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Environmental impact of mercury and other heavy metals

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Abstract

The environmental impact of heavy metals is reviewed. One significant source of emissions of heavy metals to air is waste incineration. Consumer batteries contributes significantly to this problem, as well as to heavy metal leakage to groundwater from landfill deposits. The situation in Sweden is used as an example to describe how the deposition from the atmosphere still is increasing the load of heavy metals, like mercury, cadmium and lead, in top soils and aquatic sediments. Critical factors and effect levels for Hg, Cd, Pb, Cu, Zn and As are discussed. Specific questions like mercury contents in present battery waste and heavy metal contents in new and future secondary batteries are addressed.

Keywords: Sweden; Mercury; Cadmium; Lead; Arsenic; Chromium; Heavy metals; Environmental impact

1. Introduction

Emission of heavy metals to the environment have generally decreased in Europe during the last decade. Evident environmental improvements have also been registered in many locally polluted areas. However, the levels of heavy metal pollution are still unacceptably high in several regions. Another unacceptable feature is that the concentrations of certain heavy metals like mercury, cadmium and lead have increased manifold in different kinds of top soils in large areas during the 20th century. The problem we face today is that the deposition, although generally decreased, is still too high leading to continuously increasing concentrations in already contaminated terrestrial and aquatic ecosystems and agricultural soils in large areas. The situation in Sweden will be used as an example to describe how deposition from the atmosphere is still increasing the load of certain heavy metals in top soils and aquatic sediments. Some data from two recent reports on heavy metals in the Swedish environment [1,2] will be summarized, as well as specific aspects on mercury pollution [3].

One significant source of emission of heavy metals to air is waste incineration, and certainly unsorted waste-containing batteries, for example, contributes to this route of pollution on local (< 50–100 km) and regional (< 1000–2000 km) scales. Local effects on ground or surface water from landfill disposals containing heavy metals may also be severe [4]. Therefore, and for sustainable use of natural resources, batteries should be removed from waste and recycled.

2. Heavy metals in batteries

One major problem today is to separate different kinds of batteries as a function of their content of heavy metals (Fig. 1). For example 80 tons of used batteries, mainly primary batteries, recently collected in Göteborg, Sweden, contained as much as 900 ppm of mercury, although mercury cells had been removed from this batch. This is alarming, since most batteries sold in the last few years in Sweden are declared as 'mercury-free', which means that the maximum amount of mercury should not exceed 250 ppm. There may be several reasons for this high content of mercury: (i) batteries produced before the mercury regulations in Sweden are included to a higher fraction than expected; (ii) batteries sold during the last few years contain more mercury than expected, or (iii) mercury batteries have not been removed efficiently in the sorting procedure.

This example focuses on the needs for better marking of battery contents. This will probably be even more important in the future, when different kinds of secondary batteries, for example, the metal hydride batteries (Fig. 1 and Table 1), will constitute a greater part of the market. Although one may argue that the total amount of discarded batteries will decrease when moving over from primary to secondary batteries, the applications of different types of batteries will increase, as well as the content of different kinds of valuable metals for an improved and diversified battery performance.

With the implementation of a reliable battery marking system, one may be able to sort mixed batteries in more or less harmful categories, and to recycle the battery materials in the

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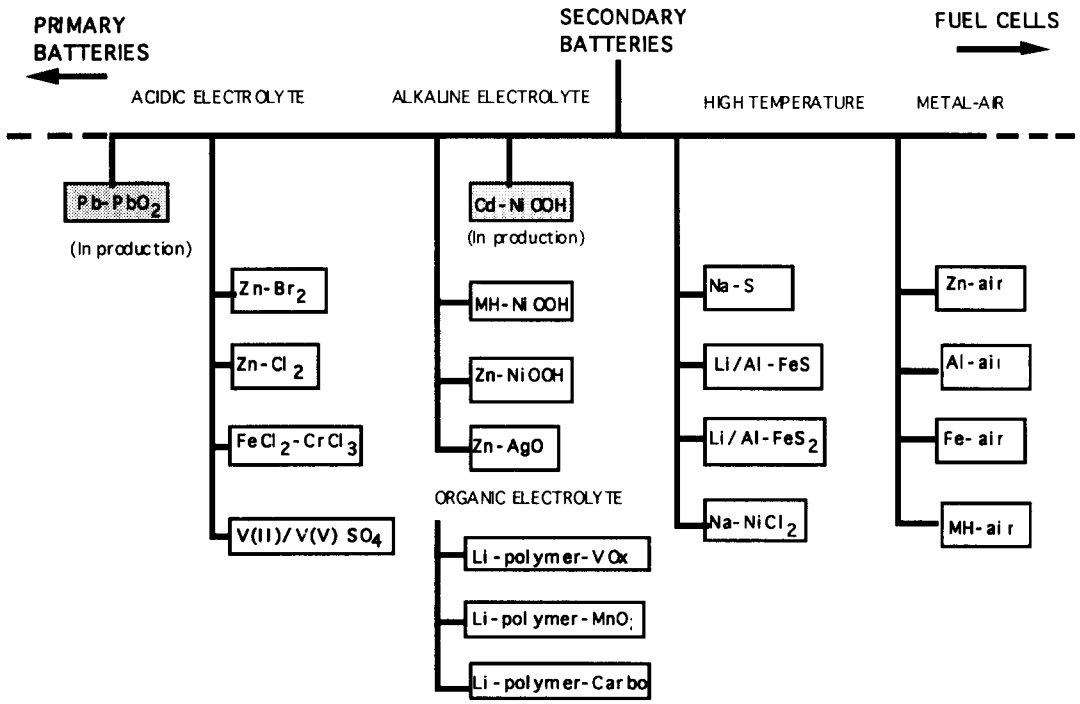

Fig. 1. Examples of different primary and secondary battery systems.

Table 1
Potential alloys for metal hydride electrodes

AB_2-type (based on rare earth metals)
$LaNi_{5-x}M_x$ (M = Cu, Al, Mn, Co)
$La_{0.8}Nd_{0.2}Ni_{2.5}Co_{2.4}Si_{0.1}$
$La_{0.9}Zr_{0.1}Ni_{4.5}Al_{0.5}Mm_{0.85}Zr_{0.15}Ni_{4.0}Al_{0.8}V_{0.2}$
$MmNi_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3}$ (Mischmetal)
AB/A_2B-type (based on titanium)
Ti_2Ni–$TiNi_{1-x}M_x$ (M = V, Cr, Mn, Co, Cu, Fe)
$Ti_{1-y}Zr_yNi_x$ (x = 0.5–1.5)
AB_2-type
$Ti_{1-y}Zr_yNi_{2-x}M_x$ (M = V, Cr, Fe, Mn, Al, Co)
$ZrNi_{1.6}V_{0.4}$
$ZrNi_{1.2}Mn_{0.3}Cr_{0.2}V_{0.3}$

Table 2
Criteria for drinking water used by the Swedish Food Administration [a]

Metal	Usable with remarks	Not usable
Al	100–500	
Zn	300–1000	
Cu	300–1000	
Cd	1	5
Pb	10	50
Hg		1
As	10	
Cr		50

[a] The figures (μg/l) for Al, Zn and Cu are so-called technical criteria, while those for Cd, Pb, Hg, As and Cr are based on health aspects.

most economically efficient way. Specific battery types with large applications, like the lead/acid and the nickel–cadmium batteries, should be recycled separately.

3. Swedish research on the effects of heavy metals

The Swedish Environmental Protection Board has traditionally followed the fate of heavy metals in the environment, since mining and metallurgical processes are large industrial activities in Sweden. Furthermore, previous production of chlorine-bleached paper pulp have resulted in mercury-contaminated fibre banks in several watersheds, as well as mercury contamination directly from the chlor-alkali plants. During the 1970s–1980s waste incineration became a dominant source of heavy metal emissions to air, especially mercury, partly due to batteries in household and industrial wastes.

One difficulty that arises when the environmental effects of heavy metals is to be evaluated is the estimation of the so-called critical factors or concentration levels. The criteria for Swedish drinking water are not very precise and list only a few metals [1,5], see Table 2.

Several investigations of the concentrations of heavy metals in forest top soil layers and in lake sediments have been performed in Sweden during the last twenty years. Maps of the concentrations of heavy metals in mosses makes it possible to estimate the yearly deposition, since the type of moss collected only takes up materials from air. Fig. 2 shows the concentration of Cd and Cr in moss in 1990 [6] and the total amount of these metals in forest mor layers [7].

It is evident from Fig. 2(a) that the deposition patterns of Cd and Cr are rather different. The higher amounts of Cd in the south-western part of Sweden and a declining gradient towards the northern parts indicate that most of the Cd deposition is long range transported, mainly from sources in Europe. Cr on the other hand is concentrated to areas where

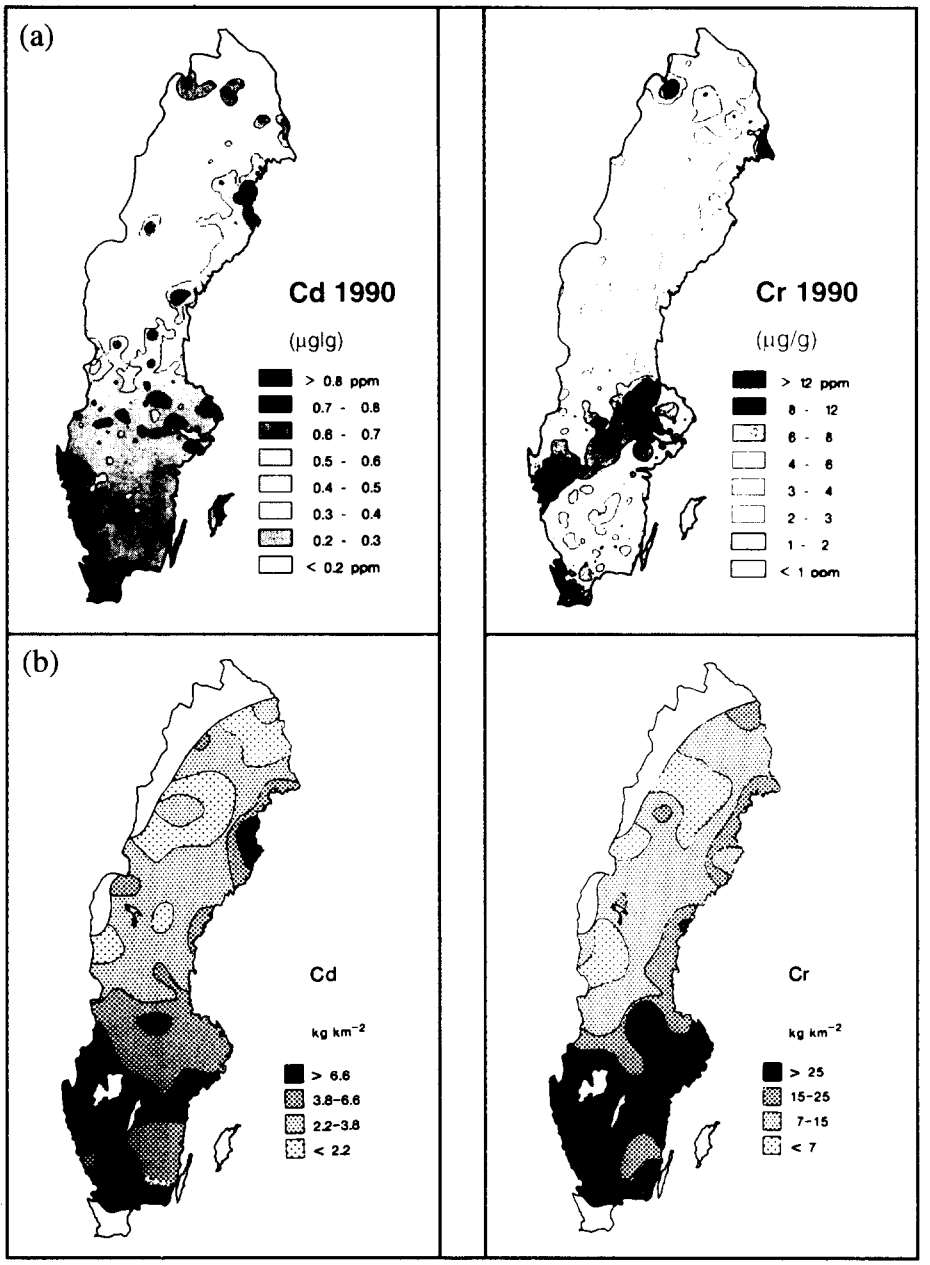

Fig. 2. (a) Cd and Cr concentrations in moss 1990 [6], and (b) their total amounts in forest mor layers in Sweden [7].

metallurgical processing takes place, i.e., Cr is not subject to long range transport.

The total load in the mor layer reflects the deposition over the last 200 years or so as shown in Fig. 2(b). Based on the information in Fig. 2(a), it is evident that both Cr and Cd have been long distance transported for this historical period, as well as emitted from industrial activities in Sweden.

Earlier moss studies show that the deposition of certain metals have decreased substantially during the period 1975–1990, see Table 3. The figures in this table are very encouraging. They show how 'cleaner' processes in Sweden and Europe have resulted in a much better situation with respect to deposition of heavy metals over Sweden. Unleaded gasoline or reduced lead concentrations in lead gasoline have given a substantial reduction of lead deposition during the period 1975–1990. Flue gas cleaning in energy or metal production processes have improved the situation for other metals.

The remaining problem is that many (or most) heavy metals are still increasing their concentration in forest top solids and lake sediments. If the metal concentration already exceeds a critical level at some or numerous locations, this means that the deposition rate has to be reduced further. For mercury, for example, it has been shown that the deposition rate has to be decreased by 80% to reduce mercury in top soils and sediments. This drastic reduction is needed in order to restore mercury concentration in lake fish levels below 0.5 mg/kg in most Swedish lakes, which is one of the Swedish

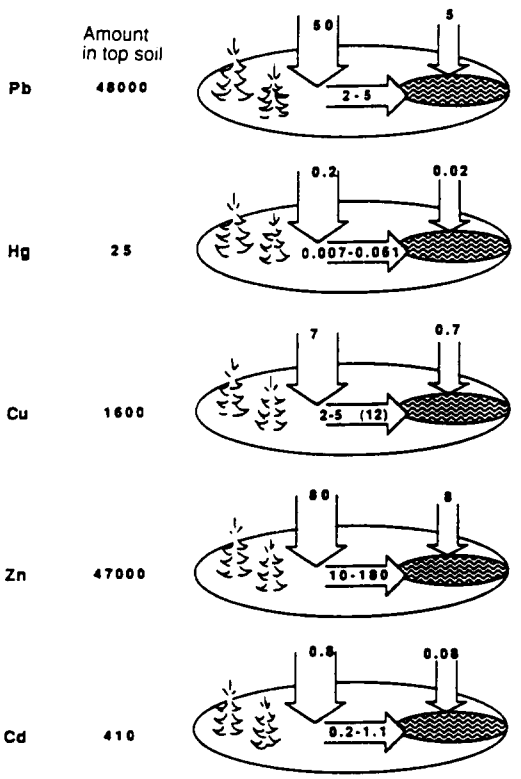

Fig. 3. Fluxes of metals (kg/year) and total amount of metals in the mor layer (kg/10 km^2) for a normal lake, 1 km^2, and a normal watershed around it (10 km^2) in southern Sweden.

Table 3
Decrease in heavy metal deposition over Sweden during the last 15 years

	Decrease (%)						
	Pb	Cd	Cr	Cu	Zn	Ni	V
1975–1985 [8]	50	48	5	7	21	28	5
1985–1990 [1]	30	15	5–10	15	0	23	25

Table 4
Critical factors for heavy metals in forest mor layers and in agricultural soils. The critical factors are the lowest relative concentration increase that has been observed to generate some negative environmental effects [7]

Type of soil	Cd	Cr^{3+}	Cu	Hg	Ni	Pb	Zn	V
Foret mor layer	5	>10	3	3	5	3	5	3
Agricultural soil			4		10		3	

Table 5
Heavy metal concentrations (mg/kg) in the forest mor layer at which biological effects will occur. The lower levels have been estimated for different regions in Sweden [1]

Region	Cd	Cr^{3+}	Cu	Hg	Pb	Zn
Northern Sweden	2.7	>20	18	0.6	75	270
Mid Sweden	3.1	>20	17	0.7	100	280
Southern Sweden	3.5	>36	20	0.8	180	280

environmental objectives. Fig. 3 indicates a continuous accumulation of heavy metals in a typical watershed around a lake, from about 1‰ for Pb to about 8‰ for Hg per annum.

4. Effects and critical factors

The effects of heavy metals on solids are difficult to relate precisely to concentration limits of the different metals. Soil factors like acidity, concentration of humic and fulvic acids as well as concentrations of base cations influence the availability of heavy metals and their effects on the microbiology in soils. Effects of heavy metal pollution may first be noticed on the soil respiration, on humic degradation processes and nitrogen mineralization. Specific enzymatic reactions are also sensitive to metal pollution [9].

Several investigations have shown that the sensitivity of microbiological activity to heavy metals depends on the background concentration. A certain level of contamination of a heavy metal may have worse effects in an area with a low natural background of the metal in question compared with areas with higher background values. This may be interpreted so that the active microorganisms may have been modified and adopted a higher tolerance towards heavy metals if the natural levels are higher. This has led Tyler [9] to formulate critical factors, i.e., the ratio between the contaminated and background concentrations for heavy metals rather than concentration limits, see Table 4.

If the critical factors are applied to background values estimated for different parts of Sweden, levels of heavy metals may be calculated at which negative environmental effects will occur due to the heavy metal pollution, see Table 5. When reading this table, one should keep in mind the uncertainties depending on local variations of different soil factors, as was discussed above.

Accumulation of heavy metals in lake or sea sediments is an environmental risk for the microbiological activity in such systems. Much sediment data has been collected in Sweden and surrounding coastal waters. In Fig. 4(a) a number of lakes are indicated as region 2. Sediment samples from 0 to 1 cm depth from these lakes were taken and analysed for some heavy metals and the results are displayed in Fig. 4(b) [10].

Table 6
Proposed classification of sea sediments with respect to effects of heavy metals [1,11]. The classification values are compared with measured values (μg/g dry substance) in sediment samples from the Baltic Sea [12]

Classification	Zn	Cu	Cd	Pb	As
'Effects possible'	120	70	5	42	33
'Effects plausible'	270	390	9	110	85
Measured values:					
Baltic Sea	330	55	2	60	13
Bothnian Sea	200	38	0.3	44	26
Bothnian Gulf	139	43	0.6	40	107

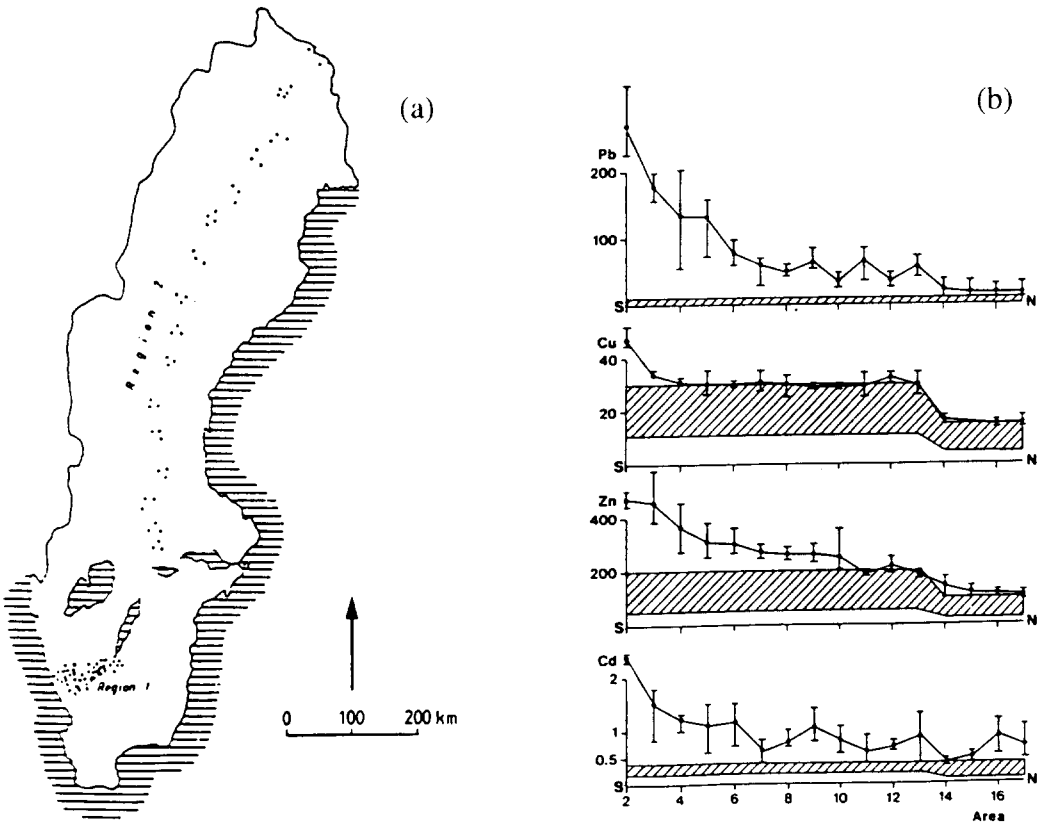

Fig. 4. (a) Map of Sweden showing the location of lakes used for sediment sampling in Norrland (region 2); (b) concentrations of heavy metals in surface sediments in lakes from south to north in region 2. The dashed areas indicate normal background values [10].

There are no generally accepted critical limits for heavy metals in sediments. Of course, such limits will vary between different kinds of lakes, coastal waters and oceanic areas. Notter [2] proposed the classification of sediments in two levels, 'effects possible' and 'effects plausible'. The values given in Table 6 are based on data from Long and Morgan [11].

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