metals given as limit values and quality criteria. The reference is given In parenthesises.

Element	Limit values/quality criteria			
	Drinking water (µg/L)	Soil (mg/kg)	Stack gas (C-values) (mg/m^3)	Air (B- values) (mg/m^3)
Antimony	5 (4)		0.5 (1)	0.001 (2, 3)
Beryllium			0.1 (2)	0.00001 (2, 3)
Bismuth				
Boron	300 (4)		0.003* (7)	
Gallium				
Indium				
Lithium	1,000 (7)	500 (8)		0.01 (3)
Molybdenum	20 (7)	2 (5)		0.005 (3)
Palladium			5 (1)	
Platinum			5 (6)	
Vanadium			0.5 (6)	0.0003 (3)

* temporary value.

(1) Directive 2000/76/EC, (2) Danish EPA 2001. Luftvejledningen - Begrænsning af luftforurening fra virksomheder Vejledning nr. 2/2001, (3) Danish EPA 1996. B-værdier. Orientering fra Miljøstyrelsen, 15/1996, (4) MINISTRY OF Environment and Energy 2001. Bekendtgørelse om vandkvalitet og tilsyn med vandforsyningsanlæg, (5) Danish EPA 1997. Økotoksikologiske jordkvalitetskriterier. Arbejdsrapport nr. 82, (6) Danish EPA 1990. Begrænsning af luftforurening fra virksomheder. Vejledning nr. 6, (7) Danish EPA 2001. Environmental Factors and Health (in English).

4 Evaluation of Potential Impacts

4.1 Evaluation of the 11 metals

As mentioned in chapter 3, the metals are used in very different quantities and the also the concentration in the waste streams vary greatly. In the following, the metals are evaluated one by one by collating information related to exposure (uses, consumption, dispersal and levels in the environment) with their inherent potential for adverse environmental effects.

4.1.1 Antimony

Among the metals in the second rank, antimony is the one which is used in highest amounts in Denmark. The use of antimony in batteries, pigments, plastic and cosmetics can result in losses to and dispersal in the environment. Especially sewage sludge and solid waste contain antimony. Energy production based on fossil fuels will result in atmospheric emission of antimony and antimony in stack gas cleaning residuals.

In the waste streams analysed in this study, relatively high concentrations of antimony were found in leachate and sewage sludge. The concentration in leachate of 8 µg/L is under the lowest NOEC-value for living organisms found in the literature. Adverse environmental effects from percolation of leachate are therefore not expected to be due to the content of antimony.

In sewage sludge the concentration of antimony is on the same level as the background concentration found for soil, while the concentration in compost is in the low end of the concentration range in soil. Use of these types of biowaste for fertilisation or soil improvement is not expected to increase the concentration of antimony in the affected areas.

Inhalation of antimony as antimony trioxide is dangerous and can result in CMR-effects.

4.1.2 Beryllium

The light-alloy metal beryllium is known as damaging to human health, and exposure to high concentrations of beryllium is known as a problem in the working environment. It is classified as carcinogenic and sensitizing.

Beryllium is used in e.g. electronics, but due to the low use of beryllium it is unlikely that the exposure will result in adverse effects on health and environment. In the working environment toxic effects from beryllium have been observed.

The concentration of beryllium is under the detection limit in leachate and treated waste water. Emission of stack gas from MSW incineration is regarded as an important way of dispersal. However, the concentration measured in stack gas is approx. 40 times below the limit value of 0.1 mg/m^3. The emission of beryllium from stack gas is in the form of beryllium oxide. This compound is relatively immobile in the pH interval found in most soils. Low concentrations of beryllium is found in compost, sewage sludge and sludge from sediment from road runoff retention basins.

Critical exposure of beryllium primarily occurs in the working environment and use of beryllium in e.g. electronics is not expected to result in adverse effects on health or environment.

4.1.3 Bismuth

The use of bismuth in e.g. electronics, pigments, plastic and cosmetics can result in environmental exposure, and especially sewage sludge and solid waste contain bismuth. Bismuth can be used instead of antimony in electronic equipment. The consumed amount of bismuth is approx. 36 tonnes/year, or 20 times less than the consumption of antimony.

Coal and oil contain bismuth. Therefore, energy production based on fossil fuels contributes to the overall emission of bismuth.

In this study, bismuth was found in low concentrations in sewage sludge, sediment from road runoff retention basins and leachate. The amount of data regarding the environmental toxicity is too sparse for proper evaluation of its effects on health and in the environment. Due to the potential for bioaccumulation bismuth might cause adverse environmental and health effects if the consumption increases.

4.1.4 Boron

Boron in the form of sodium borate is used as bleaching agent in detergents. Boron compounds are also used in e.g. plastic, flame retardants and as dietary supplement. On a weight basis, borate is the most important use of boron Waste water and sewage sludge contain high boron concentrations.

The concentration of boron is high in all waste products analysed as part of this study. Of the 11 metals in the second rank, boron is the metal found in the highest concentration in all types of waste except sediment from road runoff retention basins. Based on the collected information regarding aquatic toxicity, boron is not regarded as dangerous to aquatic organisms. The concentration in treated municipal waste water is a factor 100 lower than the NOEC-value for ***Daphnia magna***.

No quality criteria exist for the concentration of boron in soil and compost. Boron is added to farmland when sewage sludge is applied as a soil improving agent, but there is not sufficient data to evaluate its effect on soil organisms. Being an essential micro-nutrient, no adverse effects of boron are expected at the concentrations found in this study.

The use of domestic products containing boron can possibly cause sensitization.

4.1.5 Gallium

Electronic equipment is the most important source of exposure to gallium and, hence, solid waste, stack gas and gas cleaning residuals from waste incineration are expected to contain gallium. The consumption is expected to increase, and this will possibly also increase gallium concentration in the waste streams. This was confirmed from the analyses conducted in this study. Gallium was found primarily in sewage sludge, compost from municipal household waste and leachate.

Due to the content of gallium in fossil fuels, energy production based on this energy source will add to the total emission of gallium.

The environmental toxicity of gallium in not well documented. Hence, it was not possible to evaluate if gallium in emissions or waste products pose any risk. Because of the low consumption of gallium, it is not expected to cause adverse effects on health or environment at present.

4.1.6 Indium

The global consumption of indium is increasing faster than any of the metals included in this study. The yearly use in Denmark is only about 1 ton. Indium is used in LCD-displays, batteries and electronics. The most important route of dispersal to the environment is through solid waste and residuals from waste incineration.

The concentration of indium was low in all samples from the analysed waste types. No data was found regarding environmental toxicity of indium, and, consequently, the possible environmental impacts of indium can not be assessed. However, due to the low consumption of indium and the low concentrations found in waste, the actual risk of adverse effects on environment and health is considered to be low.

4.1.7 Lithium

Lithium is used in e.g. electronics, perfume, plastic and in the pharmaceutical industry. The wide application spectrum means that lithium is found in many waste types. Lithium discharged with waste water or disposed at landfills can be found in the treated waste water and landfill leachate due to its high solubility in water.

According to the analyses conducted during this study, leachate from landfills contain 50-200 µg/L of lithium, while leachate from landfills with gas cleaning residuals contain approx. 300 µg/L. Compost and sewage sludge contain high concentrations of lithium.

Compared to the aquatic toxicity, the concentration of lithium in treated waste water is approx. 10 times lower than the NOEC for fish. Compared to the quality criteria for soil, the concentration in sewage sludge and compost is approx. a factor of 100 lower. Lithium seems not to show adverse effects on the environment at the present level and pattern of dispersal.

Experiments with experimental animals have shown that lithium can have reprotoxic effects, and increasing consumption might therefore result in adverse effects on health and environment.

4.1.8 Molybdenum

With a yearly consumption of 275 tonnes, molybdenum is among the most used among the second rank metals. Molybdenum is used in alloys of steel and to specialty steel/stainless steel, as flame retardant, and in colour pigments, plastic and dietary supplements. Due to this wide spectrum of uses, molybdenum can be found in both waste water, sewage sludge and landfill leachate.

The acute toxicity measured in test with ***Daphnia magna*** is low and moderately low for algae. However, the data is not sufficient to allow a thorough evaluation. The level in waste water is approx. a factor of 1000 lower than the LC_{50} for daphnia, but close to the limit in drinking water. The content in sewage sludge and compost exceed the soil quality criteria of 2 mg/kg. The content in stack gas from municipal solid waste incineration and leachate from landfills with waste gas residuals is high.

Based on the high concentration of molybdenum in all analysed waste types, the exposure of the environment to molybdenum is regarded as significant. The limited amount of data regarding its toxicity makes it impossible to evaluate the potential for adverse environmental and health effects from molybdenum exposure.

4.1.9 Palladium

The use of palladium in Denmark is at present limited with a consumption of only 2.4 tonnes per year. The consumption is expected to increase. The main use is in printed circuit boards, catalysts and metal alloys.

The date regarding environmental toxicity is very limited. From the data presented in the data sheet, it can be seen that palladium chloride has a very low effect concentration on ***Tubifex tubifex*** and should as such be regarded as very toxic to aquatic organisms.

In the examined waste streams palladium was found in leachate, treated waste water and sewage sludge. The concentration in treated waste water is approx. a factor of 100 lower than the EC_{50}-value for the organism mentioned above.

The environmental toxicity of palladiums is not well documented, and the concentration found in especially waste water can therefore not be evaluated properly with regard to possible environmental impact.

4.1.10 Platinum

Consumption of platinum for catalytic combustion of exhaust gas from e.g. car engines (both gasoline and diesel powered) is regarded as the quantitatively most important use of platinum. Platinum is also used in the electronics industry, the petrochemical industry and the pharmaceutical industry. 1.3 tonnes of platinum is used in Denmark yearly, and the consumption is expected be relatively constant.

Despite of the variety of uses of platinum, the concentration found in all waste streams were low.

The data on the environmental toxicology of platinum is very limited. Hexachloro platinum acid has an effect concentration on ***Tubifex tubifex*** of 61 µg/L and is therefore very toxic to this aquatic organism. In treated waste water the concentration was found to be approximately 1,000 times lower. It is expected that the consumption should increase significantly before adverse health and environmental effects from platinum exposure can be observed.

4.1.11 Vanadium

Approximately 100 tonnes/year of vanadium is used in Denmark in e.g. alloys, catalysts, pigments and dietary supplement. The many different uses and the large amounts can result in dispersal of vanadium from most waste streams.

Vanadium is found in fossil fuels and is emitted from coal-fired power plants and this is assumed to be the main source of emission to the environment. From the 6.7×10^6 tonnes of coal consumed in Denmark in year 2000 (Danmarks Statistik 2001) and an average concentration of vanadium of 60 mg/kg (Sternbeck and Östlund 1999), the total amount of vanadium in emissions and residuals from coal based energy production was approx. 400 tonnes.

Compost, sewage sludge and sediment from road runoff retention basins contain high concentrations of vanadium. Compared to antimony (the metal with highest consumption in Denmark among the second rank metals, the concentration of vanadium was higher in all the analysed waste streams. Due to the high background concentration in soil, the use of sewage sludge as a soil improving agent is not expected to result in adverse effects despite its high vanadium concentration.

Vanadium is regarded as toxic to aquatic organisms. However, only limited data regarding environmental toxicity exist. It is especially the solid waste that contains much vanadium, and vanadium is therefore not regarded as a significant potential risk for the aquatic environment. Certain vanadium compounds are carcinogenic, mutagenic and/or reprotoxic.

4.2 The classic heavy metals versus the second rank metals

An overlap in the use areas for the second rank metals and e.g. lead, cadmium, chromium and mercury exists. The amounts consumed of especially lead and chromium are much higher than the consumption of the second rank metals, see Table 3.1 and Table 4.1.

Table 4.1 Uses and consumption of the classic heavy metals.

Element	Uses	Consumption (tonnes/year)
Lead	Rechargeable accumulators, plumbing purposes, alloys, ammunition, pigments, ceramic products. PVC-stabilisers, fishing tackles	15,500-19,800[1]
Cadmium	Batteries, electronic components, plastic, alloys, pigments, ornaments	43-71[2]
Chromium	Impregnation , electro galvanisation, tanning, alloys, glass, enamel paint, plastic, textiles, catalysts	6,000-11,000[3]
Mercury	Batteries, electrolyses, electronic components, thermometers and measurement/control equipment, dental fillings	6.4-9.4[4]

1Miljøstyrelsen (1996), 2Miljøstyrelsen (2000), 3Miljøstyrelsen (1985), 4Miljøstyrelsen (1996a).

The effects of the traditional heavy metals on health and environment are well known. Table 4.2 gives an overview of health effects and environmental toxicology for lead, cadmium, chromium and mercury. Especially lead, cadmium and mercury have significant adverse effects on health and environment.

Table 4.2 Selected adverse effects of heavy metals on health and environment. From Miljøstyrelsen (1995).

Element	Human toxicology	Environmental toxicology
Lead	Neurotoxic and accumulate in bones - effects especially children	Acute and chronic toxicity on plants, animals and micro-organisms
Cadmium	Acutely toxic and can cause serious damage on the kidney	Acute and chronic toxicity on aquatic and terrestrial organisms and can have reprotoxic effects
Chromium	Chromium is an essential micro-nutrient, but can give allergy and cancer	Toxicity on aquatic organisms, especially chromium (VI).
Mercury	Toxicity is due to organic Hg-compounds which are easily assimilated and affects the brain	Acute and chronic toxicity - especially on higher animals

Also some of the metals in the second rank have significant adverse health and environmental effects, e.g. beryllium, which is carcinogenic. To provoke such effect, inhalation of beryllium over an extended period of time is required. Certain boron, molybdenum, platinum and vanadium compounds have adverse health effects on health, e.g. sensitizing effects. Information regarding gallium, indium, palladium, platinum and vanadium was too limited for evaluation on their health and environmental effects.

The consumption of beryllium, gallium, indium, palladium and platinum is relatively low. Therefore, the use of these metals poses only a little risk for adverse environmental effects. The use of fossil fuels can result in significant dispersal due to emissions from stack gas and gas cleaning residuals.

4.3 Data quality

The elements in the second rank have until now not received as much attention as the classic heavy metals with regard to adverse effects on human health and the environment. Thus, the data on environmental toxicity was lacking both depth and width, i.e. test results for organisms on more than one trophic level and several tests with the same organism. The data found in the data sheets are therefore in most cases not sufficient for conducting a thorough evaluation.

The second rank metals can be used in many organic and inorganic compounds. Data on the organic compounds have not been included in this study due to low importance in relation with production, use and waste disposal, which is the issue of this report. All the inorganic compounds have been included in the description and evaluation of the health and environmental effects of each metal. However, the behaviour of each single metal species regarding solubility and thus exposure of test organisms was not considered.

5 Conclusions

The data on the metals in the second rank is limited and not sufficient to draw firm conclusions on their effects on health and environment. From the evaluation of the available data and by comparison with information on the traditional heavy metals the following conclusions are drawn:

- Antimony, beryllium, boron, molybdenum, platinum and vanadium are classified as damaging to health- and/or environment, however typically based on data on exposure in the working environment.
- Antimony, beryllium, lithium and vanadium have carcinogenic, mutagenic and/or reprotoxic properties.
- Antimony, bismuth, boron, palladium and platinum have sensitizing effects.
- Beryllium, boron, gallium, indium, lithium, molybdenum, platinum and vanadium are poorly studied with regard to their health effects.
- Antimony, beryllium, bismuth, palladium, and platinum are considered as toxic or very toxic in the aquatic environment.
- Gallium, indium, palladium, platinum and vanadium can not be evaluated due to limited data on environmental effects.
- The consumption of almost all metals in the second rank is increasing, but at present beryllium, gallium, indium, palladium and platinum are used in small amounts with little risk of significant exposure.
- Boron, indium and lithium are, with the present consumption and uses not likely to pose adverse effects on health and environment.

Based on the above conclusions and considering the magnitude of the consumption at present, the metals antimony, bismuth, lithium and vanadium are regarded as the most problematic of the metals studied. Because of the high emission of vanadium from combustion of fossil fuels the overall effects of vanadium from other uses are regarded as relatively limited.

Beryllium, lithium and molybdenum can potentially result in adverse effects if the consumption increases.

Antimony, beryllium, lithium and molybdenum are considered to be the most relevant among the 11 metals for further clarification regarding their patterns of use and exposure. Bismuth and palladium might be included among these due to the fact that they have sensitization properties, have a potential for adverse environmental effects and have an increasing consumption.

6 Literature

1 Miljøstyrelsen (1995). Tungmetaller, Redegørelse fra Miljøstyrelsen, nr. 1, 1995

2 Denmarks Statistik (2001). Statistikbanken. www.statistikbanken.dk

3 Zenk MH (1996) Heavy metal detoxification in higher plants - a review. Gene, 17, 21-30

4 Nozaki Yoshiyuki (1997) A Fresh Look at Element Distribution in the North Pacific. EOS, Online Supplement, American Geophysical Union. http://www.agu.org/eos_elec/97025e.html 15/6/01

5 Miljøstyrelsen (1996). Massestrømsanalyse for bly, Miljøprojekt nr. 327, 1996.

6 Miljøstyrelsen (2000). Massestrømsanalyse for cadmium, Miljøprojekt nr. 557, 2000

7 Miljøstyrelsen (1996a). Massestrømsanalyse for kviksølv, Miljøprojekt nr. 344, 1996

8 Miljøstyrelsen (1985). Forbrug and forurening med arsen, krom, kobalt og nikkel, Orientering fra Miljøstyrelsen nr. 7, 1985.

9 Sternbeck and Östlund (1999). Nya metaller och metalloider i samhället

The literature used in the description and evaluation of each metal can be found at the end of each datasheet (Appendix A).

Appendix A

Table of Contents

1 Antimony

1.1 Identity

Table 1.1
CAS No., EINECS No and molecular weight for antimony

Antimony (Sb)	CAS No.	7440-36-0
	EINECS No.	231-146-5
	Molecular weight	121,75

1.2 Physico-chemical properties

Antimony is a metalloid from the same group in the periodical table as arsenic and phosphorus (group VB). Normally it has the valences +3 (Sb(III)) and +5 (Sb(V)). Metallic antimony has a crystalline structure with a bluish white color and has a metallic lustre. Antimony is not attached with diluted acid or base.

Typical compounds of antimony are sulfides, hydroxides, and oxides [1, 2]. Metallic antimony is insoluble in water, whereas the oxides Sb_2O_5 and Sb_2O_3 and sulfides of antimony are slightly soluble in water. Table 1.2 shows selected physico-chemical data for metallic antimony (data from [3]).

Table 1.2
Physico-chemical data for metallic antimony

Antimony (Sb)	Valence	-III, 0, III, V
	Density (g/cm^3)	6,68 g/cm^3
	Melting point (°C)	630
	Boiling point (°C)	1637
	Solubility in water	insoluble

1.3 Uses and consumption

1.3.1 Uses

Antimony is used for:

- Production of high alloy steel
- Lead alloy in batteries
- Flame retardant in textiles, plastic and electronic components
- Yellow pigments (Sb_2S_3)
- Ceramics, enamel and glassware
- Infrared detectors
- Plastic/rubber (as stabilizer)
- Lubricant

- Certain medical/pharmaceutical products
- Cosmetics

Antimony is used as metallic antimony in alloys and as salts. Within the EU, antimony is used in the following high volume compounds: diantimony trioxide (CAS No. 1309-64-4), antimony trisulfide (CAS No. 1345-04-6) and sodium hexahydroxoantimonate (CAS No. 33908-66-6) [4]. Antimony is also found in cosmetics [7, 13, 17].

1.3.2 Consumption

The global production of antimony has been approximately 150,000 tons/year and. It has increased in the last years. China accounts for approximately 70 % of the production. Based on the per capita-consumption in USA, the consumption in Denmark is estimated be to approximately 840 tons per year in 1995/1996 [9].

The price fluctuates with the supply form China [14]. The major producing countries are China (100,000 t/year), South Africa (6,000 t/year), Bolivia (5,000 t/year), and Russia (3,000 t/year). Major antimony reserves are found in the countries mentioned above and in the USA and Kyrgyzstan.

As seen in Table 1.3, the consumption is expected to decrease in a few of the use categories. However, the overall consumption is expected to increase.

Table 1.3
Expected trend in the Danish consumption of antimony within different use categories [9]

Compound	Typical use	Assumed tendency
Sb_2O_3/Sb	Alloy metal	Decreasing
$SbCl_3$	Flame retardant in textiles	Unknown
Sb_2O_3	General flame retardant	Decreasing
	Paint	Unknown
	Glass	Decreasing
	Ceramics	Decreasing
	Plastic	Unknown
	Rubber	Unknown
	Lubricant	Unknown
SbS_3	Yellow pigments	Unknown
SbS_3	Infrared detectors	Increasing
TiO_2 containing Sb & Cr	Paint	Unknown
TiO_2 containing Sb & Cr	Plastic	Unknown
TiO_2 containing Sb & Ni	Paint	Unknown
Unknown	Catalyst in production of fluorinate compounds and synthetic fibres.	Unknown

In Table 1.4, the estimated Danish consumption of approximately 840 tons/year is divided into five categories based on the distribution in USA in 1996 [9].

Table 1.4
The relative distribution of the consumption in USA and the estimated Danish use of antimony in 1996 based on [9]

	Flame retardants	Lead alloys	Chemicals, plastic, pigments	Ceramics, glassware	Other
Distribution in USA (1996)	62%	15%	10%	8%	5%
Yearly consumption in DK	521 tons	126 tons	84 tons	68 tons	42 tons

1.4 Emissions to and occurrence in the environment

Antimony is found in trace concentrations in coal and oil. Consequently, it is emitted to the environment from combustion of fossil fuels. Emission from industry and combustion of fossil fuels has resulted in significant increase in the total emission of antimony through the last 50 years [9].

Antimony is found in solid waste due to the use of antimony oxide as flame retardant in e.g. plastics, textiles and electronic equipment. It is estimated that both combustion and land filling of solid waste will result in emission of antimony. A Swedish study showed that antimony in cinder, fly ash and stack gas condensate from waste incineration is 526 µg/kg dw, 425 µg/kg dw and approximately 1 mg/L, respectively [9]. 0.1-1 % of the antimony in the waste is emitted to the atmosphere by incineration, depending on the type of waste gas cleaning applied.

Swedish experience shows that the level of antimony in arable land increases significantly by sludge amendment.

The concentration of antimony in fresh and sea water (primarily as $Sb(OH)_6^-$) is low, see Table 1.5. The data are literature values, which do not necessarily reflect the background concentration in Denmark. 25-75 ng/L of antimony has been found in the Baltic Sea. Antimony can be associated with particulate matter. In the environment, a considerable amount of antimony is found as methylated antimony [9].

Table 1.5
Typical background concentration of antimony in the environment. Data from [9, 12, 16]

Concentrations	Fresh water (µg/L)	Sea water (µg/L)	Sediment (mg/kg)	Soil (mg/kg)	Earth crust (mg/kg)
Typical background concentration	0.01 - 5	0.18 - 5.6	1.2	0.2 - 10	0.2

A limited investigation of the levels of antimony (and the other elements covered by this study) in the major emissions and waste streams in society was conducted in the autumn of 2001, see Table 1.6.

In the waste streams antimony was found primarily in sewage sludge and sediment from road runoff retention basins. The concentration of antimony was relatively high in leachate compared to the other metals measured as part of this study. The concentration was low in stack gas.

Table 1.6
Levels of antimony in selected emissions and waste products from measurements conducted as part of this study in the autumn of 2001.

Emission/waste type	Unit	Sb-concentration
Compost:		
Compost from household waste	µg/kg dw	380
Compost from garden waste	µg/kg dw	180
Landfill leachate:		
Landfill 1	µg/L	8.0
Landfill 2	µg/L	3.40
Stack gas from MSW incineration:*		
MSW incinerator 1, semi-dry gas cleaning	µg/m^3	0.4
MSW incinerator 2, wet gas cleaning	µg/m^3	<5
MSW gas cleaning residuals:*		
Landfill leachate, semi-dry gas cleaning	µg/L	1.94
Landfill leachate, wet gas cleaning	µg/L	8.80
*Waste water and sludge from municipal WWTP**:*		
WWTP 1, effluent	µg/L	0.45
WWTP 2, effluent	µg/L	1.32
WWTP 1, sludge	µg/kg dw	3,300
WWTP 2, sludge	µg/kg dw	4,900
Road runoff retention basins, sediment:		
Motorway 1	µg/kg dw	3,860
Motorway 2	µg/kg dw	580

*Municipal solid waste

**Waste water treatment plant

1.5 Danger classification

Antimony compounds are found on the Danish list of dangerous compounds. Antimony tetra oxide (Sb_2O_4), antimony pentoxide (Sb_2O_5), antimony trisulfide (Sb_2S_3), antimony pentasulfide (Sb_2S_5) are classified as ***harmful*** with risk phrase R20/22 (harmful by inhalation and if swallowed) and ***dangerous for environment*** with risk phrase R51/53 (toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment) [8].

Within the EU, antimony trioxide is classified as ***carcinogenic*** (category Carc3) with R-phrase R40 (possible risk of irreversible effects) [8]. EU is currently evaluating the compound in order to assess its environmental classification and risk phrases.

Antimony chlorides are classified as ***corrosive*** and ***dangerous for environment*** and antimony trifluoride is classified as ***toxic*** and ***dangerous for environment*** [8].

Table 1.7
EU-classification of antimony and antimony compounds [8]

	Health	Environment
Metallic antimony	-	-
Antimony compounds with exception of:	Xn; R20/22	N; R51/53
Antimony trioxide	Carc3; R40	-
Antimony trichloride	C; R34	N; R51/53
Antimony pentachloride	C; R34	N; R51/53
Antimony trifluoride	T: R23/24/25	N; R51/53

- not classified

1.6 Toxicology

Epidemiological investigations have shown that antimony in the form of antimony trioxide can result in dermatitis and possibly it has adverse effects on female reproduction. Studies with rats have shown that inhalation of antimony trioxide can result in teratogenic effects. Neither IARC nor EPA has evaluated the carcinogenic characteristics of antimony, but antimony trioxide is classified as ***carcinogenic*** in category 3 within the EU (carcinogenic in experimental animals). Effects at low concentration are observed by exposure by inhalation, and lung neoplasms have been observed in experimental animals; apparently female animals are more sensitive than males [9].

Increased concentrations can be found in selected working environments and in the air close to e.g. metallurgical industry, coal fired power plants and incinerators. Metallic antimony and certain trivalent antimony compounds have highest potential for exposure while pentavalent compounds are less problematic [15].

1.7 Environmental properties

1.7.1 Environmental chemistry

Salts of antimony form hydrated antimony compounds in aqueous environments. Sb(III) is found as $Sb(OH)_3$ in most aquatic environments while the dominating species of Sb(V) in aqueous environments is $Sb(OH)_6^-$ (pH > 3) [2]. Formation of complexes with organic matter is not important for the overall antimony flux. The mobility of antimony in soil and sediment is controlled of binding to clay and minerals, and precipitation with oxides of Fe, Al and Mn [2].

Biomethylation of antimony is observed in the environment as for tin, arsenic and other related metals. Apparently, methylated antimony compounds do not have any significant adverse environmental effect [2], but other references report that methylated antimony is very toxic [7].

1.7.2 Environmental toxicology

Antimony trioxide showed 50% inhibition of growth (EC_{50}) on the fresh water alga ***Selenastrum capricornutum*** at 0.7 mg/L, while the no observed effect concentration was 0.2 mg/L. [5]. Therefore, the compound is classified as very toxic to algae. The EC_{50} on ***Daphnia magna*** (measured as immobilisation) of the compound antimony trioxide was 423-555 mg/L. Antimony trichloride had a LC_{50}-value of 12.1 mg/L on ***Daphnia magna***. The LC_{50} of antimony trichloride on rainbow trout in a long term test (28 days) was 0.66 mg/L.

Antimony chloroxide had a no observed effect concentration of 0.03 mg/L on the fresh water alga ***Chlorella vulgaris*** after three months' exposure.

Table 1.8
Selected test results for environmental toxicity of antimony (mg/L). Data from [5]

Organism	Latin name	EC_{50}/LC_{50} (mg/L)	NOEC (mg/L)	Compound
Algae	*Chlorella vulgaris*		0.032 (3 month)	SbClO
	Selenastrum capricornutum	0.7 - 1.0 (24-96 hours)	0.2 (96 hours)	Sb_4O_6
Crustaceans	*Daphnia magna*	423 - 555 (24 - 48 hours)		Sb_4O_6
	Daphnia magna	12.1 (48 hours)		$SbCl_3$
Worms	*Tubifex tubifex*	108 - 920 (24 - 48 hours)		Sb_4O_6
Fish	*Oncorhynchus mykiss*	0.66 (28 days)		$SbCl_3$

1.7.3 Bioaccumulation

The available information on bioaccumulation of antimony does not give reason to view antimony as bioaccumulating. The highest concentrations are observed for macro algae with a bioconcentration faction (BCF) of 7 to 17. Certain plants do, however, accumulate considerably more antimony. Values for bivalves, crustacean, and fish are lower [5].

1.8 Conclusions

Increased industrial use and combustion of fossil fuels have resulted in increased emission to the atmosphere. This has enhanced the dry and wet deposition. Antimony compounds are generally harmful, but selected compounds have other effects. Antimony trioxide is on the list of dangerous compounds and classified as carcinogenic in category Carc3. Antimony trifluoride is toxic to humans and aquatic organisms.

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2 Beryllium

2.1 Identity

Table 2.1
CAS No., EINECS No. and molecular weight for beryllium

Beryllium (Be)	CAS No.	7440-41-7
	EINECS No.	231-150-7
	Molecular weight	9.01

2.2 Physico-chemical properties

Beryllium is a group 2 element (IIA) in the periodic table, and the metal has the valence +2 (Be(II)) [12]. Metallic beryllium has low density and is a light-alloy metal. It is not soluble in cold water, but has low solubility in warm water. It is soluble in weak acids and bases [10].

Common compounds of the beryllium ion are beryllium hydroxide, beryllium chloride and beryllium sulfate. The solubility of the salts in water at neutral pH is relatively low, and is highest for beryllium chloride. Beryllium can also bind covalently and in the environment it forms organometallic compounds as e.g. $(CH_3)_2Be$ [7]. The table below shows selected physico-chemical data for metallic beryllium.

Table 2.2
Physico-chemical data for metallic beryllium. Data from [1, 2]

Beryllium (Be)	Valence	II
	Density (g/cm^3)	1.85
	Melting point (°C)	1,278
	Boiling point (°C)	2,970
	Solubility in water (g/L)	insoluble

2.3 Uses and consumption

2.3.1 Uses

Beryllium is used in the metal and electronics industry (televisions, calculator and computers) [18] and in the oil and gas industry [6, 17]. In Sweden, the aviation industry uses it in beryllium-copper alloys [6]. In Denmark, the most important use of beryllium is assumed to be the oil and gas industry where it is used in beryllium-copper alloys (pipelines and other submerged applications).

Additional fields of beryllium use are dental alloys [18, 20], sports equipment (golf ball and bike frames), air bags [21], X-ray equipment [22], additive to rocket fuel [22], ceramic/composite material [19, 20], and nuclear equipment [20].

2.3.2 Consumption

The global production of beryllium has in recent years been approximately 300-350 tons/year. USA consumed 240 tons of beryllium in 1997 [17].

The Danish consumption is assumed to be about 5 tons per year (it is assumed that the per capita consumption in Denmark and USA are identical).

2.4 Emissions to and occurrence in the environment

A significant emission of beryllium in Denmark comes from the use and disposal of metal and electronic equipment. Coal contains typically 0.5-3 mg Be/kg and oil about 0.002 mg/kg [6]. Therefore, incineration of fossil fuels results in production of waste products with beryllium and/or emission of beryllium to the atmosphere.

The concentration of beryllium in the aquatic environment is 0.0056-1 µg/L, see Table 2.3. The background concentration in the aquatic environment is 0.3 µg/L in fresh water [14]. In soil, concentrations between 0.01 and 40 mg/kg are reported. Beryllium is also found in waste water in concentration of less than 2 µg/L. In waste water treatment plants the highest concentrations are typically in the floating material in the primary clarifier. An increase in beryllium concentration in sludge in plants with sludge treatment can not be observed [9]. The results of sludge analysis are given in Table 2.4 (analysis performed in this study) corresponds to results from a previous study [9].

The fraction of beryllium used in consumer products will follow the waste streams and it is assumed that both combustion and disposal of solid waste can result in emission of beryllium to the environment. The concentrations of beryllium are according to Table 2.4 very low in waste gas from MSW incinerators and in leachate from landfill with MSW gas cleaning residuals.

From incineration of fossil fuels beryllium is emitted primarily as BeO. In Table 2.3 the typical background concentrations of beryllium in different environments are shown.

Table 2.3
Typical background concentration of beryllium in the environment. Data from [6, 14]

Concentrations	Fresh water (µg/L)	Sea water (µg/L)	Sediment (mg/kg)	Soil (mg/kg)	Earth crust (mg/kg)
Typical background concentration	0.01 - 1	0.0056	2	0.01 - 40	2.6

A limited investigation of the levels of beryllium (and the other elements covered by this study) in the major emissions and waste streams in society was conducted in the autumn of 2001, see Table 2.4. The level of beryllium in the waste streams is low in all waste types. The concentration of beryllium in road runoff retention basins was similar to the concentration of e.g. bismuth and palladium.

Table 2.4
Levels of beryllium in selected emissions and waste products from measurements conducted as part of this study in the autumn of 2001.

Emission/waste type	Unit	Be-concentration
Compost:		
Compost from household waste	µg/kg dw	330
Compost from garden waste	µg/kg dw	270
Landfill leachate:		
Landfill 1	µg/L	<0.03
Landfill 2	µg/L	<0.03
Stack gas from MSW incineration:*		
MSW incinerator 1, semi-dry gas cleaning	µg/m^3	<2.6
MSW incinerator 2, wet gas cleaning	µg/m^3	<0.2
MSW gas cleaning residuals:*		
Landfill leachate, semi-dry gas cleaning	µg/L	<0.03
Landfill leachate, wet gas cleaning	µg/L	<0.03
*Waste water and sludge from municipal WWTP**:*		
WWTP 1, effluent	µg/L	<0.03
WWTP 2, effluent	µg/L	<0.03
WWTP 1, sludge	µg/kg dw	400
WWTP 2, sludge	µg/kg dw	252
Road runoff retention basins, sediment:		
Motorway 1	µg/kg dw	780
Motorway 2	µg/kg dw	780

*Municipal solid waste

**Waste water treatment plant

2.5 Danger classification

Beryllium has been recognised as problematic in the working environment since the 1970'ies. Beryllium and beryllium compounds are, except beryllium aluminum silicates, on the Danish list of dangerous compounds as ***very toxic*** when inhaled, ***toxic*** with risk of serious damage to health by prolonged exposure through inhalation, ***carcinogenic*** in category Carc2, ***irritant*** and ***sensitizing*** (R43) [4, 11]. Beryllium compounds except beryllium aluminum silicates are furthermore classified as ***dangerous for environment*** with risk phrase R51/53 (toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment).

Table 2.5
Classification of and risk phrases for beryllium and beryllium compounds

	Be	Be-compounds
Health	Carc2;R49 T;R25-48/23 Tx;R26 Xi;R36/37/38 R43	Carc2;R49 T;R25-48/23 Tx;R26 Xi;R36/37/38 R43
Environment	-	N;R51/53

2.6 Toxicology

The toxicological effects of beryllium are due to the mode of action of the divalent beryllium ion, which can substitute Mg^{2+} in enzymes and thereby inactivate them.

Based of data on toxicity to animals and limited data on its human toxicology, inhaled beryllium is regarded as a possible carcinogen (group B2) by US EPA. Cancer can develop from exposure to high doses or chronic exposure of the lungs. Also oral intake is toxic [15].

According to IARC, there is sufficient evidence to classify beryllium and beryllium compounds as carcinogenic in humans and animals (Group 1) [3].

2.7 Environmental properties

2.7.1 Environmental chemistry

The salts of beryllium are in most cases the only beryllium compounds which will result in adverse effects on the environment. In the aquatic environment beryllium is found as beryllium ions (Be^{2+}) or hydroxides. In aquatic ecosystems the concentration of beryllium ions is low since the salts have relatively low solubility at the pH, which in found in these environments. In fresh water beryllium is found as Be^{2+} and $BeOH^{+}$, while the hydroxides are dominant in sea water [6]. The solubility of beryllium salts and thereby the concentration of beryllium ions in the water phase increases with decreasing pH [7].

Uptake of beryllium ions instead other metal ions can be observed. Metal ions are used in the metabolic functions of cells, and beryllium can substitute Mg^{2+} in enzymes and thereby deactivate enzymatically catalysed reactions.

Beryllium oxide (BeO) originating from combustion of fossil fuels is deposited by dry and wet deposition. In this form it is relatively immobile at pH values from 4 to 8 [7]. Only a limited amount of beryllium is therefore released by leaching from the soil environment.

2.7.2 Environmental toxicology

The acute toxicity of beryllium salts on ***Daphnia magna*** in the aquatic environment varies with a factor 10^4 depending on which salt is used in the toxicological test. As seen in Table 2.6, the EC_{50} is 0.050 mg/L for $BeCl_2$, whereas it is between 236 and 538 mg/L for $Be(OH)_2$ depending on water hardness. This large difference in toxicity is due mainly to the different solubility of the compounds.

Table 2.6
Selected test results for environmental toxicity of beryllium. Data from AQUIRE [5]

Organism	Latin name	EC_{50}/LC_{50} (mg/L)	Duration	Compound
Crustacean	*Daphnia magna*	0.05 - 0.90	24 - 96 hours	$BeCl_2$
	Daphnia magna	1.19 - 6.32	48 hours	$BeSO_4$
Crustacean	*Daphnia magna*	236 - 538	48 hours	$Be(OH)_2$
Fish	*Oncorhynchus mykiss*	0.38		$BeCl_2$

2.7.3 Bioaccumulation

The bioaccumulation of beryllium is low at all levels of the food web. However, bioconcentration in the aquatic environment has been observed on one occasion [6, 8]. It was the case in areas with intensive combustion of coal, which resulted in high concentrations of beryllium in the aquatic environments and aquatic organisms. Natural organometallic compounds with beryllium are not known.

2.8 Conclusions

Beryllium is used primarily in electronic equipment. The salts of beryllium are in most cases the only beryllium compounds, which can result in adverse environmental effects. In aquatic ecosystems the concentration of beryllium ions is low because the low solubility of the beryllium salts at the pH found in these environments. Beryllium has chronic effects (carcinogenic) on humans and animals. Beryllium compounds with high solubility exhibit adverse effects on aquatic standard test organisms at concentrations below 1 mg/L.

2.9 References

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3 Bismuth

3.1 Identity

Table 3.1
CAS No., EINECS No and molecular weight for bismuth

Bismuth (Bi)	CAS No.	7440-69-9
	EINECS No.	231-177-4
	Molecular weight	208.98

Bismuth is a rare metal, which typically is produced as a by-product during the refining of other metals [1].

3.2 Physico-chemical properties

Bismuth is found in group VB in the periodic table and it has the valences +3 (Bi(III)) and +5 (Bi(V)). Bismuth has a density of 9.80 g/cm^3. It belongs to class B of the heavy metals, where the very toxic metals such as lead, thallium and mercury are found also [6]. Bioavailable bismuth is found as e.g. BiO^+ or $Bi(OH)_2^+$.

Table 3.2
Physico-chemical data for metallic bismuth. Data from [2, 8]

Bismuth (Bi)	Valence	III, V
	Density (g/cm^3)	9.8
	Melting point (°C)	271
	Boiling point (°C)	1,500
	Solubility in water (g/L)	insoluble

3.3 Uses and consumption

3.3.1 Uses

Bismuth has a wide range of uses and is often used as substitute for other metals, especially lead [13]. Below the most common uses are mentioned.

Antimony and bismuth can replace each other in several products [10]. Often bismuth, gallium and indium are used together in e.g. semi conductors [14]. Bismuth is used alone in metal alloys where a low melting point is required, in the petrochemical industry, ceramics, glass, pigments, electronics, plastic, fuses and optical instruments.

Bismuth is used to decrease the melting point of alloys when added in low concentrations. Good examples are Woods and Roses metals, which both contain bismuth, lead, and tin. These are used in thermal fuses in automatic fire protection installations [10].

An expanding area where bismuth is used (as a bismuth-molybdenum compound), is as a catalyst in the production of acrylonitrile and polyurethane foams [12].

The salts of bismuth have a low toxicity and they are therefore widely used in the pharmaceutical and cosmetic industry [6].

Additional areas where bismuth is used are in pigments/paint (often as a substitute for Cd-, Pb- and Cr-pigments), catalysts, super conducting materials, ceramic coloring, lubricants, flame retardants, glassware, ammunition, fluorescent lamps, prevention of tin-pest, and batteries [11, 12].

Substitution of organotin compounds in agricultural pesticides and marine antifoulants with organobismuth compounds decrease the marine-life toxicity problems. [12].

3.3.2 Consumption

The global production of bismuth (often as a by-product in mining of lead, tin, cobber, wolfram, silver, and gold) was 4,000 tons in 1996. The consumption in USA was approximately 1700 tons.

Assuming that the per capita consumption in Denmark and USA are identical, the Danish consumption is about 36 tons per year based on 1996 figures [6]. In Table 3.3 the distribution of the use in the USA is shown. From this distribution the yearly consumption in Denmark is calculated. The recycling percentage of bismuth is low.

Table 3.3
The relative distribution of USA's and Denmark’s consumption of bismuth in 1997 [6]

	Chemicals and pharmaceuticals	Alloys	Other
Distribution in USA	62%	35%	3%
Yearly consumption in DK	22 tons	13 tons	1 ton

3.4 Emissions to and occurrence in the environment

Metallic bismuth is found in nature, but the background concentration in the aquatic and terrestrial environment is low, see Table 3.4.

Table 3.4
Typical background concentration of bismuth in the environment. Data from [8]

Concentrations	Fresh water (µg/L)	Sea water (µg/L)	Sediment (mg/kg)	Soil (mg/kg)	Earth crust (mg/kg)
Typical background concentration	0.02	0.015 - 0.02	0.4	0.1 - 13	0.048

Bismuth is found in concentrations of up to 2.3 mg/kg in waste products from incineration of coal [6]. In oil the concentrations of bismuth can be as high as 0.4 mg/kg. Combustion of fossil fuels is assumed to account for a significant part of the total emission in Denmark. Use of bismuth in e.g. cosmetics, chemicals and other consumer products brings bismuth into solid waste and municipal waste water. This was confirmed by a Danish study, in which bismuth was found in waste water and in sludge from waste water treatment plants [3]. It is assumed that bismuth is emitted from incinerators as $BiCl_3$ [6]. The major part of the emission comes from incineration of municipal solid waste. Cinders and fly ash from coal fired power stations contain 2.6-8 and 9.4-14 mg/kg Bi, respectively [6].

In the analysis of emissions and waste carried out as part of this study, bismuth was identified primarily in sewage sludge and sludge from runoff retention basins, see Table 3.5. In stack gas, treated municipal waste water, and leachate from landfills, the concentration of bismuth is close to the detection limit.

Table 3.5
Levels of bismuth in selected emissions and waste products from measurements conducted as part of this study in the autumn of 2001.

Emission/waste type	Unit	Bi-concentration
Compost:		
Compost from household waste	µg/kg dw	204
Compost from garden waste	µg/kg dw	76
Landfill leachate:		
Landfill 1	µg/L	<0.2
Landfill 2	µg/L	<0.2
Stack gas from MSW incineration:*		
MSW incinerator 1, semi-dry gas cleaning	µg/m^3	<0.016
MSW incinerator 2, wet gas cleaning	µg/m^3	
MSW gas cleaning residuals:*		
Landfill leachate, semi-dry gas cleaning	µg/L	<0.2
Landfill leachate, wet gas cleaning	µg/L	<0.2
*Waste water and sludge from municipal WWTP**:*		
WWTP 1, effluent	µg/L	<0.03
WWTP 2, effluent	µg/L	<0.03
WWTP 1, sludge	µg/kg dw	1,850
WWTP 2, sludge	µg/kg dw	1,130
Road runoff retention basins, sediment:		
Motorway 1	µg/kg dw	510
Motorway 2	µg/kg dw	330

*Municipal solid waste

**Waste water treatment plant

3.5 Danger classification

Bismuth or inorganic bismuth compounds are not on the Danish list of dangerous compounds [7].

3.6 Toxicology

Adverse effects of bismuth and bismuth compounds in humans have been observed from medical treatment rather than exposure from the working environment [9]. In past days, therapeutic treatment with bismuth was often prolonged, and this chronic exposure resulted in symptoms of poisoning. The symptoms resemble those of lead and mercury: hyper salivation, stomatitis, and greyish pale colour of the gums. From prolonged exposure damages on the central nervous system are observed, e.g. absent-mindedness and amnesia, insomnia and encephalitis [15].

Some investigations show that bismuth can be transformed from compounds with low toxicity to compounds with higher toxicity by intestinal bacteria.

Organic $Bi(CH_3)_3$ has a relatively high vapor pressure and can irritate the respiratory tract and the eyes conjunctiva [9].

There is no evidence of carcinogenicity, mutagenicity, or teratogenicity from exposure to bismuth compounds [9].

3.7 Environmental properties

Bismuth is often marketed as an environmentally friendly alternative to the traditional, more toxic heavy metals. Under the present level of exposure and emission to the environment, no adverse effects of bismuth have been observed on humans and animals [6]. According to a Swedish study, no biological functions of bismuth are known. Furthermore, negative effects in the environment are not likely unless the emission increases significantly compared to the present level [6].

3.7.1 Environmental chemistry

Bismuth occurs in fresh and sea water as hydroxides ($Bi(OH)_2^+$ and $Bi(OH)_3^0$). In the aquatic environment bismuth is associated with particulate matter with a high retention time in the aquatic environment. Bismuth can be methylated in the environment. In this form, bismuth has high lipophilicity and it can bioaccumulate in lipid-rich environments. If plants take up the metal, it can be partly or completely deactivated by complexation with phytochelatin. Deactivation of enzymes, which are affected by metals, is thereby avoided. The fact that this mechanism of defence is active with bismuth (and other metals, e.g. Cd^{2+} and Pb^{2+}) indicates that the metal can affect biological functions. The metal has high affinity to particles (comparable with leads metal affinity) [6].

3.7.2 Environmental toxicology

Only limited information regarding the environmental toxicology of bismuth and bismuth compounds is available. Bismuth nitrate has high acute toxicity in the aquatic environment and EC_{50} has been determined to 0.66 mg/L in a four day test using ***Tubifex tubifex*** as test organism. According to this result, the compound should be classified as very toxic to aquatic organisms.

Table 3.6
Test results for environmental toxicity. Data from [4]

Organism	Latin name	EC_{50} (mg/L)	LD_{50} (mg/kg)	Compound
Worms	*Tubifex tubifex*	0.66 - 1.48 (1 - 4 days)		BiN_3O_9
Mammal (mouse)	*Peromyscus maniculatus*		320 (3 days)	$C_{18}H_{15}Bi$

3.7.3 Bioaccumulation

The available data on environmental fate of bismuth is not sufficient to conclude on its ability to bioaccumulate. In the marine environment, bismuth is typically associated with particulate matter.

3.8 Conclusions

The physical properties of bismuth make it a good substitute for certain heavy metals. The metal is used in e.g. cosmetics where it shows no adverse effects in low concentrations. Bismuth is dispersed from diffuse sources and the concentration of bismuth in the environment is generally low. High concentrations of bismuth in sewage sludge and in ash from waste incineration were observed. The environmental toxicity of bismuth is generally low compared to other heavy metals.

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4 Boron

4.1 Identity

Table 4.1
CAS No., EINECS No. and molecular weight for boron

Boron(B)	CAS No.	7440-42-8
	EINECS No.	231-151-2
	Molecular weight	10.81

4.2 Physico-chemical properties

Boron is not found in its elemental form in nature but it occurs commonly as boric acid ($B(OH)_3$), borate compounds such as $B(OH)_4^-$ and $Na_2O{\bullet}2B_2O_3{\bullet}10H_2O$ (sodium borate), boron halides (e.g. BCl_3) and boron hydrides as e.g. B_2H_6 [2, 13]. While boric acid and borates are water soluble, most boron halides and hydride hydrolyses with contact with water, forming boric acid. Boric acid in the aquatic environment is found as $B(OH)_4^-$. Metallic boron is not water soluble. Below selected physico-chemical data for metallic boron are shown (data from [1, 3]).

Table 4.2
Physico-chemical data for metallic boron

Boron(B)	Valence	III
	Density (g/cm^3)	2.3
	Melting point (°C)	2,180
	Boiling point (°C)	3,650
	Solubility in water (g/L)	insoluble

4.3 Uses and consumption

4.3.1 Uses

Boron is used in form of sodium borate as bleaching agent in detergents. On a weight basis, this is the most important use of boron [8, 14].

Enamel can be based on borates. These can also be the starting point in the formation of glass from supercooling of borate. The borates have also a capacity to dissolve oxides and can therefore be used as a flux [14].

Boron is used in low concentration in metal alloys (especially steel) acting as a hardener. In a wide range of products such as plastics, oil, fat and other materials where increased thermal conductivity are required, boron is used as additive [18]. It is especially the compounds triisopropyl borate (TIPB) and triphenyl boron (TPB), which are in focus as e.g. catalysts [19].

Boron trioxide (also named boron oxide) is used together with SiO_2 and Na_2CO_3 for preparation of heat resistant Pyrex glass and as flame retardant in paint.

Weak solutions of boric acid, $B(OH)_3$ are used for mouth and eye rinsing purposes [6].

Boron compounds are used as dietary supplement. It is believed to impede losses of calcium, phosphor and magnesium through the urine [16, 17].

The boron compounds are used in tanning of skin, in cosmetics, photographical materials, soaps and detergents. Certain pesticides and wood preservatives can contain boron compounds [15].

The layered structure of boric acid is utilised in lubricants. The compound boron nitride can form both graphite- and diamond like structures [14]. Boric acid and borax ($Na_2B_4O_7$) are used as combined flame retardant and biocide in some alternative building isolation materials (wool, paper and flax).

Metal alloys with boron have increased hardness and melting point and can therefore be used where such properties are required [14].

A new product based on boron is the so-called "Boron Nitride Nanotubes", which is used for surface treatment where a very hard surface is required such as the exterior of airplane windows [20]. Boron nitride can in many occasions replace fluoro-based polymers and is also used in paints [23, 24].

4.3.2 Consumption

The consumption of detergents in Denmark with and without bleaching agents is approximately 36,000 tons pr. year [8]. If assumably half of this amount contains 15% borate as bleaching agent, 2,700 tons of borate is consumed yearly. With a boron content of 18%, the boron consumption is approximately 500 tons.

4.4 Emissions to and occurrence in the environment

Boron exists naturally in the environment and is found in e.g. sea water as $B(OH)_4^-$ in the mg/L-range.

The use of borate and boric acid in industry and households are the major emission sources, while only a small part of the boron emission comes from combustion of fossil fuels.

Table 4.3 shows the background concentration of boron in the aquatic and terrestrial environment.

Table 4.3
Typical background concentration of boron in the environment. Data from [2, 11]

Concentrations	Fresh water (µg/L)	Sea water (µg/L)	Sediment (mg/kg)	Soil (mg/kg)	Earth crust (mg/kg)
Typical background concentration	7 - 500	4,440	100	2 - 270	10

A limited investigation of the levels of boron (and the other elements covered by this study) in the major emissions and waste streams in society was conducted in the autumn of 2001, see Table 4.4.

In Danish waste streams very high concentrations of boron are found in sludge and compost. Boron is also among the metals which are found in highest concentration in sediment from runoff retention basins, see Table 4.4. Boron concentration is low in treated waste water and leachate from landfills.

Table 4.4
Levels of boron in selected emissions and waste products from measurements conducted as part of this study in the autumn of 2001.

Emission/waste type	Unit	B-concentration
Compost:		
Compost from household waste	µg/kg dw	34,000
Compost from garden waste	µg/kg dw	32,000
Landfill leachate:		
Landfill 1	µg/L	9,400
Landfill 2	µg/L	1,700
Stack gas from MSW incineration:*		
MSW incinerator 1, semi-dry gas cleaning	µg/m^3	-
MSW incinerator 2, wet gas cleaning	µg/m^3	-
MSW gas cleaning residuals:*		
Landfill leachate, semi-dry gas cleaning	µg/L	1,090
Landfill leachate, wet gas cleaning	µg/L	1,180
*Waste water and sludge from municipal WWTP**:*		
WWTP 1, effluent	µg/L	710
WWTP 2, effluent	µg/L	880
WWTP 1, sludge	µg/kg dw	50,000
WWTP 2, sludge	µg/kg dw	102,000
Road runoff retention basins, sediment:		
Motorway 1	µg/kg dw	45,000
Motorway 2	µg/kg dw	42,000

*Municipal solid waste

**Waste water treatment plant

4.5 Danger classification

The boron compounds boron tribromide, boron trichloride and boron triflouride are listed on the Danish list of dangerous compounds and are classified as very toxic when inhaled and/or ingestion. Furthermore, these compounds are corrosive [10]. Inorganic and organic boron compounds are not regarded as carcinogenic. The boron compounds should be labelled with the risk sentence R14 (reacts violently with water).

Table 4.5
Classification of and risk phrases for boron compounds. Data from [10]

B-compounds	Physico-chemical properties	Health
Boron tribromide	R14	Tx, R26/28 C, R35
Boron trichloride	R14	Tx, R26/28 C, R34
Boron trifluoride	R14	Tx, R26 C, R35

4.6 Toxicology

Chronic exposure to boron, boric acid and boron derivates in working and indoor environments from ingestion, uptake through skin or mucous membrane results in loss of appetite, loss of weight, vomiting, mild diarrhea, skin eruption and anaemia [25].

Investigations with mouse, rat and dog exposed to sodium borate and boric acid for prolonged periods show that males are more sensitive than females, and that the testicles are the target organ. Depending on the dose effects vary from minor impairment of spermatozoon formation to complete testicle atrophy. Congenital malformation has been observed in experimental animals [26].

No inorganic or organic boron compounds have been tested positive for carcinogenic effects.

4.7 Environmental properties

4.7.1 Environmental chemistry

Most boron compounds have relatively high water solubility and are regarded as mobile. In aquatic environments, boron is found primarily as $B(OH)_4^-$ from which metal complexes are formed [2]. In soil, sorption of boron compound depends on soil pH, content of aluminum oxides and ion oxides, particle size, and content of organic material.

4.7.2 Environmental toxicology

Boron is an essential nutrient for plants, but can also be phytotoxic in high concentrations. The environmental toxicity is low, see Table 4.6. The data on acute aquatic toxicity of boron compounds stated as EC_{50} shows, that adverse effects in aquatic organisms are not likely to occur under normal circumstances. In the terrestrial environment, the LC_{50} is 10,000 ppm for quail and mallard.

Table 4.6
test results for environmental toxicity of boron. Data from [5, 12]

Organism	Latin name	EC_{50} (mg/L)	LD_{50} (mg/kg)	NOEL/NOEC (mg/L)	Compound
Crustacean	*Daphnia magna*	658 - 875 (2 days)		80 (21 days)	$B(OH)_3$
Crustacean	*Daphnia magna*	21.3 (2 days)			BF_3
Aquatic plant (duckweed)	*Lemna minor*	60 (4dage)			B
Bird (quail)	*Colinus virginianus*		10,000 (8 days)		$B_8Na_2O_{13}$
Bird (mallard)	*Anas platyrhynchos*		10,000 (8 days)		$B_8Na_2O_{13}$
Bird (mallard)	*Anas platyrhynchos*			100 - 400 (9 weeks)*	B

* LD_{50} (mg/kg)

4.7.3 Bioaccumulation

Being an essential micronutrient, boron is assimilated by microorganisms and plants [2]. Boron is found in animals and plants and is accumulated in e.g. algae and plants, but food web magnification is not expected.

4.8 Conclusions

Boron is used in industry and households as e.g. bleaching agent in detergents. Boron halides are classified as toxic by ingestion and inhalation. Boron is found as $B(OH)_4^-$ in aquatic environment. This compound has low acute toxicity on aquatic organisms.

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5 Gallium

5.1 Identity

Table 5.1
CAS No., EINECS No and molecular weight for gallium

Gallium (Ga)	CAS No.	7440-55-3
	EINECS No.	231-163-8
	Molecular weight	69.72

5.2 Physico-chemical properties

Gallium is in the same group in the periodic table as boron and aluminum and can have the valences +2 (Ga(II)) and +3 (Ga(III)), though +3 is the normal valence. It is a heavy metal among the transition elements cadmium and lead. Gallium is one of few metals with a melting point close to room temperature.

Table 5.2
Physico-chemical data for metallic gallium. Data from [1, 3]

Gallium (Ga)	Valence	II, III
	Density (g/cm^3)	5.904
	Melting point (°C)	29.8
	Boiling point (°C)	2,403
	Solubility in water (g/L)	Insoluble

5.3 Uses and consumption

5.3.1 Uses

Gallium is used mostly in the electronics industry. It is used together with indium and arsenic in e.g. photo-voltaic cells for automation. These are grouped according to their composition, e.g.: InGaAs and HgCdTe [10]. The consumption of gallium is expected to increase as the used of the classical heavy metals is phased out. This applies especially for mercury, which in many cases can be substituted with gallium [13, 18].

Gallium (together with arsenic or as gallium phosphide) is used in solar cells, transistors, semi conductors, laser equipment (especially violet and blue laser), light emitting transistors, photoelectric cells, DVD's, CD's, and for electronic cooling [6, 12-15, 17-20]. An expansion of the electronics industry is assumed to account for the major part of any increment in consumption in the coming years.

Gallium is used in metal alloys for e.g. dental purposes [13, 18].

5.3.2 Consumption

The yearly consumption in Denmark is assumed to be small. Based on the per capita consumption in USA, the consumption is estimated to be about 0.15-0.24 tons/year.

Table 5.3
The relative distribution of the gallium consumption in USA and the consumption in Denmark in 1997, based on [6]

	integrated circuits	Other electronics	Other
Distribution in USA	40%	59%	1%
Yearly consumption in DK	90 kg	140 kg	2 kg

5.4 Emissions to and occurrence in the environment

The background concentration of gallium in the aquatic environment is low. In sediment and soil, the concentration of gallium is up to 100 mg/kg. Coal and oil contain gallium in concentrations of 1-35 mg/kg and 0.01-1.2 mg/kg, respectively, and combustion of fossil fuels therefore contributes to the emission of gallium to the environment. A Swedish study showed that the gallium concentration in ash from incineration of coal was between 4 and 7 mg/kg [6]. Despite the increment in the use of gallium the last 10 to 20 years, it is estimated that natural weathering of gallium still accounts for a considerable part of the total gallium emission [8].

Table 5.4
Typical background concentration of gallium in the environment. Data from [8]

Concentrations	Fresh water (µg/L)	Sea water (µg/L)	Sediment (mg/kg)	Soil (mg/kg)	Earth crust (mg/kg)
Typical background concentration	0.09	0.03	18	2 - 100	18

A limited investigation of the levels of gallium (and the other elements covered by this study) in the major emissions and waste streams in society was conducted in the autumn of 2001, see Table 5.5.

In Danish waste streams, gallium was found mainly in compost and sewage sludge and sediment from road runoff retention basins. A low gallium concentration was found in stack gas, cleaned waste water, and landfill leachate, se Table 5.5.

Table 5.5
Levels of gallium in selected emissions and waste products from measurements conducted as part of this study in the autumn of 2001.

Emission/waste type	Unit	Ga-concentration
Compost:		
Compost from household waste	µg/kg dw	1,900
Compost from garden waste	µg/kg dw	1,600
Landfill leachate:		
Landfill 1	µg/L	0.22
Landfill 2	µg/L	0.25
Stack gas from MSW incineration:*		
MSW incinerator 1, semi-dry gas cleaning	µg/m^3	<0.11
MSW incinerator 2, wet gas cleaning	µg/m^3	<0.2
MSW gas cleaning residuals:*		
Landfill leachate, semi-dry gas cleaning	µg/L	0.19
Landfill leachate, wet gas cleaning	µg/L	0.28
*Waste water and sludge from municipal WWTP**:*		
WWTP 1, effluent	µg/L	0.12
WWTP 2, effluent	µg/L	<0.02
WWTP 1, sludge	µg/kg dw	6,400
WWTP 2, sludge	µg/kg dw	2,200
Road runoff retention basins, sediment:		
Motorway 1	µg/kg dw	5,200
Motorway 2	µg/kg dw	4,300

*Municipal solid waste

**Waste water treatment plant

5.5 Danger classification

Gallium or inorganic gallium compounds are not on the list of dangerous compounds [7].

5.6 Toxicology

Low gallium assimilation can be observed from the gastrointestinal tract and the toxicity from ingestion is considered to be low. In animal experiments gallium caused kidney injury and had toxic effects on muscle nerves. Blindness and paralysis has been reported in rats and aplastic changes have been reported in dogs. The assimilation pattern was not stated but is assumed to be intravenous. No additional data regarding toxicology of gallium or effects related to exposure from working environment was found [22]. Data regarding the use of different gallium compounds for therapeutic purposes are available but not directly applicable to describe gallium toxicity.

5.7 Environmental properties

5.7.1 Environmental chemistry

Gallium is biologically reactive and forms stable complexes with nitrogen and sulphur groups in living organic material. In the aquatic environment organisms such as algae can assimilate gallium. As for nutrients, gallium is assimilated and released again with the decomposition of dead organic material. However, a fraction of gallium will bind to other particulate matter.

Gallium is found as $Ga(OH)_4^-$ in fresh and sea water. The solubility is strongly dependent on the pH-value. $Ga(OH)_4^-$ is highly soluble at low pH-values while the solubility is low a neutral and high pH-values.

Compared to aluminum, which also forms low soluble hydroxides, gallium will to a lesser degree be present in acidic environments [6].

5.7.2 Environmental toxicology

The toxicity of $GaCl_3$ on rainbow trout is the only test result found regarding the environmental toxicity of gallium. With a LC_{50}-value of 3.5 mg/L for a 28 days test, it is regarded as toxic to aquatic organisms [5]. According to [6], gallium is somewhat more toxic than zinc.

Table 5.6
Test results for environmental toxicity. Data from [5]

Organism-	Latin name	LC_{50} (mg/L)	Compound
Fish	*Oncorhynchus mykiss*	3.5 (28 days)	$GaCl_3$

5.7.3 Bioaccumulation

It is not known if gallium is assimilated in different organisms and whether it can accumulate in the food web.

5.8 Conclusions

The use of gallium has increased in the last decades, mainly due to applications in the electronics industry. Weathering accounts compared to anthropogenic emission for a considerable part of the total gallium emission to the environment. The increased use of gallium has resulted in an increase of gallium in the waste streams. A certain amount of the total emission comes from fossil fuel combustion. The available data regarding fate and effect of gallium in the environment is not sufficient to allow a thorough evaluation. It is assumed that gallium is less toxic than the heavy metals cadmium and lead, but more toxic than zinc.

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6 Indium

6.1 Identity

Table 6.1
CAS No., EINECS No. and molecular weight for indium

Indium (In)	CAS No.	7440-74-6
	EINECS No.	231-180-0
	Molecular weight	114.82

6.2 Physico-chemical properties

Indium is a very soft, silvery-white metal. It belongs to the same group in the periodic table (IIIB) as boron and aluminum. +3 (In(III)) is the typical valence, but valences +1 and +2 can also be seen [1]. With a density of 7.3 g/cm^3, indium is a heavy metal belonging to the transition elements together with e.g. cadmium and lead. Indium dissolves slowly in diluted acids and fast in hot, concentrated acids. The metal is not attacked by bases [11].

Table 6.2
Physico-chemical data for metallic indium. Data from [1, 3]

Indium (In)	Valence	I, II, III
	Density (g/cm^3)	7.3
	Melting point (°C)	156
	Boiling point (°C)	2,000
	Solubility in water (g/L)	insoluble

6.3 Uses and consumption

6.3.1 Uses

The most important use of indium in USA today is in liquid crystal displays (LCD) [17].

Indium is used in high-efficient solar cells such as $CuInSe_2$ and InP, in electronics in combination with phosphorus, selenium, copper, tellurium, tin, arsenic, nitrogen, mercury, silver, sulphur, zinc, lead, gallium and bismuth (especially semi conductors [13]) and in selected metal alloys of e.g. tin, bismuth, gold, lead and zinc [2, 13, 15]. The gallium-indium alloys are important since they are liquid at ambient temperature and are used in for transmission of both heat and electricity. Lasers, cameras and IR-detection equipment are other areas where indium is used [15, 17].

Indium is used in sodium lamps, as an additive in chemical products, and in mercury-free dry cells. [14]. As a substitute for mercury in alkaline batteries, indium compounds such as indium hydroxide, indium acetate, and indium sulphate are used [15].

To avoid thermal damages when materials with different coefficient of conductivity are combined, indium is often in the soldering material to decrease the thermal stress [15].

By use of galvanic processes, metal surfaces can be covered with indium in order to achieve surface hardness and resistance to corrosion [16].

In dentistry, as much as 10% of indium is used in gold alloys.

6.3.2 Consumption

The world production of indium was between 200 and 240 tons/year in 1995-1997 [6]. The consumption of indium has increased more than any other metal in the last 15 year. The expansion of the electronics industry is assumed to account for the major part of this increment [8].
From the per capita consumption in USA, the Danish consumption is estimated to be approximately 1 ton/year.

Table 6.3

The relative distribution of USA's consumption and the Danish use of indium in 1997 based on [8]

	LCD displays	Alloys	Electronics incl. batteries	Other
Distribution in USA	50%	33%	12%	5%
Yearly consumption in DK	480 kg	320 kg	120 kg	50 kg

In Sweden, the recycling of indium is low and 0.4-1.0 tons of indium is disposed of yearly. This corresponds to a recycling of 25-62 %. With the Swedish conditions applied in Denmark, the disposal of indium will amount to approximately 0.2-0.6 tons yearly.

6.4 Emissions to and occurrence in the environment

As seen in Table 6.4, the concentration of indium is very low in seawater and earth crust.

The high increase in indium consumption during the last decades will be reflected in emission from use and waste handling. Only sparse information on emissions is available from Danish and Swedish investigations. High concentrations were observed in sewage sludge from waste water treatment plants receiving waste water from industries using indium [8].

Usage of indium in electronics will probably in the future be reflected in increased indium concentration in the waste streams. A Danish investigation from 1996 showed that the concentration of indium in waste water and sewage sludge was low [4]. This was confirmed with the results from the present study, see Table 6.5. The concentration of indium was relatively low compared to the concentration of the other metals that were measured. A Swedish study showed that cinder and fly ash from waste incineration were rich in indium (0.8-3.1 mg/kg), whereas the concentration is sediments and sewage sludge was low [8].

During waste incineration indium will be in the liquid phase due to its low melting point, and indium will adsorb on the smallest particles. Indium compounds with low boiling point such as e.g. indium chloride will be on gaseous form during waste incineration and therefore constitute a potential risk of indium dispersion.

The low concentrations of indium in coal results in low indium emission related to coal combustion [8].

Table 6.4
Typical background concentration of indium in the environment. Data from [2, 10]

Concentrations	Sea water (µg/L)	Sediment (mg/kg)	Soil (mg/kg)	Earth crust (mg/kg)
Typical background concentration	0.00011	0.044	0.7 - 3	0.049

Table 6.5
Levels of indium in selected emissions and waste products from measurements conducted as part of this study in the autumn of 2001.

Emission/waste type	Unit	In-concentration
Compost:		
Compost from household waste	µg/kg dw	20
Compost from garden waste	µg/kg dw	14
Landfill leachate:		
Landfill 1	µg/L	<0.04
Landfill 2	µg/L	<0.04
Stack gas from MSW incineration:*		
MSW incinerator 1, semi-dry gas cleaning	µg/m^3	<0.045
MSW incinerator 2, wet gas cleaning	µg/m^3	<0.2
MSW gas cleaning residuals:*		
Landfill leachate, semi-dry gas cleaning	µg/L	<0.04
Landfill leachate, wet gas cleaning	µg/L	<0.04
*Waste water and sludge from municipal WWTP**:*		
WWTP 1, effluent	µg/L	<0.009
WWTP 2, effluent	µg/L	<0.009
WWTP 1, sludge	µg/kg dw	34
WWTP 2, sludge	µg/kg dw	94
Road runoff retention basins, sediment:		
Motorway 1	µg/kg dw	61
Motorway 2	µg/kg dw	68

*Municipal solid waste

**Waste water treatment plant

6.5 Danger classification

Indium or inorganic indium compounds are not listed on the Danish list of dangerous compounds [9].

6.6 Toxicology

The toxicological data for indium is limited. No data was found in the standard works of reference [7, 12]. Indium can impede protein synthesis, thereby affecting numerous essential physiological processes, including detoxification of organic carcinogens [8]. Intravenous indium chloride exposure to mice had a toxic effect on the kidney and resulted in necrosis of the liver [18]. As for gallium, data regarding therapeutic use of indium compounds is available. However, these data can not be used to describe the toxicology of indium.

6.7 Environmental properties

The information on the environmental properties of indium is sparse. It is expected that its environmental properties are similar to the properties of gallium.

6.7.1 Environmental chemistry

Distribution of indium in the soil between particle-bound and mobile forms of the element is not known. Indium is probably found as hydroxides, whose solubility depends on the pH.

$In(OH)_2^+$ and $In(OH)_3^0$ are the typical compounds in the aquatic environment. It is possible that indium is biologically reactive and can form stable complexes with nitrogen and sulphur in living organic material. In the aquatic environment, indium is expected to be assimilated by e.g. algae [8]. A fraction will, however, be sorbed on particulate matter.

6.7.2 Environmental toxicology

No data on environmental toxicity was found for indium by searching in the AQUIRE database [5].

6.7.3 Bioaccumulation

It is not known if indium can bioaccumulate.

6.8 Conclusions

Indium is used in e.g. the electronics industry, and the consumption has increased significantly in recent years. This increase has resulted in higher amounts of indium in the waste. However, concentrations are still low in e.g. wastewater and compost. The available data regarding environmental fate of indium is not sufficient for proper evaluation.

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7 Lithium

7.1 Identity

Table 7.1
CAS No., EINECS No. and molecular weight for lithium

Lithium (Li)	CAS No.	7439-93-2
	EINECS No.	231-102-5
	Molecular weight	6.94

7.2 Physico-chemical properties

Lithium has the lowest density of all metals and is the lightest of those elements that are solid at room temperature. It is a group 1A element in the periodic table and has the valence +1 (Li(I)). Lithium is generally very reactive and reacts explosively with water. Li_2O is formed when lithium is burned. Lithium salts as e.g. Li_2CO_3, LiF and Li_2PO_4 are all only slightly soluble in water [1].

Table 7.2
Physico-chemical data for metallic lithium. Data from [1, 2]

Lithium (Li)	Valence	I
	Density (g/cm^3)	0.534
	Melting point (°C)	179
	Boiling point (°C)	1,336
	Solubility in water (g/L)	reacts explosively with water

7.3 Uses and consumption

7.3.1 Uses

An important use of lithium is as cathode (oxides of lithium) or anode material (metallic lithium) in batteries for electronic equipment. These batteries are especially used in equipment where low weight is required, e.g. cameras and portable video recorders, mobile phones and portable PC's [10. 11, 13].

Lithium is used in many lightweight metal alloys e.g. together with magnesium and aluminum in airplanes and cars [13, 20]. It is also used as additive in lead alloys [20].

The aluminum industry use significant amounts of lithium in the form of lithium carbonate for the production of aluminum and Al-Li-alloys [12].

In the production of glass and ceramics, lithium carbonate, lithium fluoride, lithium sulfate, lithium phosphate, and lithium orthophosphate are used as additives [13, 20].

Lithium compounds are added to some types of cement. For example, lithium sulfate is used as a general additive and lithium nitrate as inhibitor of the undesired alkali-silica-reactivity [13].

In the production of synthetic rubber, different lithium compounds are used [20]. In textiles, lithium chloride can be used as stabilizer [13]. Lubricants can contain lithium hydroxide [13].

Medicine for treatment of patients with mental disorders often contains lithium [14, 21], e.g. use of lithium carbonate in the treatment of manic-depression [15, 16, 18, 19, 21].

The compounds lithium aluminum hydride and lithium boron hydride are often used as reducing agents in chemical synthesis. Numerous lithium compounds find application in chemical synthesis [13].

7.3.2 Consumption

The global production was 11,000 tons in 1996-1997, and the consumption in USA was approximately 2,800 tons. From the per capita consumption in USA it is estimated that the Danish consumption of lithium is approximately 55-60 tons.

Table 7.3
The relative distribution of the global consumption and the Danish use of Lithium in 1996 based on [5]

	Ceramics and glass	Aluminum production	Synthetic rubber and medicine	Chemicals	Lubricants	Batteries	Other
Global distribution	20%	18%	13%	25%	11%	7%	4%
Consumption in Denmark	11 tons	10 tons	7 tons	14 tons	6 tons	4 tons	2 tons

7.4 Emissions to and occurrence in the environment

Generally, lithium is not regarded as having adverse effects on the environment, and it is found naturally in the aquatic and terrestrial environment. In fresh water and sea water lithium is found as Li^+. Furthermore, it can be found as Li_2CO_3, LiCl or Li_2O in the terrestrial environment. Emission of lithium originates from e.g. combustion of fossil fuels or waste. In coal and oil the concentration of lithium is 10-50 mg/kg and approximately 0.002 mg/kg, respectively [5]. The concentration of lithium in waste from incinerators and in sewage sludge is low [5]. The concentration is high in leachate from landfills where MSW gas cleaning residuals have been disposed.

Table 7.4
Typical background concentration of lithium in the environment. Data from [4, 7]

Concentrations	Fresh water (µg/L)	Sea water (µg/L)	Sediment (mg/kg)	Soil (mg/kg)	Earth crust (mg/kg)
Typical background concentration	0.07 - 40	170 - 194	56	3 - 350	20

A limited investigation of the levels of lithium (and the other elements covered by this study) in the major emissions and waste streams in society was conducted in the autumn of 2001, see Table 7.5.

Lithium was found in all environmental samples in relatively high concentrations. The concentration was high in especially compost, waste water, sewage sludge and sediment from road runoff retention basins, while the concentration in effluent from waste water treatment plants was low.

Table 7.5
Levels of lithium in selected emissions and waste products from measurements conducted as part of this study in the autumn of 2001.

Emission/waste type	Unit	Li-concentration
Compost:		
Compost from household waste	µg/kg dw	4,640
Compost from garden waste	µg/kg dw	4,690
Landfill leachate:		
Landfill 1	µg/L	201
Landfill 2	µg/L	49.4
Stack gas from MSW incineration:*		
MSW incinerator 1, semi-dry gas cleaning	µg/m^3	<9.1
MSW incinerator 2, wet gas cleaning	µg/m^3	1.0
MSW gas cleaning residuals:*		
Landfill leachate, semi-dry gas cleaning	µg/L	285
Landfill leachate, wet gas cleaning	µg/L	367
*Waste water and sludge from municipal WWTP**:*		
WWTP 1, effluent	µg/L	11.4
WWTP 2, effluent	µg/L	21.2
WWTP 1, sludge	µg/kg dw	6,060
WWTP 2, sludge	µg/kg dw	5,015
Road runoff retention basins, sediment:		
Motorway 1	µg/kg dw	16,300
Motorway 2	µg/kg dw	15,500

*Municipal solid waste

**Waste water treatment plant

7.5 Danger classification

Lithium, lithium aluminum hydride, and lithium methanolate are found on the Danish list of dangerous substances. The latter is along with metallic lithium classified as ***corrosive***. No lithium compounds are classified for adverse environmental effects [6].

Table 7.6
Classification of and risk phrases for lithium and lithium compounds

	Physico-chemical properties	Health
Lithium	F, R14/15	C, R34
Lithium aluminum hydride	F, R15	-
Lithium methanolate	F, R11 R14	C, R34

7.6 Toxicology

The primary target organ for lithium toxicity is the central nervous system. Lithium is therefore used therapeutically on membrane transport proteins in the central nervous system when treating manic-depression. Lithium is moderately toxic with lethal dose of LiCl in rats of 526-840 mg/kg body weight [22]. After chronic exposure to 1 mEq/L decreased brain weight was observed in male offspring [22]. Chemically, lithium resembles sodium, but is more toxic: in humans 5 g LiCl can result in fatal poisoning [8]. In therapeutic doses, damages on the central nervous system and the kidneys have been reported [23].

7.7 Environmental properties

7.7.1 Environmental chemistry

Lithium is found primarily as Li+ in the aquatic environment. A release of lithium-containing waste can result in wide dispersal due to low biological uptake and sorption to particulate matter.

7.7.2 Environmental toxicology

The lithium concentration in fresh water and sea water is on the µg/L-level. The acute toxicity of lithium is low, and lithium is considered as not being acutely toxic to aquatic organisms at the concentrations found in treated municipal waste water. The acute environmental effect concentration measured as EC_{50} on ***Daphnia magna*** was determined to be 33-197 mg/L, which is at least 1000 times higher than the level in fresh water. Both lithium chloride and lithium sulphate has high water solubility, and the compounds will dissociate in aqueous environment.

Table 7.7
Test results for environmental toxicity. Data from [3]

Organism	Latin name	EC_{50}/LC_{50} (mg/L)	NOEC, (mg/L)	Compound
mollusc	*Dreissena polymorpha*	185 -232 (24 hours)		LiCl
crustacean	*Daphnia magna*	33 - 197 (24 hours)		Li_2SO_4
worms	*Tubifex tubifex*	9.3 - 44.8 (24 - 96 hours)		Li_2SO_4
fish	*Pimephales promelas*	1 - 6.4 (26 days)	0.200 - 5,4 (26 days)	LiCl
fish	*Tanichthys albonubes*	9 - 62 (48 hours)		LiCl
earth worms	*Eisenia fetida*	10 mmol/kg soil (7 weeks)		LiCl

7.7.3 Bioaccumulation

No data regarding bioaccumulation of lithium was found, but based on its low affinity to particles it is not expected to bioaccumulate.

7.8 Conclusions

Lithium is used in e.g. batteries, lubricants, ceramics and chemicals. No point sources, which can give adverse effects in the environment, have been identified. Lithium is mainly found on ion form in the environment and is not expected to bioaccumulate. Toxicity and environmental toxicity are low.

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8 Molybdenum

8.1 Identity

Table 8.1
CAS No., EINECS No and molecular weight for Molybdenum

Molybdenum (Mo)	CAS No.	7439-98-7
	EINECS No.	231-107-2
	Molecular weight	95.94

8.2 Physico-chemical properties

Molybdenum is a heavy metal belonging to group VIA in the periodic table. It occurs in valences from -2 to +6 [11]. The high oxidation numbers are most common and stable [12]. Metallic molybdenum has a silver-white metal glance. Molybdenum is oxidized at high temperature. It is not soluble in water, but has high solubility in concentrated sulphuric acid and nitric acid.

Table 8.2
Physico-chemical data for metallic molybdenum. Data from [1,3, 8]

Molybdenum (Mo)	Valence	II, III, IV, V, VI
	Density (g/cm^3)	10.28
	Melting point (°C)	2,622
	Boiling point (°C)	4,825
	Solubility in water (g/L)	Insoluble

8.3 Uses and consumption

8.3.1 Uses

Molybdenum is used in alloys of steel and for specialty steel/stainless steel [4, 24, 30]. It is also used widely in:

- catalysts for the chemical industry, especially the petrochemical industry [27, 31]
- color pigments (lead molybdenum) [27, 32]
- plastic [4]

It has been used mainly in metal alloys, e.g. special alloys to airplanes, weapons, [31], electronic components [22], sports equipment (petanque-balls, skies and hockey skates [19, 20], but is also used in alloys for electrodes [31].

Molybdenum trioxide is used as a flame retardant in e.g. polyester products [26].

The layered structure of molybdenum sulphide is utilised in lubricants for the automobile industry due to its high heat resistance [24, 27, 31]. Molybdenum has also a good conductivity and has therefore been applied in heating elements in high temperature furnaces [18].

Molybdenum is sold as dietary supplement and vitamins to animals and humans [21, 23, 32] and as plant nutrient for soils being deficient with respect to molybdenum [31].

8.3.2 Consumption

About 250 kg of molybdenum was discharged from industrial sources in Denmark in 1998 [6].

In the USA, 15,000 tons of molybdenum was used in 2000 [27]. From the per capita consumption in USA it is estimated that the Danish consumption is 275 tons per year.

8.4 Emissions to and occurrence in the environment

Anthropogenic discharges of molybdenum come from many industrial uses, combustion of fossil fuels and incineration of waste.

The content of molybdenum in fossil fuels is not known, but the concentration of molybdenum in air is approximately a factor of 10 higher in the urban environment than in countryside areas [15]. The concentration of molybdenum in fly ash, cinders and sewage sludge is 26-49, 2.5-14 and 1.4-17.4 mg/kg dw respectively [14, 16, 17]. This is supported by the high concentration of molybdenum observed in waste gas and in leachate from land fills where waste products from waste gas cleaning have been disposed (Table 8.4).

Molybdenum occurs naturally in aquatic and terrestrial environments at low concentrations. In fresh water the concentration of molybdenum is between 0.03 and 10 µg/L and is typically found as MoO_4^{2-} in oxidised environments. Table 8.3 shows the typical concentration of molybdenum in the environment.

Table 8.3
Typical background concentration of molybdenum in the environment. Data from [9, 16]

Concentrations	Fresh water (µg/L)	Sea water (µg/L)	Sediment mg/kg)	Soil (mg/kg)	Earth crust (mg/kg)
Typical background concentration	0.03 - 10	4 - 10	2	0.1 - 40	1.5

A limited investigation of the levels of molybdenum (and the other elements covered by this study) in the major emissions and waste streams in society was conducted in the autumn of 2001, see Table 8.4.

Molybdenum was found in relatively high concentrations in leachate and waste water, see Table 8.4. Sewage sludge and sediment from road runoff retention basins do also contain high molybdenum concentration compared to the other metals included in this study.

Table 8.4
Levels of molybdenum in selected emissions and waste products from measurements conducted as part of this study in the autumn of 2001.

Emission/waste type	Unit	Mo-concentration
Compost:		
Compost from household waste	µg/kg dw	2110
Compost from garden waste	µg/kg dw	880
Landfill leachate:		
Landfill 1	µg/L	0.5
Landfill 2	µg/L	8.98
Stack gas from MSW incineration:*		
MSW incinerator 1, semi-dry gas cleaning	µg/m^3	120
MSW incinerator 2, wet gas cleaning	µg/m^3	1.5
MSW gas cleaning residuals:*		
Landfill leachate, semi-dry gas cleaning	µg/L	27
Landfill leachate, wet gas cleaning	µg/L	1140
*Waste water and sludge from municipal WWTP**:*		
WWTP 1, effluent	µg/L	2.7
WWTP 2, effluent	µg/L	5.95
WWTP 1, sludge	µg/kg dw	9440
WWTP 2, sludge	µg/kg dw	13,300
Road runoff retention basins, sediment:		
Motorway 1	µg/kg dw	10,900
Motorway 2	µg/kg dw	3,700

*Municipal solid waste

**Waste water treatment plant

8.5 Danger classification

MoO_3 is, except from molybdenum orange (lead chromate molybdate sulphate, CI pigment red 104) and a molybdenum-doped vanadium compound [7], the only inorganic molybdenum compound, which is found on the Danish list of dangerous compounds. Molybdenum trioxide is classified as ***harmful*** with risk phrases R48/20/22 (harmful: danger of serious damage to health by prolonged exposure through inhalation and if swallowed) and irritant for eyes and respiratory system.

Table 8.5
Classification of and risk phrases for molybdenum and molybdenum compounds

	Mo-trioxid
Health	Xn; R48/20/22 Xi; R36/37

8.6 Toxicology

Molybdenum forms part of many enzymes and is regarded as an essential metal. Hence, both deficiency effects and toxic effects can be observed depending on molybdenum concentration. Long term exposure of low molybdenum concentrations does not result in chronic adverse effects. It seems, however, that there is a relation between low cobber metabolism and assimilation of molybdenum, and the importance of excretion from the kidneys could indicate that sensible individuals are to be found among groups with these characteristics [8]. Typical effects from sub-chronic and chronic oral exposure of experimental animals to high molybdenum concentrations are destabilization of the gastrointestinal tract, growth retardation, anaemia, bone deformity, sterility, and kidney and liver abnormalities.

8.7 Environmental properties

Molybdenum is an essential micro-nutrient, which forms part of several enzymes in bacteria, fungi, plants and mammals [9]. Among the molybdenum-containing enzymes are oxidases, dehydrogenases and nitrogenases [13].

8.7.1 Environmental chemistry

Some molybdenum compounds, e.g. MoO_3, can evaporate, while molybdenum in the terrestrial environment is relatively immobile. The sorption potential in soil is high (0.15-2.02 mg/g) and depends on the content of clay and organic matter. Molybdenum is found as MoO_4^{2-} in the aquatic environment. Transport of molybdenum in soil and groundwater reservoirs occurs slowly, depending on pH and content of sulphate and phosphate.

Amendment of sewage sludge on farm land results in molybdenum supply to the soil. After intensive sludge amendment the concentration of molybdenum can be as high as three times the background concentration [2].

MoO_4^{2-} as found in the aquatic environment can be reduced and precipitate when the environment turns anoxic. Under these conditions, molybdenum forms compounds of low solubility such as ion monosulphides. Molybdenum can also adsorb to ion oxides or organic matter and thereby be removed from the water phase [2].

8.7.2 Environmental toxicology

Results from environmental toxicity tests with molybdenum and molybdenum compounds are shown in Table 8.6. The acute toxicity measured as LC_{50} on ***Daphnia magna*** is low: 2.848 mg Na_2MoO_4/L [10]. The toxicity of an unspecified Mo-compound and MoO_3 to algae and crustaceans are higher, but does not enough to result in a classification as dangerous for aquatic organisms. Ruminants have been observed to develop anaemia, growth retardation and diarrhea when grazing on pastureland with 20-100 ppm molybdenum [11, 15].

Table 8.6
Test results for environmental toxicity. Data from [5, 10]

Organism	Latin name	EC_{50} /LC_{50} (mg/L)	Compound
Algae	*Gymnodinium splendens*	4.5 - 100 (48 hours)	Mo
	Thalassiosira guillardii	52 - 100 (48 hours)	Mo
Crustacean	*Daphnia magna*	2.848	Na2MoO4
	Americamysis bahia	180 (96 hours)	MoO3

8.7.3 Bioaccumulation

Molybdenum is an essential micro-nutrient and it is assimilated naturally in all parts of the food web. No bioaccumulation of the metal has been observed in lipid rich biota. It is not expected that molybdenum biomagnifies in the food web.

8.8 Conclusions

Molybdenum is used in industry in e.g. alloys and lubricants. The consumption has increased partly because of its use as a substitute for cobber due to its low toxicity. Molybdenum occurs naturally in all environments and is an essential micro nutrient. Amendment of sewage sludge on farmland and resulting increments in molybdenum concentration is not expected to give adverse effects if current sludge amendment procedures are followed. Molybdenum and inorganic molybdenum compounds are not to be classified as dangerous for aquatic organisms.

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9 Palladium

9.1 Identity

Table 9.1
CAS No., EINECS No and molecular weight for palladium

Palladium (Pd)	CAS No.	7440-05-3
	EINECS No.	231-115-6
	Molecular weight	106.42

9.2 Physico-chemical properties

Palladium is a heavy metal belonging to the platinum group in the periodic table. It has in most cases the valence +2 (Pd(II)), but +3 (Pd(III)) and +4 (Pd(IV)) are also possible [1]. Palladium is attacked by sulphuric acid and nitric acid [1]. The physico-chemical properties of Pd(II)-compounds resembles the platinum (Pt(II)) compounds. However, the Pd(II)-compounds are generally more reactive and have higher solubility in water. Table 9.2 shows selected data on palladium's physico-chemical properties (data from [2, 6]).

Table 9.2
Physico-chemical data for metallic palladium

Palladium (Pd)	Valence	II, III, IV
	Density (g/cm^3)	12.02
	Melting point (°C)	1,555
	Boiling point (°C)	3,167
	Solubility in water (g/L)	Insoluble

9.3 Uses and consumption

9.3.1 Uses

The expansion of the electronics industry is supposed to account for the major part of the recent increase in consumption, e.g. from the use in printed circuit boards [8]. Palladium is also used in significant amounts in catalytic converters in automobiles [8].

Sweden recycles palladium from electronic equipment and catalytic converters and a similar trend is expected in Denmark due to requirements in the national legislation on waste handling [3, 8].

A special use of palladium in Sweden and Denmark is in the alloying of gold in dentistry [8].

According to Swedish experience, palladium is used as the pure metal or as $PdCl_2$ [8].

9.3.2 Consumption

The global consumption has increased significantly throughout the 20th century [8], and the global production was 240 tons in 1997. From the per capita consumption in USA, the Danish consumption is estimated to approximately 2.4 tons Pd/year [8].

Table 9.3
The relative distribution of the global consumption and the Danish use of Palladium in 1997 based on [8]

	Catalysts	Electronics	Medicine	Chemical industry	Other
Global distribution	40%	33%	18%	25%	11%
Yearly consumption in DK	960 kg	792 kg	432 kg	600 kg	264 kg

Since the 1990's the most significant area of consumption has shifted from the electronic industry to catalysts (including catalytic converters) [8].

9.4 Emissions to and occurrence in the environment

The analysis of waste streams conducted in relation to this study is the only available information on palladium concentration in the environment in Denmark. A Swedish study showed that the level of palladium is highest in lake sediment, sewage sludge, and leachate from waste disposals, cinders, and fly ash [8].

The use of palladium in catalytic converters in automobiles leads to emission on the same level as the platinum-emission. In Sweden this emission is expected to be approximately 3 kg Pd/year which corresponds to 1.8 kg in Denmark. 90 µg/L of palladium is found in road runoff water in Sweden.

Palladium in consumer products will primarily end as solid waste. From the high concentrations found at different waste treatment facilities in Sweden, it is expected that combustion and disposal of solid waste can result in palladium release.

Palladium used in printed circuit boards shall be recycled according to a Danish government order [3].

In aqueous and terrestrial environment palladium is found in low concentrations. Sea water has a concentration of palladium of approximately 0.06 µg/L. Typical concentrations of palladium in the environment are shown in Table 9.4.

Table 9.4
Typical background concentration of palladium in the environment. - indicates that the value is unknown. Data from [5, 7, 8, 12]

Concentrations	Fresh water (µg/L)	Sea water (µg/L)	Sediment (mg/kg)	Soil (mg/kg)	Earth crust (mg/kg)
Typical background concentration	-	0.06	0.175-0.445	0.0004	0.0006

A limited investigation of the levels of palladium (and the other elements covered by this study) in the major emissions and waste streams in society was conducted in the autumn of 2001, see Table 9.5.

Table 9.5 shows the palladium concentration in selected emissions and waste products in Denmark. The level of palladium is generally a little higher than that of platinum. In landfill leachate, sewage sludge and sediment from road runoff retention basins the highest concentrations were found. In treated waste water the concentration of palladium was 0.7-0.9 µg/L.

Table 9.5
Levels of palladium in selected emissions and waste products from measurements conducted as part of this study in the autumn of 2001. When the average of two measurements had a deviation of more than ±50% both measurements are reported.

Emission/waste type	Unit	Pd-concentration
Compost:		
Compost from household waste	µg/kg dw	455
Compost from garden waste	µg/kg dw	250
Landfill leachate:		
Landfill 1	µg/L	2.7
Landfill 2	µg/L	1.1
Stack gas from MSW incineration:*		
MSW incinerator 1, semi-dry gas cleaning	µg/m^3	0.24
MSW incinerator 2, wet gas cleaning	µg/m^3	<0.2
MSW gas cleaning residuals:*		
Landfill leachate, semi-dry gas cleaning	µg/L	0.065 - 0.89
Landfill leachate, wet gas cleaning	µg/L	<0.03
*Waste water and sludge from municipal WWTP**:*		
WWTP 1, effluent	µg/L	0.95
WWTP 2, effluent	µg/L	0.74
WWTP 1, sludge	µg/kg dw	1,020
WWTP 2, sludge	µg/kg dw	990
Road runoff retention basins, sediment:		
Motorway 1	µg/kg dw	850
Motorway 2	µg/kg dw	990

*Municipal solid waste

**Waste water treatment plant

9.5 Danger classification

Palladium or palladium compounds are not listed on the Danish list of dangerous compounds or the list of undesired compounds [9, 10].

9.6 Toxicology

Palladium has not been identified as acute toxic or causing CMR effects. Contact dermatitis has been reported from exposure of metallic palladium and palladium alloys [11]. Individuals suffering from nickel allergy also seem to react on palladium.

9.7 Environmental properties

The use of palladium in electronic equipment and catalytic converters rises concern of the possibility of palladium dispersion due to the relatively high mobility of the Pd(II)-compounds. The data available is not sufficient to enable a thorough analysis of its environmental effects.

9.7.1 Environmental chemistry

Palladium is found as $Pd(OH)_2^0$ in fresh water, and $Pd(OH)_2^0$ and $PdCl_4^{2-}$ in sea water. Palladium can also bind to organic matter in aquatic environments [8]. The palladium assimilated by algae and plankton is released during degradation of organic material.

The relatively high solubility of Pd(II)-ion compounds can result in fast dispersion, impeding accumulation in recipients or other environments that receive palladium, e.g. sludge amended farmland.

Palladium can decrease the enzymatic activity in the organisms that assimilate the metal, due to its ability to bind amino acids.

It is not known whether combustion of palladium rich waste results in emission and subsequent atmospheric deposition, or if the metal immobilises in cinder or in the waste gas cleaning residuals.

9.7.2 Environmental toxicology

Only limited information on the environmental toxicity of palladium was obtained from searching in databases. The only environmental toxicity test found was with the organism ***Tubifex tubifex***. The acute toxicity of $PdCl_2$ measured as EC_{50} (assessed as immobilisation) had a value of 237 µg/L. Based on the result of this test, $PdCl_2$ should be classified as very toxic to aquatic organisms.

Table 9.6
Test results for environmental toxicity (mg/L). Data from AQUIRE [4]

Organism	Latin name	EC_{50} (µg/L)	Compound
Worms	*Tubifex tubifex*	142 - 237 (24 - 48 hours)	$PdCl_2$

9.7.3 Bioaccumulation

No data on bioaccumulation of palladium or palladium compounds were found.

9.8 Conclusions

The consumption of palladium is increasing due to growth in the use of electronic equipment and catalytic converters for automobiles. This is likely to result in increasing emissions too. Only few data on palladium in waste streams and the environment is available from the literature. Measurements conducted as part of this study show that the palladiums concentration are high in sewage sludge, sediment from road runoff retention basins, and in compost. Palladium (II) compounds are expected to have high mobility due to their high water solubility. There is not sufficient data to evaluate the environmental toxicity of palladium.

9.9 References

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10 Platinum

10.1 Identity

Table 10.1
CAS No., EINECS No. and molecular weight for platinum. Data from [3]

Platinum (Pt)	CAS No.	7440-06-4
	EINECS No.	231-116-1
	Molecular weight	195.08

10.2 Physico-chemical properties

Platinum is a heavy metal belonging to group VIII in the periodic table (the platinum group). The valences +2 (Pt(II)), and +4 (Pt(IV)) are most common, but +3 and +6 are also possible [1, 2].
In its pure form platinum is silver-white. It is not oxidised even at high temperatures. Platinum cannot be dissolved in concentrated hydrochloric acid or nitric acid, but dissolves as gold in aqua regia, forming H_2PtCl_6 [1]. Furthermore it is attacked by hot, concentrated sulphuric acid or phosphoric acid, and can be dissolved in molten alkali salts. Platinum binds to organic matter as Pt^{2+} or as $Pt(OH)_2^0$ in the aqueous environment.

Table 10.2 shows selected physico-chemical data for platinum.

Table 10.2
Physico-chemical data for metallic platinum. Data from [1, 9]

Platinum (Pt)	Valence	II,, III, IV, VI
	Density (g/cm^3)	21.45
	Melting point (°C)	1,772
	Boiling point (°C)	3,827
	Solubility in water (g/L)	Insoluble

10.3 Uses and consumption

10.3.1 Uses

The use of platinum to catalytically convert nitrous gasses from e.g. car engines (both gasoline and diesel) is regarded as the quantitatively most important. The content of platinum in a catalytic converter of an automobile is on average about 1.5 g [7].

The catalytic properties of platinum are also used in the chemical and especially in the petrochemical industry [7]. The amount of platinum used in jewellery is similar to what is used for catalytic conversion purposes [7].

In the electronics industry platinum is used for especially in the production of printed circuit boards. Platinum used in printed circuit board shall be recycled according to a Danish government order [4].

Other uses in the electronics industry are high temperature thermometers, thermo elements, crucibles and other laboratory equipment [11].

Platinum is used in displays for computers and televisions [7].

Some medicals contain platinum, e.g. cis-platinum, $Pt(NH_3)Cl_2$, used in cancer treatment [7].

Platinum is used for special equipment in e.g. airplanes, automobiles, electronics and the pharmaceutical industry [8].

10.3.2 Consumption

The global production was 150 tons in 1995, and the consumption in USA was approximately 60 tons [7]. From the per capita consumption in USA, the Danish consumption is assumed to be 1.1-1.3 tons per year (1995 numbers).

The Danish consumption is probably higher today, even though platinum in recent years has been replaced with the cheaper palladium. The development of fuel cells for use in the automobile industry possibly equalizes the decreasing consumption for catalytic converters.

In Table 10.3, the yearly consumption of 1.1-1.3 tons in Denmark is divided into consumption areas.

Table 10.3
The relative distribution of global consumption and the Danish use of platinum in 1996 based on [7]

	Catalytic incineration	Jewellery	Electronics	Glass	Chemical and petrochemical industry	Other including medicine
Global distribution	35.5%	37.5%	5%	5%	8%	9%
Yearly consumption in DK	380 - 450 kg	410 - 470	50 - 60	50 - 60	90 - 100	100 - 110

Due to the high market price on platinum its recycling has economical interest. In USA, the recycling is estimated to account for 30-40 % of the consumption. If this recycling percentage is also valid in Denmark, the yearly loss to the Danish environment is 560-900 kg.

10.4 Emissions to and occurrence in the environment

The concentration of platinum in the aquatic and terrestrial environment is very low, see Table 10.4.

Table 10.4
Typical background concentration of platinum in the environment. Data from [6, 7, 10]

Concentrations	Fresh water (µg/L)	Sediment (µg/kg)	Soil (µg/kg)	Earth crust (µg/kg)
Typical background concentration	0.04 - 0.3	0.1	0.4	1.0

From the literature search no data on the platinum level in Danish waste was found. Hence, the measurements conducted as part of this study, are the only available data on emissions and waste streams, see Table 10.5. A Swedish study confirmed that the platinum concentration in general was lower than the concentration of palladium [7]. I cinder, fly ash, sludge and sediment 30, 87, 34 and 4.2 µg/kg dw was found, respectively [7].

Table 10.5
Levels of platinum in selected emissions and waste products from measurements conducted as part of this study in the autumn of 2001.

Emission/waste type	Unit	Pt-concentration
Compost:		
Compost from household waste	µg/kg dw	6.9
Compost from garden waste	µg/kg dw	2.7
Landfill leachate:		
Landfill 1	µg/L	<0.03
Landfill 2	µg/L	<0.03
Stack gas from MSW incineration:*		
MSW incinerator 1, semi-dry gas cleaning	µg/m^3	<0.041
MSW incinerator 2, wet gas cleaning	µg/m^3	<0.2
MSW gas cleaning residuals:*		
Landfill leachate, semi-dry gas cleaning	µg/L	<0.03
Landfill leachate, wet gas cleaning	µg/L	0.22
*Waste water and sludge from municipal WWTP**:*		
WWTP 1, effluent	µg/L	0.084
WWTP 2, effluent	µg/L	0.060
WWTP 1, sludge	µg/kg dw	19
WWTP 2, sludge	µg/kg dw	28
Road runoff retention basins, sediment:		
Motorway 1	µg/kg dw	16
Motorway 2	µg/kg dw	10

*Municipal solid waste

**Waste water treatment plant

Due to the commercial interest in platinum recycling, the emissions from waste are assumed to be lower than emissions related to the use of platinum containing products. This is confirmed by the low concentrations found in waste from Swedish incineration plants.

Emission of platinum is a result of its use in catalytic converters, and the concentration of platinum is high close to roads with a heavy traffic load [7]. Despite this, the concentration of platinum is low in sediment from road runoff retention basins compared to palladium, see Table 10.5. Since platinum has been detected in sediments of lakes close to urban areas it seems probable that emission of platinum from motor vehicle catalysts can be spread over medium to long distances [7]. Coal contains platinum in a concentration of 0.001 to 1.7 mg/kg [7], and it is expected that a minor amount of platinum will be emitted from coal-fired power plants.

The concentration of platinum in different environmental matrices is given in Table 10.4. Compared to e.g. palladium, soil and earth crust has a relatively high concentration of platinum.

10.5 Danger classification

Several platinum compounds such as chloro platinates are ***toxic*** by ingestion, ***sensitizing*** and ***irritating*** to skin and/or can result in serious eye damage [8]. Platinum compounds found on the Danish list of dangerous compounds are not classified as dangerous to the aquatic environment. According to [7], platinum should be classified as dangerous to the environment with risk sentence R50 (very toxic to aquatic organisms).

Table 10.6
Classification of and risk phrases for platinum compounds

	Health
Tetrachloro platinates with exception of:	T; R25 Xi; R41 R42/43
Diammonium tetrachloroplatinate	T; R25 Xi; R38-41 R42/43
Dipotassium tetrachloroplatinate	T; R25 Xi; R38-41 R42/43
Disodium tetrachloroplatinate	T; R25 Xi; R38-41 R42/43
Hexachloro platinic acid	T; R25 C; R34 R42/43
Hexachloro platinates	T; R25 Xi; R41 R42/43

10.6 Toxicology

Platinum it its metallic form is relatively harmless, but allergic dermatitis from especially complex salts is known [9, 13]. Platinum is as the other noble metals relatively toxic on ionic form or soluble form. This type of exposure is, however, rare due the high price of the metal. Chloroplatinates are ***toxic*** by ingestion and ***irritating*** to skin.

10.7 Environmental properties

10.7.1 Environmental chemistry

Platinum is found as $Pt(OH)_2^0$ in fresh water or bound to organic matter as Pt(II). In seawater $PtCl_4^{2-}$ is also seen. Platinum can be assimilated by algae and plankton in the aquatic environment, and is released once the organic material degrades. It is not strongly bound to particles. No volatile Pt-compounds exist, and platinum is predominantly found in soil, sediment and the aquatic environment [7]. Platinum emitted from catalytic converters can be distributed over significant distances and will accumulate in e.g. sediment. It has been shown that platinum emitted from catalytic converters is biologically available.

10.7.2 Environmental toxicology

Hexachloro platinum acid has an acute toxicity on ***Tubifex tubifex*** of 61 µg/L determined in a 96-hour test, see Table 10.7. According to this result, hexachloro platinum acid is very toxic to aquatic organisms.

Table 10.7
Test results for environmental toxicity. Data from Aquire [5]

Organism	Latin name	EC_{50}/LC_{50} (µg/L)	Compound
Worms	*Lumbriculus variegatus*	397 - 897 (96 hours)	$PtCl_6H_2$
Worms	*Tubifex tubifex*	61 - 95 (24 - 96 hours t)	$PtCl_6H_2$

10.7.3 Bioaccumulation

Platinum is not an essential micro nutrient, and the available information does not give any reason to regard platinum as bioaccumulating.

10.8 Conclusions

The catalytic properties of platinum are widely used in the chemical and the petrochemical industry. Platinum-containing waste is collected for recycling, and emission is related mainly from use of products with platinum. The concentration of platinum in areas with much traffic is high, and platinum can be distributed over relatively long distances according to the wind conditions. The concentration of platinum in sludge and fly ash is low. Several platinum compounds are toxic, and hexachloro platinum acid is toxic to aquatic organisms.

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11 Vanadium

11.1 Identity

Table 11.1
CAS No., EINECS No. and molecular weight for vanadium

Vanadium (V)	CAS No.	7440-62-2
	EINECS No.	231-171-1
	Molecular weight	50.94

11.2 Physico-chemical properties

Vanadium is found in group VA in the periodic table. The metal can have the valences +2 and +5 (V(II) to V(V)) [1]. In water vanadium is normally found as the vanadyl (V(IV)) or vanadate ion (V(V)). Chemical compounds based on the vanadate ion are normally water soluble. Vanadium is attacked by sulphuric acid and nitric acid [1]. Selected physico-chemical data for vanadium are shown in Table 11.2.

Table 11.2
Physico-chemical data for metallic vanadium. Data from [1, 3, 12, 21]

Vanadium (V)	Valence	II, III, IV, V
	Density (g/cm^3)	6.11
	Melting point (°C)	1929
	Boiling point (°C)	3407
	Solubility in water (g/L)	Insoluble

11.3 Uses and consumption

11.3.1 Uses

Vanadium is primarily used as alloy metal. It increases the hardness of steel and is found in up to 5% in titanium alloys, 2 % in hard steel, 0.03 % in trade steel and 0.08 % in other steel [2]. Vanadium is used in catalytic converters (V_2O_5) and in e.g. pigments ($BiVO_4$) [9]. Vanadium is also found as vanadium carbide and is furthermore used in some types of wires and metal plates where ductility is required [16]. The use of organic vanadium compounds has also been reported [17].

Vanadium is used in many dietary supplements and in vitamin tablets [14, 15].

Vanadium is also used as pigment in pottery, ceramics and colourful precious stones [18, 19].

11.3.2 Consumption

The steel industry is the most important purchaser of vanadium [9].

The global production of new vanadium was approximately 35,000 tons/year in 1990. The production has thus tripled since the 1960's. Based on the per capita-consumption in USA, the consumption in Denmark is estimated be to approximately 95 tons.

Table 11.3
The relative distribution of the vanadium use in USA and the estimated consumption in Denmark in 1998 based on [9]

	Carbon steel	High alloy steel	Low alloy steel	Tools steel	Other (catalysts/ pigments)
Distribution in USA	38%	19%	20%	11%	9%
Yearly consumption in DK	36 tons	18 tons	19 tons	11 tons	9 tons

Recovery is primarily from catalytic converters. Vanadium is produced from oil ash in some countries. In Sweden, high alloy steel (which contains 1.5-3.5 % vanadium) is remelted to vanadium steel [9].

11.4 Emissions and environmental concentrations

By weathering, a considerable amount of vanadium is emitted to the environment. The amount is 0.6 million tons/year on a global scale [13]. Point source emission of vanadium is observed from metallurgic manufacturing facilities.

Burning of fossil fuels is the most important anthropogenic source of vanadium emission to the atmosphere [7]. Vanadium is emitted from coal-fired power plants and when combusting oil for house heating. These sources are considered the most important sources of vanadium emission in Denmark. From the annual use of coal in Denmark in 2000 of 6.7×10^6 tons [20] and an average vanadium content of 10-60 mg/kg [9], the amount of vanadium in emissions and residuals from coal-based power generation is 67-400 tons. Oil can contain up to 400 mg/kg.

In Europe, the atmospheric emission from anthropogenic sources is estimated to 34,500 tons/year. Atmospheric emissions are introduced into the aquatic and terrestrial environments by both dry and wet deposition [7].

The background level of vanadium in the earth crust is high. In the aquatic environment the background level is at the lower µg/L-level, see Table 11.4.

Table 11.4
Typical background concentration of vanadium in the environment. Data from [4, 6, 13]

Concentrations	Fresh water (µg/L)	Sea water (µg/L)	Sediment (mg/kg)	Soil (mg/kg)	Earth crust (mg/kg)
Typical background concentration	0.01 - 20	0.9 - 2.5	105	3 - 500	160

A Swedish study showed that the concentration of vanadium in different types of waste was not higher than e.g. the background level in sediment [9]. The concentration of vanadium is high in the Danish waste streams compared to the other metals discussed in this report, see Table 11.5.

The vanadium concentration in wastewater has been reported to be 1.6-6.5 and 2.1-2.8 µg/L for influent and effluent, respectively [4]. The concentration in dewatered sewage sludge is 4.5-25.7 mg/kg [4], see also Table 11.5.

Table 11.5
Levels of vanadium in selected emissions and waste products from measurements conducted as part of this study in the autumn of 2001.

Emission/waste type	Unit	V-concentration
Compost:		
Compost from household waste	µg/kg dw	18,700
Compost from garden waste	µg/kg dw	11,900
Landfill leachate:		
Landfill 1	µg/L	83
Landfill 2	µg/L	56
Stack gas from MSW incineration:*		
MSW incinerator 1, semi-dry gas cleaning	µg/m^3	<50
MSW incinerator 2, wet gas cleaning	µg/m^3	<5
MSW gas cleaning residuals:*		
Landfill leachate, semi-dry gas cleaning	µg/L	29.3
Landfill leachate, wet gas cleaning	µg/L	215
*Waste water and sludge from municipal WWTP**:*		
WWTP 1, effluent	µg/L	1.59
WWTP 2, effluent	µg/L	2.28
WWTP 1, sludge	µg/kg dw	23,000
WWTP 2, sludge	µg/kg dw	21,800
Road runoff retention basins, sediment:		
Motorway 1	µg/kg dw	69,000
Motorway 2	µg/kg dw	46,000

*Municipal solid waste

**Waste water treatment plant

11.5 Danger classification

Vanadium pentaoxide (V_2O_5) is on the list of dangerous compounds and is classified as ***harmful***, ***irritant***, and ***mutagenic*** in category 3 (Mut3), ***toxic*** with danger of serious damage to health by prolonged exposure through inhalation, and ***reprotoxic*** in category 3 (Rep3) [10]. Vanadium pentaoxide is furthermore classified as ***dangerous for environment*** with risk phrases R51/53 (toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment) [10]. Vanadyl pyrofosfate is sensitizing and divanadyl pyrofosfate is sensitizing and toxic to aquatic organisms and may cause long-term adverse effects in the aquatic environment.

Table 11.6 shows an overview of the classification and risk phrases for vanadium compounds.

Table 11.6
Classification and risk phrases for vanadium compounds

Vanadium compounds	Health	Environment
Vanadium pentaoxide	Xn; R20/22, Xi; R37, Mut3; R40. T; R48/23, Repr3; R63	N; R51/53
Divanadyl pyrophosphate	Xn; R22, Xi; R41 - 43	N; R51/53

11.6 Toxicology

The metallic form of vanadium does not seem to pose any significant risk to human health [12]. However, some vanadium compounds exist, which are toxic and have mutagenic and reprotoxic effects. Vanadium compounds are only poorly absorbed through the gastrointestinal tract but assimilation through the lungs occurs easier. Therefore, toxic effects are normally limited to the respiratory tract. Bronchitis and pneumonia are observed after industrial exposure. Therapeutic ingestion of vanadium can cause destabilization in the gastrointestinal tract, changes in the clinical-chemical parameters related with renal function, and effects of the central nervous system. These effects are primarily observed after exposure of high concentrations of vanadium.

11.7 Environmental properties

The environmental properties of vanadium are primarily determined by the vanadyl and vanadate compounds, in e.g vanadium with redox state IV and V. Vanadium is characterised by the fact that a large fraction is bound to organic matter such as sediment. Vanadium is an essential metal to certain species of algae, and in certain bacteria vanadium can substitute molybdenum [13]. It is not known if vanadium is essential to all organisms.

11.7.1 Environmental chemistry

Vanadium is found in the atmosphere bound to particulate matter and it will be removed by both wet and dry deposition. Vanadium emitted during combustion of oil can be distributed widely due to formation of small particles with high atmospheric retention times [7].

The mobility of vanadium in soil depends on the pH-value. In neutral or poorly alkaline environments, vanadium is relatively mobile compared to other metals, whereas the mobility decreases in acidic environments. In the presence of humic acids the mobile anionic metavanadate compounds (V(V)) are transformed into cationic vanadyl compounds (V(IV)). This can result in accumulation of vanadium [7].

A certain mobility of vanadium under unsaturated, oxidizing conditions has been observed. The mobility is low under reducing conditions. Vanadium can sorb to clayey soil particles.

In the aquatic environment vanadium is found as the vanadate compounds HVO_4^{2-} and VO_3^- in both fresh and sea water. However, the vanadyl compounds VO^{2+} and $VO(OH)^+$ dominate under reducing conditions. In the aquatic environment algae and plankton assimilate vanadium, and a considerable part of the total vanadium pool will be associated with organic material under both oxidizing and reducing conditions. Vanadium will be released in connection with degradation of organic material [7].

Vanadium can precipitate by reaction with manganese oxide and ferro hydroxide ($Fe(OH)_3$).

11.7.2 Environmental toxicology

The available data on environmental toxicity is limited to two tests on trout (with the compound vanadium pentaoxide). Based on these, vanadium pentaoxide should be classified as toxic to aquatic organisms.

Table 11.7
Test results for environmental toxicity

Organism	Latin name	LC_{50} (mg/L)	Compound
Fish	*Oncorhynchus mykiss*	2 - 6,4 (4 - 7 days)	V_2O_5
Fish	*Salvelinus fontinalis*	2 - 36 (3 - 30 days)	V_2O_5

11.7.3 Bioaccumulation

Bioconcentration factors of 1,900 and 400 for plant and animal plankton, respectively, have been reported from a study in Lake Michigan. However, lower bioconcentration factors were found for other organisms [7]. Accumulation of vanadium in plants was observed in the vicinity of a rolling mill in concentration of up to 19.3 mg/kg dw, which was the double of the concentration in the controls [7].

11.8 Conclusions

Vanadium is used in alloy steel and in catalytic converters. Combustion of coal is probably the most important anthropogenic emission source. Vanadium pentaoxide is classified as mutagenic and reprotoxic in category 3. The data on vanadium environmental toxicology is limited. If the environmental toxicity data is used to classify vanadium pentaoxide, it will be classified as toxic to aquatic organisms.

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12 Danger Classification and Risk Sentences

Tx	Very toxic
T	Toxic
Xn	Harmful
C	Corrosive
Xi	Irritant
Carc1	Substances known to be carcinogenic to man
Carc2	Substances which should be regarded as if they are carcinogenic to ma.
Carc3	Substances which cause concern for man owing to possible carcinogenic effects but in respect of which the available information is not adequate for making a satisfactory assessment
Mut1	Substances known to be mutagenic to man
Mut2	Substances which should be regarded as if they are mutagenic to man
Mut3	Substances which cause concern for man owing to possible mutagenic effects
Rep1	Substances known to impair fertility in humans
Rep2	Substances known to cause developmental toxicity in humans
Rep3	Substances which cause concern for human fertility
R4	Forms very sensitive explosive metallic compounds
R14	Reacts violently with water
R22	Harmful if swallowed
R25	Toxic if swallowed
R26	Very toxic by inhalation
R37	Irritating to respiratory system
R40	Possible risks of irreversible effects
R41	Risk of serious damage to eyes
R43	May cause sensitization by skin contact
R49	May cause cancer by inhalation
R51	Toxic to aquatic organisms
R52	Harmful to aquatic organisms
R53	May cause long-term adverse effects in the aquatic environment
R63	Possible risk of harm to the unborn child
R20/22	Harmful by inhalation and if swallowed
R36/37/38	Irritating to eyes, respiratory system and skin
R42/43	May cause sensitization by inhalation and skin contact

R48/20/22	Harmful: danger of serious damage to health by prolonged exposure through inhalation and if swallowed
R48/23	Toxic: danger of serious damage to health by prolonged exposure through inhalation
R51/53	Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment
R52/53	Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment