

Cadmium in Wood Ash Used as Fertilizer in Forestry: Risks to the Environment and Human Health

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FOREWORD

The aim of this report is to estimate the impacts of cadmium (Cd) in wood ash used as fertilizer in forestry on forest soil and on forest biota, and to assess the related human health and environmental risks.

The assessment has been performed by applying, as appropriate, the adopted EU principles on risk assessment of New and Existing Substances (TGD, Technical Guidance Document). The work has been carried out on the basis of available literature and other information relating to the occurrence of cadmium in the forest ecosystem in Finland, the environmental hazards of cadmium, as well as its health risks.

The work has been commissioned by the Finnish Ministry of Agriculture and Forestry. Persons and institutions in charge include:

Senior Adviser Jukka Malm, Finnish Environment Institute: Project coordination, Senior Adviser Jaana Pasanen, Finnish Environment Institute: Environmental risks, Dr. Kimmo Louekari, Finnish Institute of Occupational Health.

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EXECUTIVE SUMMARY

Environmental aspects

The toxicity of cadmium to terrestrial organism shows a variable pattern. Plants grown in soil are generally considered insensitive to the effects of cadmium, although some exceptions do exist. Cadmium exhibits moderate and low toxicity to avian species in subacute exposure. Microorganisms and terrestrial invertebrates show moderate or high sensitivity to cadmium.

The effects of cadmium in ash on soil biota are hard to prove and distinguish from the effects of the increased pH of the soil. The increase of pH after ash treatment seems to cause the most prominent effects on biota. In general, soil microbes seem to benefit at least from the short-term effects of ash treatments; soil respiration and microbial activity has increased. However, the microbial community has changed. The short-term effects of ash fertilization on soil fauna seem to be adverse, although there are some species which benefit from the increase of soil pH.

No clear trend of increase of cadmium content in mushrooms was noticed, although according to one recent study a slight increase of cadmium, not statistically significant, could be seen in mushrooms. The general trend of increasing concentrations of cadmium in berries is also lacking, although a slight increase of cadmium concentrations in lingon- and cloudberries and stems of blueberries after ash treatment could be noticed in two studies.

Ash fertilization increased total concentrations of cadmium in peat and mineral soils. In peat soils cadmium concentrations even doubled. However, the fate and impacts of easily mobile and bioavailable extractable fractions of cadmium are still unclear. The extractable content of cadmium seemed to increase at least some years after ash fertilization. However, no direct conclusions can be drawn on the basis of the limited number of available studies. In fact, available data on extractable background cadmium concentrations and concentrations after ash treatment do not enable a quantitative risk assessment to be carried out.

A drastic increase of extractable concentrations of cadmium shown in some studies was quite surprising, because according to the general understanding of the behaviour of cadmium with increasing pH the situation should be the opposite. Especially humus layer has a large capacity to retain cadmium and bind it in a less bioavailable form, especially if pH increases. Depending on the quantity and quality of ash used, pH can increase 1-2 units after ash treatment. In general, the mobility of cadmium tends to decrease and its adsorption on soil increase when pH increases. It has been generally known that the soil pH is one of the most important factors determining not only the short-term, but also the long-term variations in the uptake of cadmium by organisms and the vertical and horizontal mobility of cadmium in the soil.

Human health aspects

Diet is the main source of human exposure to cadmium. Cereals, vegetables and potatoes cause most of the average dietary intake of cadmium in Finland (9.5 µg/day). In some sub-populations, long-term dietary intake of cadmium is 20-30 µg/day in Finland. Normally only 5 % of the cadmium in food is absorbed in the gastrointestinal tract. However, studies on humans and experimental animals show that a deficiency of iron, which is not uncommon among women increases the rate of absorption (up to 10 %).

There is some evidence that cadmium concentration of lingon berries and mushrooms is slightly increased by ash fertilisation. Some mushroom species accumulate more cadmium several years after ash fertilisation. There is no evidence that the level of cadmium in blueberries, in perch of forest lakes would be affected by ash fertilisation. The cadmium content in liver and kidney of elk has increased over about 20 years, but reason of this trend remains to be elucidated. The preliminary assessment showed that the cadmium bal-

ance of forest soil is not dramatically changed by ash fertilisation.

The consumption of “forest foods”: i.e. berries, mushrooms and liver and kidney of elk by an average Finnish consumer is low. The average intake of cadmium from berries and elk liver and kidney is considered negligible. The intake of cadmium from forest mushrooms by average consumer is approximately 0.5 µg/day.

In the reasonable worst case scenario for recreational hunters and their family members, it was assumed that they annually eat a few meals containing liver or kidney of elk. Based on food consumption studies, it was estimated that they eat twice as much forest mushrooms as the average consumer and twice as much forest berries as the average inhabitant of Northern Finland. In addition, it is assumed that these foods come from ash fertilized areas. The dietary intake of cadmium is clearly higher among this consumer group (about 17.4 µg/day) as compared with an average Finnish consumer (9.5 µg/day). As such this intake is considered to be safe. However, in case recreational hunters or their family members are also heavy smokers and have iron deficiency, which increases the absorption of cadmium, their body burden of cadmium might reach critical level and cause adverse health effects.

These main factors of total cadmium exposure: high dietary intake of cadmium (due to consumption of “forest foods”), increased absorption and smoking are considered in the risk assessment. The corresponding urinary levels of cadmium and the critical urinary levels that are associated with health effects are compared. It is concluded that for the risk group, the urinary Cd level is about 2-3 µg/l. This is also the level of urinary excretion of cadmium associated with risk of cadmium-induced kidney dysfunction and bone effects, which are due to the increased excretion of cadmium. It is noteworthy, that the number of people (among the recreational hunters and their family members) affected by all the three risk factors (and having the urinary Cd level of 2-3 µg/l) is very small.

The dietary intake of cadmium by some recreational hunters and farmers is about two-fold as compared with the average Finnish consumer. On the basis of current data, not the ash fertilization but the food consumption pattern increases the cadmium exposure of this population group. There is a need for more data on the effect of ash fertilization on the Cd-content of mushrooms and liver and kidney of elk to confirm or refute the preliminary estimates presented in this report.

Recommendations

In order to assess more reliably the effects of cadmium in wood ash used as fertilizers in forestry more comprehensive carefully planned long-term ash fertilization studies are needed, where extractable cadmium concentrations are measured in soil. Based on the current limited data on extractable cadmium concentrations in forest soil, no direct conclusions of the impact of ash fertilization can be drawn. Also long-term studies on leaching of cadmium from forest soil are needed.

More accurate estimates on the Cd balance (total long-term inputs and outputs) in the forest soil are needed. These can be done on the basis of the above mentioned studies on extractable cadmium concentrations and leaching studies. The instructions and application practices (e.g. frequency of ash treatment, amount of ash applied per hectare, maximum allowed concentration of cadmium in the ash) of ash fertilisation should be designed taking into account the long-term balance of cadmium in forest soil.

In addition, in order to assess the long-term trend of cadmium content in berries and mushrooms more long-term studies on the effect of ash fertilization are needed. Thus, surveillance of cadmium concentrations in berries and mushrooms e.g. in experimental areas founded by the Finnish Forest Research Institute should be continued.

The effect of ash fertilisation on the level of cadmium in liver and kidney of elk and hare should be studied. It seems reasonable to retain the current recommendations given to the rec-

reational hunters for avoidance of frequent consumption of liver and kidney of the elk and hare.

Despite the uncertainties in this preliminary risk assessment, it can be recommended that a maximum allowed concentration of cadmium in wood ash used as fertilizer in forest be established. In addition, the use of ash without liming effect e.g. peat ash with low pH should be considered very carefully. It can be assumed that the extractable cadmium concentrations in soil and the related environmental and health risks are likely to increase, when ash with low liming capacity is used.

1 INTRODUCTION

In Finland about 300 000 t wood and peat (about 100 000 t wood ash) ash is generated annually (Moilanen & Issakainen 2000). Nowadays much pressure has been put on recycling of wood ash to forest soils. The use of wood ash as a fertilizer in the forestry has often been regarded as a practical and cheap solution to the waste and treatment problem of ash.

Ash could be seen as a valuable resource since it contains most of the elements needed for plant nutrition and growth. According to Levula et al. (2000) apart from N and S, wood ash contains mineral nutrient (K, Mg, Ca, Zn, B, Cu and Mn) in almost the same proportion as in the stand biomass. According to Hakkila (1992, ref. in Silfverberg 1996) about 20 000 hectares could be fertilized annually in Finland using the annual production of 100 000 t of good-quality wood ash with a dose of 5000 kg/ha. According to Silfverberg (1996) the need for the regeneration of peatland forests will be increased, because extensive areas of older forest stands are now approaching the final felling stage due to the large drainage of peatlands in the 1960's and 1970's (Paavilainen and Tiihonen 1988, ref. in Silfverberg 1996). Approximately 5.9 million hectares of peatlands have been drained in Finland (Aarne 1993, ref. in Silfverberg 1996).

The environmental and health issues through diet with ash is that it contains heavy metals e.g. Cu, Zn, Mn, Pb, Cd, Cr, Hg, Ni. Some of these metals (Mn, Cu, Zn) are essential trace elements of plants, but others (Cd, Hg, Pb) are harmful and toxic for biota. Cadmium is considered to be the

most problematic of these heavy metals, because of its severe toxicity and relatively high mobility and enrichment in the environment (Levula et al. 2000). According to Egnell et al. (1998) wood ash can also contain radioactive substances and organic environmental toxins e.g. dioxins and furans.

In this report, wood ash is mainly considered, although other types of ash e.g. peat ash, wood ash with sludge has also been used in forest fertilization experiments. The impacts of ash fertilization on cadmium concentrations in peat and mineral soils are both considered. However, the drained peatlands (peat soils) are generally considered to be "the target area" of ash fertilization. In case of mineral soils the study has been focused on the humus layer, because it is biologically the most active part of the soil and it is also the most vulnerable to the effects of deposition.

In most of the studies referred to in this report, cadmium content is expressed as total concentrations (e.g. extracted by HNO_3 acid). There is limited information available about exchangeable cadmium concentrations (e.g. cadmium extracted by NH_4 acetate, KNO_3 , acid ammonium acetate EDTA). However, the toxicity of cadmium is mainly related to its bioavailability, and therefore concentrations expressed as extractable, exchangeable or mobile are the most important ones in risk assessment.

Because of relative shortage of data on effects of cadmium containing ash not only peer reviewed publications but also domestic publications and reports have been referred to in this report.

2 GENERAL INFORMATION ABOUT WOOD ASH USED AS FERTILIZER

2.1 The history of wood ash fertilization

The first Finnish wood ash experiments on drained peatlands started in 1937 by the Finnish Forestry Research Institute. The main aim was to compare the capacity of ash and lime stone to reduce the acidity of peat soil (Lukkala 1951, ref. in Silfverberg 1996). In Sweden, early fertilization activities in 1910 were followed by small-scale trials (Silfverberg 1996). In general, a large-scale application of wood ash in forests has been a rather uncommon practice abroad.

The 1960's was a period of rather low research activity on ash fertilization, primarily due to the increasing use of commercial forest fertilizers (Silfverberg 1996). In the late 1970's, when several of the wood ash fertilized peatland stands of Scots pine (*Pinus sylvestris* L.) were still growing vigorously interest in wood ash again increased. During the period 1977-1985 about 170 ash fertilization experiments were laid out on peatlands by the Finnish Forest Research Institute. The main purpose of these was to compare different types and doses of wood ash with commercial fertilizers, particularly PK fertilizers (Paavilainen 1980, ref. in Silfverberg 1996).

The best results of ash fertilization have been gained in nitrogen-rich peatlands, where there has been a shortage of potassium and phosphorus. Still after 30-40 years of wood ash fertilization pH-value and the content of nutrients of the peat have been clearly higher in fertilized areas than in untreated areas (Silfverberg and Huikari 1985). However, in mineral soils wood ash has not increased stand growth. The benefits of using wood ash in mineral soils are mainly associated with its role as an ameliorative agent and stimulator of the biological activity of the soil, rather than as a source of nutrients (Levula et al. 2000).

Besides the drained peatlands, wood-ash fertilization has been considered to be suitable for a range of special sites such as stands suffering from nutritional disorders, peat cut-away areas and afforested peatlands (Veijalainen et al. 1984,

Kaunisto 1987, Ferm et al. 1992, ref. in Silfverberg 1996). In addition to the growth increment, the other advantages of ash fertilization are a long time increase of store of nutrients in peatlands (Veijalainen et al. 1984, ref. in Silfverberg 1996), smaller risk of damages to the trees than with (N)PK fertilization (Huikari 1977, Reinikainen 1980, ref. in Silfverberg 1996), a reduced rotation time and the need for additional fertilization (Ferm et al. 1992, ref. in Silfverberg 1996). According to Silfverberg (1996) a loading effect of ash fertilization on water courses through leaching could also be less than that of commercial fertilizers, because well-burned wood ash contains practically no nitrogen, and phosphorus is in a less soluble form than in commercial PK fertilizers.

2.2 The type of ash used

There is very limited information available about the type of wood ash used in the former ash fertilization experiments. Very often it has only been stated that peat or wood ash were used. Further information about wood ash used e.g. species and part of trees is lacking. It has been suggested that in older fertilization experiments especially high doses of birch wood ash has been used in peat soils, because liming effects, the increase of pH, can be seen still tens of years after ash fertilization. At present, experiments of wood ash combined with other materials such as sludge, have also been made.

In general, peat ash is not considered as good as wood ash in forest fertilization, because it contains less nutrients (especially K) and the solubility of nutrients is poor. Due to the very low pH value of peat ash, its liming capacity is also much lower than in wood ash. The pH of wood ash is 12-13 (Hytönen & Nurmi 1997).

Solubility of ash has been regulated by granulating or hardening of ash. Granulation and hardening makes very reactive untreated loose ash less reactive and easier to handle at spreading.

Dusting of ash has considered to be hazardous to people, who spread the ash (Eriksson 1998). Granulation of ash increases the volume weight, decreases the dust problem and permits the addition of supplementary nutrient e.g. nitrogen-rich sludge (Veijalainen 1993, ref. in Silfverberg 1996) or biotite containing slowly soluble potassium (Kaunisto et al. 1993, ref. in Silfverberg 1996). According to Eriksson (1998) a slow release rate of ash is preferable in order to minimize the bio-availability of heavy metals contained in the ash

2.3 Cadmium in wood ash

The physical and chemical quality of ash varies significantly depending on many factors e.g. tree species, growing site, part, size and age of the tree, logging technique, fuel used and burning technique (Hytönen & Nurmi 1997). According to Korpilahti (2001) the cadmium concentration in wood ash of power plants in Finland varies from some mg/kg to about 30 mg/kg (table 1). According to the analyses carried out by the Plant Production Inspection Centre of ash intended to be use in agricultural fields, the content of cadmium has varied from < 0.3 mg/kg dw as high as 60 mg/kg dw. Concentrations have exceeded many times the national limit of cadmium content in ash used in agricultural purposes, which is < 3 mg/kg dw (Rainio 2001).

In Finland preliminary guideline values of cadmium for soil are 0.5 mg/kg dw (targeted value) and 10 mg/kg dw (limit value) (Saastuneet maa-alueet ja niiden käsittely Suomessa 1994). A new proposed targeted value of cadmium for soil is 0.3 mg/kg dw (Assmuth 1997). Official guidelines are presently been prepared by the Ministry of the Environment.

Table 1. Cadmium content (mg/kg, HNO₃) of ash of different power plants in Finland. Metsä-Botnia Kaskinen and Äänekoski and UPM Kuusankoski and Pietarsaari and Enocell are kraft pulp mills, which use mainly pine and birch bark. Voikkaa is a mechanical pulp mill, which uses spruce bark. Fortum uses mainly peat (Korpilahti 2001).

Power plant	Type of ash	Cadmium mg/kg
MB-Kaskinen	Dust 1998	10.2 – 13.9
MB-Äänekoski	Dust 1997	10.0
	Dust 1998	10.2
	Self hardened 1997	7.9
	Self hardened 1998	9.2
UPM-Voikkaa	Dust 1997	2.4 – 6.2
	Granule 1997	3.4
UPM-Kuusankoski	Granule 1997	4.0
	Self hardened 1997	4.0
UPM-Pietarsaari	Dust 1998	19.0
Enocell	Dust 1998	20.0 – 28.5
	Granule 1998	19.7 – 22.7
Fortum-Joensuu	Peat 1997	< 1.0
Fortum-Joensuu	Peat 1998	3.7
Fortum-Haapavesi	Peat 1998	3.7
Fortum-Rauhalahti	Peat 1998	<1.0

In coniferous trees cadmium concentration is highest in the phloem and bark (table 2) (Lodenius et al. 2000). According to Nilsson & Eriksson (1998) willows accumulate much cadmium and the cadmium concentration in willow ash can be as high as 70 mg/kg.

Wood ash, in general, can be divided into fly and bottom ash. The most lightest fraction of wood ash is filter fly ash. The amount of different fractions depends on the type of boilers and cadmium content of ash varies significantly in different fractions of ash. In burning processes cadmium is very easily found in filters (even 90 %) due to volatilization of cadmium. However, the proportion of the lightest fraction of the total ash generated is often only about 2-10 % (Ober-

Table 2. Cadmium concentration (mg/kg dw; means +SE) in different parts of spruces (*Picea abies*) and pines (*Pinus sylvestris*) (Reijonen unpublished according to Nuorteva 1990, ref. in Lodenius et al. 2000).

	Bark	Phloem	Young sapwood	Sapwood & heartwood	2.year needles
<i>Picea abies</i>	0.49 ± 0.03	0.85 ± 0.3	0.08 ± 0.03	0.25 ± 0.08	0.13 ± 0.02
<i>Pinus sylvestris</i>	0.49 ± 0.14	1.3 ± 0.5	0.16 ± 0.04	0.28 ± 0.06	0.25 ± 0.12

berger et al. 1997, ref. in Kepanen 2001). In general, the heavy metal content of ash increases with increasing burning temperature, because quantity of ash generated is smaller at very high temperature corresponding to the higher amounts of heavy metals concentrated (Etiégne & Campbell 1991, ref. in Kepanen 2001).

There is no definite and unambiguous information available about the fraction of different cadmium compounds and the solubility of cadmium in wood ash. According to Dahl & Obernberger (1998, ref. Kepanen 2001) and Lind et al. (1998, ref. in Kepanen 2001) cadmium is mainly as sulfates ($3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$) and silicates (CdSiO_3) in wood ash. Cadmium silicate is not soluble in water, but dissolves in acids. However, a little amount of cadmium oxide (CdO) has been found in wood ash (Dahl & Obernberger 1998, ref. in Kepanen 2001), although CdO has generally in many ash fertilization experiments been assumed to be the most probable cadmium fraction in wood ash due to the high temperature burning. Cadmium oxide is insoluble to water, but may dissolve under strong oxidizing or acidic conditions (WHO 1992).

The removal of toxic elements such as cadmium from ash has been discussed. According to Österbacka (2001) cadmium compounds are probably found on the surface of ash granules, from where they could be “cleaned” before granulation of ash and spreading of ash into the forests if suitable technique could be available.

3 CHARACTERISTICS OF FORESTS AND SOILS

3.1 Forestry land

About 65 % of forestry land can be classified as mineral soils and 34 % as mires (table 3). Forestry land consists of productive forest land 20.0, other wooded land 3.0, waste land 3.1 and roads, depots 0.2 million hectares. A site is classified as mire if it has peat layer or if the coverage of peat-forming plants is more than 75 % (Finnish statistical yearbook of forestry 2000).

3.2 Mineral and peat soils

Sediments and soils in Finland have formed during the Quaternary, the youngest period in the history of the earth, when continental ice sheets repeatedly covered northern Europe. The last ice age ended about 9000 years ago. Since then the land has been rising and the Baltic Sea receding (Koljonen & Tanskanen 1992).

The bedrock in Finland is overlain by a sedimentary cover (mineral and organic sediments) of average 7 meters thickness. Mineral sediments predominate and till, which is found nearly everywhere, is the most common of these. The till was formed from bedrock, preglacial sediments, and "in situ" weathered bedrock when the slowly flowing glacial ice dislodged, crushed, and ground the mineral matter. Till is composed of mineral and rock fragments ranging in size from boulders to clay. Organic-rich sediments, which include gyttja, peat, and mull humus, are formed through

the humification of the remains of organic matter. Organic matter accumulates as peat in bogs through humification of moss, sedge and grass (Koljonen & Tanskanen 1992).

Podzol soil predominates in areas of coniferous forest and where sediments are mostly till (Figure 1). Podzol is typically composed of horizons with total thickness less than half a metre. The topmost, litter-rich, organic layer (O) is composed of humified plant remains. This results in the formation of organic acids, which together with carbonic acids, leach iron, aluminium and other elements from the mineral soil and carry them downwards in the podzol profile. An ash-grey, leached horizon (E) composed mainly of quartz and feldspars develops. Acidity decreases toward the bottom of the leached horizon and organic compounds and dissolved elements like iron and aluminium, which migrate in solution, precipitate in the enrichment horizon (B). A reddish brown colour enrichment horizon grades downwards into mineral soil (C), which has undergone only slight chemical change (Koljonen & Tanskanen 1992).

Ecologically, a mire can be defined as an ecosystem, sustained by humid climate and a high water table, due to which partially decomposed organic matter is accumulated as peat. In practical site classification mires are divided into two

Table 3. Distribution of forestry land into mineral soils and mires, and the state of drainage of mires, 1986-1998 (Finnish statistical yearbook of forestry 2000).

	Mineral soil sites	Spruce Mires	Pine mires	Treeless mires	Mires total	Proportion of mires	Drained mires	Peat depth < 30 cm
	1000 ha	1000 ha	1000 ha	1000 ha	1000 ha	%	%	%
Whole country	17 192	2 277	4 951	1 705	8 932	34.2	53.1	22.2
Southern Finland	8 785	1 183	1 828	177	3 188	26.6	76.3	21.9
Northern Finland	8 407	1 093	3 123	1 528	5 744	40.6	40.2	22.4

main groups: 1) genuine forested mire site types (spruce and pine mires) and 2) treeless mires and sparsely forested composite site types (fens and bogs) (Laine & Vasander 1996). A mean thickness of the peat layers is 1.52 m; 23 %, or 1.17 million hectares, are over 2 m deep (Lappalainen 1996).

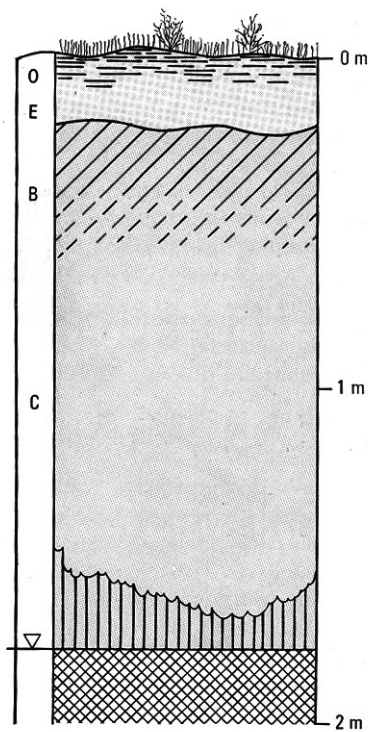


Figure 1. Profile of a podzol soil; O=organic layer, humus horizon E=eluvial horizon, B=illuvial horizon and C=parent glacial material (modified from Koljonen & Tanskanen 1992).

4 GENERAL INFORMATION ON EXPOSURE

4.1. Sources of cadmium in forest soil

Sources of Cd in soils are both natural and anthropogenic. Emissions of cadmium derive from combustion of fossil fuels, industrial manufacturing, waste incineration and cement manufacturing. In addition, the use of phosphate fertilizers contributes to the contamination of agricultural soils. Even though the emissions have decreased, the anthropogenic input is still higher than the natural release of cadmium from wind-borne soil particles, volcanoes, sea-salt spray and forest fires (Nriagu 1989).

4.1.1 Atmospheric deposition

According to Kulmala et al. (1998) the deposition (bulk) of cadmium in Finland has only been systematically monitored since 1990. According to air quality measurements made during 1997-99 in eight background stations in Finland (Finnish Meteorological Institute 1997, 1998, 1999) annual bulk deposition of cadmium was the highest in southern Finland, 0.3 g/ha, and decreased gradually to the north being 0.2 in Central Finland and 0.1 g/ha in Northern Finland (table 4). However, it can be estimated that the bulk deposition in forest could be almost doubled due to the high adsorption surface area their can-

opies present for interception (Ukonmaanaho et al. 1998, 2001). According to Ukonmaanaho et al. (2001) deposition loads of heavy metals to forested areas based on wet-only or bulk collectors placed in an open area underestimate the total deposition load to the forest. For cadmium wet and dry deposition are of equal importance. In a southern Swedish spruce forest, bulk deposition contributes to approximately 50 % of the total cadmium input to the forest floor (Bergkvist 1987).

According to Verta et al. (1990) total deposition of 0.19 g/ha/a was estimated for southern Finland and 0.094 g/ha/a for Northern Finland from snow analyses. Based on moss concentrations the estimated atmospheric deposition is <0.5-1 g/ha/a (Europe's environment 1995, ref. in Lodenius et al. 2000).

Scandinavian moss monitoring (Nordic Council of Ministers 1992) indicates that Cd deposition has clearly decreased in the Nordic countries during the years 1969-1985. During the period of 1990-97, the annual atmospheric emissions of cadmium in Finland decreased by 85%, from 6.3 to 1.1 tonnes (Melanen et al. 1999).

4.1.2 Commercial fertilizers and liming agents

Practical forest fertilization began in Finland in the early 1960s. The peak in fertilization activity was reached in 1975, when nearly 250 000 hectares of forest were fertilized. After that there was a strong decrease in the area fertilized. About half of the fertilization done so far has been on peatlands, and the other half on mineral soils (Salonen 1994). In the year 1999, totally of 21 519 hectares of forest were fertilized with commercial fertilizers (Metsätalastollinen vuosikirja 2000).

According to Hero (2001) in the year 2000, 9737 t of commercial fertilizers have been sold to the forest use, where the average use has been 450 kg/ha. In the same year, the amount of phosphorus sold in forest fertilizers has been 148 551 kg.

Table 4. Annual bulk average depositions of cadmium in eight Finnish background stations measured by Finnish Meteorological Institute during 1997-99 (Finnish Meteorological Institute 1997, 1998, 1999).

	1997	1998	1999	1997-99
Background station	g/ha	g/ha	g/ha	g/ha
Southern Finland				
Average	0.24	0.32	0.29	0.28
Central Finland				
Average	0.10	0.17	0.23	0.17
Northern Finland				
Average	0.06	0.12	0.09	0.09
Mean	0.14	0.21	0.20	0.19

The cadmium content of forest fertilizers is generally < 0.2 mg/kg or < 5 mg/kg of P. Consequently, based on the maximum amount of cadmium in phosphorus and a use recommendation of 45 kg phosphorus per forest hectare (Paavilainen 1979, ref. in Kaunisto 1997), the cadmium load of the commercial fertilizers on forest has been 0.2 g/ha in the year 2000.

In some experiments, totally about 100 ha of forests have been treated with liming agents (Kukkonen 2001). Consequently liming has not been considered in this report.

4.1.3 Wood ash

The amount of ash used in forest fertilization has varied between 2000 – 16000 kg/ha. The nutrient content of ash varies significantly. Based on the recommended use of 45 kg phosphorus per forest hectare 3000 –7000 kg ash per hectare should be spread in the forest in order to achieve the necessary phosphorus content in soil (Kaunisto 2001).

When the average amount of ash used is 5000 kg/ha and an average cadmium content 10 mg/kg dw, the cadmium load on forest soil is 50 g/ha, which is more than hundred times higher the average atmospheric deposition (table 5). When ash fertilization is done e.g. once in 50 years, the difference to the total annual atmospheric deposition over 50 years ($0.2 \times 50 = 10$ g/ha over 50 years) is five fold. According to Paavilainen (1980, ref. in Silfverberg 1996) the fertilizing effect of wood ash of 5000 kg/ha has been estimated to last 30-40 years.

According to the environmental impact assessment of ash fertilization by Egnell et al. (1998)

short-term adverse effects of ash fertilization could be acceptable if stabilized wood ash is used not more than 3000 kg dw/forest hectare during forest generation. However, it was emphasized that netto input of heavy metals to forest soil can not be allowed to increase during ash fertilization. Heavy metal input and output (e.g. via harvest of logging residues) to the forest soil should be in balance.

Table 5. Cadmium load (Cd g/ha) on forest soil with different amount of ash used and different content of cadmium in ash.

Amount of wood ash used (kg/ha)	5 mg Cd/kg ash	10 mg Cd/kg ash	20 mg Cd/kg ash	30 mg Cd/kg ash
	Cd g/ha	Cd g/ha	Cd g/ha	Cd g/ha
3000	15	30	60	90
5000	25	50	100	150
7000	35	70	140	210

5 ENVIRONMENT

5.1 Exposure assessment

Cadmium occurs at very low concentrations in the lithosphere and in topsoils. The average total content of Cd in soils lie between 0.07 and 1.1 mg/kg. However, the background Cd level in soils apparently should not exceed 0.5 mg/kg, and all higher values reflect the anthropogenic impact on the Cd status in topsoil (Kabata-Pendias and Pendias 1984).

The chemical composition of parent rock determines the natural Cd content of the soil. In addition to this, the age of the soil has a significant influence on the concentrations of total and soluble Cd in soil. According to Bergseth (1989), chemical and mineralogical analysis of soil samples from 10 European countries indicate that the samples from Portugal and Spain have the lowest total Cd content and the highest degree of weathering. The samples from Finland and Norway seem to have higher total as well as easily extractable Cd content than the samples from southern Europe. Although the bedrock is old in Finland, the soil is young as compared to the soil in Southern Europe, because Finnish soil is mainly formed after the last ice age.

Table 6. Mean cadmium content (mg/kg) and organic matter (OM) content and median pH by soil layer (Tamminen & Starr 1990).

Layer	Mean pH (range)	OM % (range)	Cadmium mg/kg dw
Humus	4.17 (3.6-5.8)	71.6 (32-95)	0.47
0-5 cm	4.35 (3.6-5.4)	7.0 (1.1-22.0)	0.24
5-20 cm	4.94 (4.3-5.5)	4.2 (1.4-11.2)	0.32
20-40 cm	5.25 (4.8-6.6)	2.5 (0.2-6.2)	0.32
60-70 cm	5.56 (4.0-7.4)	1.3 (0.3-5.6)	0.28

Table 7. Cadmium concentrations in humus layer at different percentiles (Tamminen 1998).

	Min.	25 %	50 %	75 %	99 %	Max.
Cd mg/kg	0.0	0.3	0.4	0.5	0.9	1.6

5.1.1 Background cadmium concentration in mineral soils

According to Tamminen & Starr (1990) the content of cadmium is clearly concentrated in the humus layer (table 6). Altogether 65 samples from the South of Finland were analysed for total cadmium. Different forest types did not influence the cadmium concentration.

According to Tamminen (1998) cadmium concentrations of the humus layer vary between 0.0-1.6 mg/kg dw (table 7). Samples were taken from 488 sample areas all over Finland. Concentrations increased from north to south indicating the effect of deposition.

In Sweden a mean concentration of 0.71 mg/kg dw (50 % fractile of 0.64 mg/kg dw) was found in mor layer (Andersson et al. 1991, ref. in Lodenius et al. 2000).

The natural concentration of heavy metals in soils varies regionally with the basic geology and locally with the type and genesis of the overburden. The whole Finland has been geochemically mapped on the bases of the fine fraction of till, which is the most common soil parent material in Finnish forests. In Finnish basal till (samples taken at a depth of > 60 cm) the median value of total (aqua regia extraction) cadmium is 0.19 mg/kg and bioavailable (acid ammonium acetate EDTA extraction) cadmium 0.0056 mg /kg. The bioavailable concentrations are usually only 1-3 % of the total concentrations (Tarvainen & Kallio 1999).

In addition, natural background concentrations of cadmium are high in black shale areas in Finland e.g. median value of cadmium in Talvivaara area is 15 mg/kg. Black shales, which are composed of former marine sediments are mainly situated in the East and North of Finland (Loukola-Ruskeeniemi et al. 1998, Loukola-Ruskeeniemi 2001).

5.1.2 Background cadmium concentration in peat soils

There is not much information available about cadmium concentrations in peat soils. According to Moilanen & Issakainen (2000) total cadmium concentrations in peat soils vary between 0-1.1, 0.2-0.3, 0.1-0.2 and 0.1-0.3 mg/kg at the depth of 0-10, 10-20, 20-30 and 30-40 cm, respectively. According to Silfverberg & Issakainen (1991) the mean cadmium concentration in peat soils was 0.5 and 0.3 mg/kg at the depth of 0-10 and 10-20 cm, respectively.

According to Virtanen (2001) the average and the maximum total cadmium content of peat (altogether 550 samples) in the north of Finland was 0.13 and 1.01 mg/kg dw, respectively. The quantification limit of the laboratory was 0.5 mg/kg dw.

5.1.3 Effects of ash fertilization on soil cadmium concentrations

According to Pihlström et al. (2000) the exchangeable (cadmium extracted by NH_4 acetate; pH 4.65) and total (HNO_3 acid extracted Cd) concentrations of cadmium in mineral soil humus and peat

soil more than doubled two years after ash fertilization (Figure 2). In addition, in the year 2000 concentrations of exchangeable cadmium were still in higher levels (Pihlström 2001). There were 8 controls and 3 fertilized plots in *Vaccinium* and *Myrtillus* type forest soil. In peat soil there were 7 study plots of which 2 were controls and 5 fertilized. Hardened wood ash of 6400 kg/ha was spread on these study plots in the summer 1998. The cadmium content of ash was 8-9 mg/kg dw.

According to Pihlström et al. (2000) exchangeable cadmium fractions could originate from the soil and the peat as well as from the ash itself. Already 5 months after ash fertilization pH increased 0.5 pH unit in peat soils and 1.0 units in forest soils. Approximately 1.7 years after ash fertilization the increase of pH was an average 1.5 units in all the fertilized areas. A sudden increase of pH and competition of cation exchange places after ash fertilization could cause the removal and release of cadmium from the soil and peat, although great amounts of cadmium had not yet been released from the ash itself. This indicates

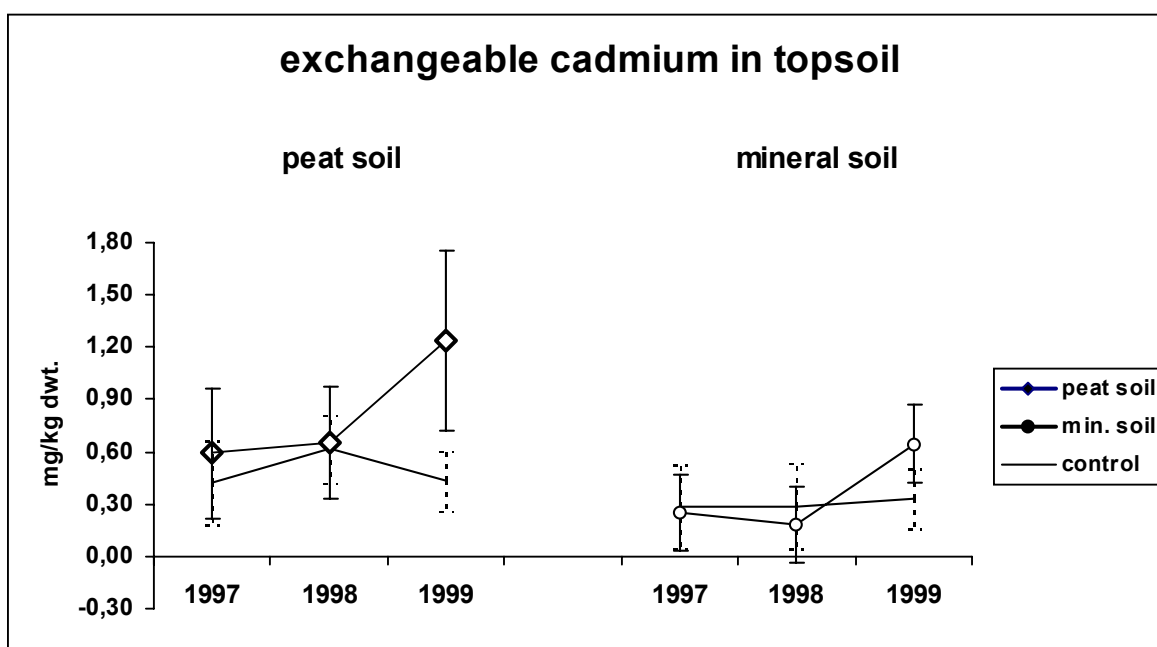


Figure 2. Exchangeable cadmium concentrations in the surface of peat soil and in humus layer of (0-7 cm) of mineral soil in 1997-1999. NB: The concentrations have been presented in dry weight. Concentrations in mineral soils would be 3-5 higher in relation to concentrations in peat soils, if calculated in wet or volume weight. Ash treatment has started in 1998, therefore the concentrations obtained in the year 1997 represent the background concentrations of the study area (Pihlström et al. 2000).

that after ash fertilization not all the cadmium is adsorbed for a long time in soil.

According to Egnell et al. (1998) easily extractable fractions of cadmium can increase or decrease after ash fertilization. There has sometimes been a trend that extractable fractions of metals were lower after high amount of ash used as compared to the controls. However, there has also been a temporary increase of extractable metal concentrations 1-2 years after ash fertilization, even when granulated ash has been used. This has been observed as increased concentrations of cadmium in needles, certain mushrooms, enchytraeid worms and soil water. The origin of cadmium released is still unclear, but probably it comes from the soil, not from the ash itself. The increase of pH after ash fertilization has varied between 0.4-2.5 units in peat soils and 0-1 unit in humus layer of mineral soils depending on the quantity and quality of ash used.

According to Bramryd & Fransman (1995, ref. in Egnell 1998) the extractable cadmium (0.05 M EDTA) content of humus layer was 8-41 % higher in fertilized study plots of 2000-7000 kg ash/ha than in control plots 10 years after ash fertilization. In the study loose ash of 2000, 7000 and 10 000 kg/ha was spread on moraine of pine forest. The cadmium content of the ash was 12 mg/kg dw. Samples were taken every year during 5 years after fertilization and then once 10 years after fertilization.

Rühling (1996, ref. in Egnell 1998) noticed also that the extractable concentration of cadmium (extracted by 0.5 M barium chloride) in humus layer was two years after ash fertilization 30-36 % higher in fertilized plots received 3 000 kg ash/ha than in controls. On the contrary, the extractable cadmium concentration in humus layer nine years after ash fertilization in another study area (Ringamåla area) was 38-96 % lower in ash fertilized plots than in control plots. Zhan et al. (1996, ref. in Kepanen 2000) state that the decrease of solubility of cationic heavy metals is only a temporary phenomenon caused by the increase of pH during ash fertilization. According to Eriksson (1998) humus substances from soil

may speed up dissolution of ash due to their acidity and complexing ability. The mor layer has a large capacity to retain different elements released from ash and, especially if pH increases, to bind heavy metals in a less bioavailable form.

Kepanen (2001) studied effects of ash treatment in the same area as Pihlström et al. (2000). Samples were taken at depths of 0-5 and 15-20 cm on mineral and peat soils two years after ash treatment of 6 400 kg/ha. The following extractions were used; water to extract cadmium in soil water, KNO_3 to extract extractable cadmium, NaOH to extract organic bound cadmium, $\text{NH}_2\text{OH}\cdot\text{HCl}$ to extract cadmium bound in oxides and HNO_3 to analyse total cadmium content. The cadmium and moisture content of ash were 9.2 mg/kg dw and 25 %, respectively. Therefore, the cadmium load was 44 g/ha. In general, cadmium was more tightly adsorbed in the surface layer of fertilized area (both mineral and peat soils) than in controls. In mineral soils a bigger percentage of cadmium was in an organic and bound residue fraction in fertilized area than in controls. Correspondingly, a bigger percentage of cadmium was in an extractable fraction in controls. In peat soils no difference were found in cadmium content and percentages of different fractions between fertilized and control areas. According to the author the reliability of the results suffer from the uneven spreading of ash and the great heterogeneity of the soils used in the study. Obviously, no direct conclusions can be drawn on the change of the content of cadmium in soil after ash fertilization due to the lack of information about background concentrations of cadmium in soils before ash treatment.

In a three week laboratory incubation study by Kepanen (2001) mineral and peat soils samples were fertilized with 5 different types of ash at the level of 10 000 kg/ha (table 8). The same extractions of cadmium were used as cited above. Ash treatment increased pH significantly. Dust ash (= untreated fly ash) treatment resulted in the highest pH increase and cadmium content in soil samples. On the contrary, granulated ash resulted in the lowest pH increase and cadmium content,

Table 8. Total cadmium content (mg/kg, HNO₃) in different types of ash and in peat and mineral soil samples and pH-values in peat and mineral soils after ash fertilization treatment in three weeks laboratory incubation study (Kepanen 2001).

	Cd mg/kg in ash	Peat soils		Mineral soils	
		pH	Cd (mg/kg)	pH	Cd (mg/kg)
Control		2.9 ± 0.1	0.30 ± 0.05	5.0 ± 0.1	0.05 ± 0.01
Dust ash of Äänekoski	5.5	8.6 ± 0.1	1.49 ± 0.07	8.5 ± 0.2	0.29 ± 0.05
Bottom ash of Äänekoski	0.2	7.6 ± 0.4	0.32 ± 0.08	8.0 ± 0.2	0.05 ± 0.00
Self hardened ash of Äänekoski	3.1	7.0 ± 0.3	0.77 ± 0.22	7.2 ± 0.2	0.10 ± 0.03
Granulated ash of Uimaharju	12.5	4.1 ± 0.7	0.23 ± 0.01	6.0 ± 0.4	0.04 ± 0.00
Dust ash of Uimaharju	12.8	7.6 ± 0.1	3.90 ± 0.29	8.1 ± 0.1	0.44 ± 0.11

Dust ash is untreated fly ash

although the cadmium content of granulated ash was high. Generally, cadmium did not seem to be very easily soluble form in the ash. In most peat and mineral soil samples cadmium could only be extracted by HNO₃. However, the control of the peat soil was an exception; cadmium was mainly extracted by KNO₃. Also the amount of cadmium bound in the organic fraction was higher in fertilized than untreated peat soil samples. This could indicate that during fertilization the easily soluble cadmium is bound more tightly in soil. The assumption was supported by the observation that the fraction of extractable cadmium was decreased after ash fertilization. In most control and treated samples of mineral soil cadmium could only be extracted by HNO₃. However, the fraction of cadmium bound in oxide (NH₂OH•HCL) was bigger in ash fertilized samples than untreated samples (Kepanen 2001).

In the short-term fertilization experiment (2-3 months) peat ash was spread 20 000 kg/ha and birch wood ash 10 000 kg/ha on mineral and peat soils. In the long-term experiment peat ash was spread on study area 2-8 years ago (Silfverberg

and Issakainen 1991). Untreated control areas were not established for all the treated areas in the long term experiment, some controls were chosen in untreated forest areas. The cadmium content in wood and peat ash was 31 and 9 mg/kg dw, respectively. The pH of the surface soil layer (0-10 cm) increased by 1.7 units in mineral soil and 1.0 unit in peat soil 2-3 months after fertilization with birch wood ash. The effects of peat ash on pH of the soil were minor. Concentrations of cadmium in all study areas were under detection limit 2-3 months after fertilization. However, 2-8 years after fertilization cadmium concentrations in fertilized peat soils had doubled and were much higher than in mineral soils (table 9).

Moilanen and Issakainen (2000, table 10) studied short- and long-term effects of ash fertilization on forests in the North of Finland. In the short-term study the impacts of different types of ash on soil and vegetation were studied 2-16 months after fertilization. Wood ash of 5000 and 15000 kg/ha was spread on peat soils. On mineral soils wood and peat ash was spread 3000 and 9000 kg/ha, respectively. The wood ash fer-

Table 9. The pH and cadmium concentration (mg/kg, HCL extraction) in mineral and peat soil 2-8 years after ash fertilization (Silfverberg & Issakainen 1991).

	Sampling depth (cm)	Control samples		Ash treated samples 20 t/ha	
		pH	Cadmium mg/kg	pH	Cadmium mg/kg
Mineral soil	0-10	3.72±0.05	0.19±0.04	3.66±0.06	0.25±0.05
	10-20	4.09±0.08	0.13±0.04	3.90±0.04	0.13±0.03
Peat soil	0-10	3.50±0.05	0.51±0.08	3.80±0.05	1.00±0.23
	10-20	3.74±0.08	0.31±0.14	3.76±0.06	0.53±0.31

tilization level of 5000 kg/ha corresponds to the addition of phosphorus in commercial PK-fertilizers. Cadmium content (mg/kg dw HCL-extract) in dust and hardened ash of Äänekoski, Metsä Botnia (90 % bark, 10% sludge), dust and granulated ash of Voikkaa, UPM (bark and sludge) and peat ash of Fortum (90 % peat, sawdust and fuel oil) was 15, 13-15, 6, 6, 3-4, respectively.

The long-term effects on soil and vegetation were studied 9-52 years after fertilization with wood ash (28 study plots) and peat ash (9 study plots). In all experiments only dust wood ash was used. Wood ash of 500-15000 kg/ha and peat ash of 4000-100 000 kg/ha was spread on the study area. The content of cadmium in wood ash was 31 mg/kg (dw HCL-extract, analysed in only one ash sample). Cadmium content in peat ash varied 3-9 mg/kg (analysed in three samples) (Moilanen & Issakainen 2000).

Dust ash resulted in the highest increase of cadmium in soil. In some samples the cadmium content had more than doubled in the upper layer

of soil. The elevated concentrations of cadmium in soil could be seen even 13 years after ash treatment. The pH increased in all fertilized study areas. The increase of pH in humus was 1.4-2.8 units in mineral soils and 0.3-1.6 units in peat soils. The direct short-term effects of fertilization were limited at the depth of 2-4 cm of the humus layer, but the decrease of acidity could also be seen at the depth of 0-10 cm. Dust wood ash of Äänekoski resulted in the highest decrease of the acidity of soil. The decrease of acidity of humus in mineral soil was still clearly seen 9-19 years after fertilization, when the pH of humus was still 1-1.4 units higher in wood ash fertilized areas than in control areas. The decrease of acidity could be even seen at the depth of 10-20 cm in some fertilized mineral soils. The decrease of acidity was much less in peat soils, where the pH of the surface peat was 0.2-0.6 unit higher than in control 14-26 years after ash fertilization (Moilanen & Issakainen 2000). According to Silfverberg & Hotanen (1989) the increases in nutrient

Table 10. Total cadmium concentration (mg/kg dw) in short- and long-term ash fertilization experiments (Moilanen & Issakainen 2000).

		Cd (mg/kg) at different depth (cm) of the soil				
		Humus layer	0-10	10-20	20-30	30-40
Dry mineral soil (18 months after ash treatment of 9000 kg/ha)	Control	0.2	*	*		
	Dust ash, Äänekoski	0.4	*	*		
	Hardened ash, Äänekoski	0.3	*	*		
	Dust ash, Voikkaa	0.3	*	0.3		
	Granulated ash, Voikkaa	0.3	*	*		
	Peat ash	0.4	0.2	*		
Ombrotrophic peatlands (18 months after ash treatment of 15 000 kg/ha)	Control		0.3	0.2	0.1	
	Dust ash, Äänekoski		0.7	0.2	0.5	
	Hardened ash, Äänekoski		0.6	0.3	2.3	
	Dust ash, Voikkaa		0.4	0.2	0.2	
	Granulated ash, Voikkaa		0.3	0.2	0.2	
Minerotrophic peatlands (18 months after ash treatment of 15 000 kg/ha)	Control		0.4	1.0	0.2	
	Dust ash, Äänekoski		6.1	0.2	0.3	
	Hardened ash, Äänekoski		0.5	0.3	0.2	
	Dust ash, Voikkaa		0.4	0.2	0.3	
	Granulated ash, Voikkaa		0.6	0.3	0.4	
Mineral soil (Paltamo) (19 years after ash treatment)	Control	0.4	0.2	0.1		
	Ash treatment	1.4	0.2	6.2		
Mineral soil (Muhos) (19 years after ash treatment)	Control	0.2	*	*		
	Ash treatment	0.2	*	*		
Organic soil (Pyhäntä) (13 years after ash treatment of 11 900 kg/ha)	Control		0.3	0.2	*	0.1
	Ash treatment		0.5	*	*	0.2
Organic soil (Muhos) (27 years after ash treatment of 5040 kg/ha)	Control		1.1	0.2	0.2	0.3
	Ash treatment		0.5	0.2	0.3	0.3

- under detection limit

concentrations and pH of the peat soils were still evident about 40 years after ash fertilization.

Eriksson (1998) studied dissolution of hardened and crushed ash in a column experiment during leaching with artificially acidified rainwater corresponding to five-year precipitations. The results show that hardened and crushed ashes dissolve relatively slowly. Cadmium seems to be strongly bound in the ash. Although total contents of heavy metals increased slightly, the exchangeable and presumably bioavailable (extracted by BaCl_2) fractions tended to decrease due to the increased pH of the mor layer induced by the ash. The most prominent effect of ash application in general, was the initial temporary increase in concentrations in the leaching water. The effect was stronger in the mor layer and coincided with an increase in electric conductivity (high salt content). This indicates that exchangeable heavy metals are mobilized from the mor layer and not from the ash.

According to Eriksson et al. (1998) within three weeks after ash application, electrical conductivity (EC) increased most in the upper 8 cm of the soil in all treatments. A hardened ash obtained from burning wood and peat fuels, which had relatively high contents of organic C and S, caused the highest increase in EC. A short-term decrease in soil pH at 1-8 cm depth was found in cases where large increases in electrical conductivity were observed. In general, the highest pH values were found after 11 months, at 0-1 cm soil depth. At all soil depths, the greatest increase in pH was obtained with an untreated, loose wood ash. The decrease in soil pH in the 1-3 cm and 3-5 cm layers caused by most ash treatments were probably the result of so-called "salt effect", where some of the cations from early dissolved neutral salts were exchanged with hydrogen ions in the upper soil layer, whereupon the latter were transported further down in the soil profile where they caused a temporary increase of acidity. Later on, when carbonates and oxides dissolved to a higher degree than neutral salts, the ashes had a more direct alkalising effect.

5.1.4 Conclusions of the effects of ash fertilization

Total concentrations of cadmium have increased in the surface of peat soil and in humus of mineral soil after ash fertilization. The increase of cadmium concentrations has generally been higher in peat soils than in mineral soils. In peat soils cadmium concentrations even doubled (e.g. from 0.5 mg/kg to 1 mg/kg Cd dw) after ash fertilization.

There are only limited number of available studies on exchangeable concentrations and the results of the fate of exchangeable (extractable) cadmium concentrations seem to be quite contradictory. In some ash fertilization studies the exchangeable cadmium concentrations have decreased and other studies increased. However, there seems to be a trend that exchangeable concentrations of cadmium would increase after ash fertilization. Exchangeable concentrations have even been noticed to double two years after ash treatment. The mechanism behind the increased exchangeable concentrations is still unclear. "Salt effects" have been considered to be one of the reasons. Cadmium is released from the soil, when ionic concentration of the soil water increases due to the easily dissolved neutral salts of ash. The competition of cationic exchange places becomes harder and cations from early dissolved neutral salts will be exchanged with hydrogen ions. A temporary increase of acidification is seen in soil water, although the solid soil material becomes alkaline. The trend in the long run is still unclear, although according to one study the exchangeable concentrations were still 8-41 % higher in fertilized area than in untreated areas 10 years after ash treatment.

Ash fertilization increases the pH (even couple of pH units) of the upper layer of peat soil and in humus layer of mineral soils. The increase of pH depends on the soil and the quantity and quality of ash used. The increase of pH is usually more prominent in mineral than in peat soils and has been seen even couple of tens of years after ash fertilization. It should however be remembered that in former ash fertilization experiments great amounts of high pH birch wood ash was often used.

In addition to the limited amount of studies available about extractable cadmium concentrations the comparison of ash fertilization studies and their results is difficult. Many studies are not fully referred to especially regarding cadmium and wood ash used. Studies also differ from each other in many methodological ways e.g. different extraction and analysis methods are used, type of ash varies significantly, amount of controls varies (especially in long-term studies they are often lacking). In general, the number of samples taken is often quite small for such a heterogeneous environment as forest soils.

5.1.5 Fate of cadmium in soil and forest

5.1.5.1 Transformation and distribution in forest soil

Most biological processes are concentrated to the humus layer. The behaviour of cadmium in deeper horizons is poorly known and probably of less important to the functioning of forest ecosystem. The mobility of cadmium is strongly dependent on pedological factors such as pH, humus content, cation exchange capacity, redox potential, as well as external factors such as temperature, precipitations, erosion, land use practice etc. Furthermore, the degree of activity, bioavailability and mobility of Cd is influenced by other factors, like competition with other metal ions (e.g. Zn), ligation by anions, composition and quantity of the soil solution (Christensen & Tjell 1990). The sorption of cadmium decrease at decreasing pH and increasing particle size. Cadmium from atmospheric deposition and litterfall is attached to humic substances in the mor horizon (Ukonmaanaho et al. 1998, 2000).

Compared to other toxic heavy metal, like lead and mercury, cadmium is exceptionally soluble in soil. Cadmium is relatively mobile between the pH levels of 4.2 – 6.6 and only moderately mobile between the pH levels of 6.7 – 8.8 (Schmitt and Sticher 1991).

The major physico-chemical reactions of Cd in the soil are sorption, complexation, precipitation, biosynthesis, biodecomposition and uptake by the roots. The principal chemical species of Cd in acid soil solution under oxic conditions are

Cd^{2+} , CdSO_4 , CdCl^+ and in alkaline conditions Cd^{2+} , CdCl^+ , CdSO_4 , CdHCO_3^+ . Soluble, exchangeable and chelated species of Cd are the most mobile in soils and these forms govern its migration and phytoavailability (Schmitt and Sticher 1991).

The dominating mechanism governing the distribution of Cd between soil and soil solution is sorption (adsorption, absorption, chemisorption, ionexchange and surface complexation).

Cadmium sorption in soils is a fast process reaching equilibrium within 1 hour, the sorption process approximately is fully reversible and the distribution of cadmium between soil and solute is independent of its origin (Cristensen & Tjell et al. 1990). This indicates that although the soil may have a significant capacity to sorb cadmium, the soil is not a permanent sink and previously sorbed cadmium may be released upon changes in the soil solution composition.

5.1.5.2 Leaching in soil and the effects of ash treatment

Generally, in natural soils formed under a cool and humid climate, the leaching of trace elements downward through the profiles is greater than their accumulation, unless there is a high input of these elements into the soil. However, specific soil properties, mainly cationic exchange capacity, control the rates of trace elements migration in the profiles (Kabata-Pendias and Pendias 1984).

The danger of leaching of nutrients and heavy metals has to be considered especially in peat soils, where the leaching is generally greater than in mineral soils. Besides, in the restoration of peatlands the fate of nutrients and heavy metals has to be considered carefully due to the radically changed moisture conditions after restoration (Pihlström et al. 2001). However, according to Piirainen (2000) leaching of cadmium from the different types of drained peatlands two years after ash fertilization was insignificant. Probably, due to the increase of pH cadmium was adsorbed in soil. Ash was spread at the level of 5000 – 6500 kg/ha and the cadmium load on peat varied 0.01–0.08 kg/ha. In general, leaching of nutrients and heavy metals seems to depend on the type of the peatlands; leaching is greater from ombrotrophic than from minerotrophic peatlands.

According to the laboratory lysimeter study with four different eluents by Lodenius & Autio (1990) cadmium was sorbed strongly to peat and sand soils, but released at low pH-values. Results indicated that pH was more important for the leaching of cadmium than the content of organic matter.

5.1.5.3 Cadmium in soil, ground and surface water

Heavy metal concentrations in headwater lakes and streams are heavily influenced by bedrock lithology, soil granulation and chemistry of the catchment, land-use such as cultivation, fertilization and ditching in the catchment area and the main hydrogeochemical parameters such as pH, alkalinity and total organic carbon (TOC) (Tärväin et al. 1997).

In the aquatic environment Cd is found in various forms: Cd^{2+} is the most important dissolved species in freshwater whereas in seawater the dissolved chloride-complexes are the most important. The pH and redox potential of water have a major effect on the physical and chemical forms of metals and metal compounds in an aquatic environment. Increasing the acidity increases the free metal ion concentration in solution.

Water hardness, contributed in most natural waters by calcium (Ca^{2+}) and magnesium (Mg^{2+}), affects bioavailability of metals by competing with metal cations for binding sites of anions in the water. The ionic competition results in a redistribution in the concentrations of metal salts, sometimes changing the ratio of a dissolved to solid-phase metal by forming insoluble salts (ICME 1995).

Cd may be bound to suspended particles. This depends on the content of the suspended material, the particle size distribution, pH, temperature and on the complexants present. The proportion of the cadmium bound to suspended material is large in fresh inland waters (>50%), small in the coastal waters (10-20%) and minor in the open ocean (1%) (Ros and Slooff 1988).

Also, it has been well established that naturally occurring dissolved organic compounds such as humic acids have a substantial effect on the

bioavailability of metals (ICME 1995). Complexation of metal ions usually reduces their effective concentration in water and, in many cases, also their biological availability and toxicity to animals. On the other hand, there is contradictory information on the interrelationships between the decreased bioaccumulation and toxicity of cadmium to fish and invertebrates in humic waters (Ramamoorthy & Blumhagen 1984, Winner 1984, Oikari et al. 1992).

The interface between the sediment and water column represents an important environment governing the fate of metals in an aquatic environment. As particulate matter falls through the water column, metals are scavenged and incorporated into the bottom sediment (ICME 1995). This phenomenon increases when large quantities of calcium carbonate precipitate. If the sediment gets anaerobic and sulphate reduction takes place, the cadmium will be bound as insoluble Cd sulphide. Remobilisation occurs when the pH decreases; as a result of the microbial process; possibly at very high sulfide concentration (>30 mg/l); by oxidation; and by decomposition of organic material (Ros & Slooff 1988).

In Finland lake water is typically very soft (mean hardness $\leq 10 \text{ mg CaCO}_3$). The median pH in Finnish lakes is 6.6 (Mannio and Vuorenmaa 1996). The proportion of acidic lakes with a pH ≤ 5 was in 1987 about 10% (Forsius et al. 1990). More than half of Finnish lakes can be classified to be brown coloured, humus lakes (colour > 40 mg Pt/l) (Mannio and Vuorenmaa 1996). Concentration of aquatic humic substances in Scandinavian inland waters varies, given as dissolved organic carbon (DOC) generally 5-20 mg C/l (Oikari et al. 1992). The high concentrations of organic matter decrease the pH values of the lakes and the humic lakes are on average more acidic than the clear water lakes (Kortelainen et al. 1989). In humic waters, elevated concentrations of especially land-derived metals are to be expected. Due to their complexing ability and their acidity, humic substances can also transport metals which in other conditions would be retained in the soils of the catchment (Mannio et al. 1993). All these typical characteristics of Finnish waters make Cd more

soluble and more bioavailable to aquatic organisms.

5.1.5.4 Cadmium budget in forest

The atmospheric inputs (bulk deposition from a forest opening and estimated total) and stream runoff (catchment) and soil leaching (plot) outputs for cadmium were studied in two forested headwater catchments in relatively remote background locations in Finland. Both catchments contains areas of forested upland, peatland, seepage lakes and ponds, and a discharge lake. (Ukonmaanaho et al. 2001).

According to the catchment-scale budget most of the atmospheric inputs of cadmium was retained somewhere within the catchment (canopy, humus layer, soil or lake sediments) (80-82 %) (table 11). Runoff outputs of cadmium was less than atmospheric total inputs. Two thirds of the inputs of cadmium to the discharge lakes was from the terrestrial part of the catchment, the remaining being directly from the atmosphere (Ukonmaanaho et al. 2001). Starr et al. (2000) estimated weathering rates of several heavy metals in the Hietajärvi area. The weathering of cadmium was almost negligible, although soil leaching losses were relatively high.

According to plot-scale studies the difference between total deposition (TD) and the soil leaching fluxes from 40 cm depth indicate the amount of retention of atmospheric (external) inputs by the canopy (adsorption), vegetation (uptake and recycling) and soil. However, at the plot-scale, soil leaching fluxes at 40 cm depth of Cd was clearly greater (>100 %) than total atmospheric inputs. Thus the terrestrial retention observed at the catchment –scale must have taken place either deeper in the upland soil or in the lowland peatland areas (Ukonmaanaho et al. 2001).

The humus layer was important in the retention of atmospheric inputs of cadmium, which was subsequently taken up and recycled. The humus layer apparently retained over 50 % of the

Table 11. Mean annual (1994-1996) input-output budgets, retention of atmospheric inputs and transfer of cadmium in Valkea-Kotinen and Hietajärvi catchments (Ukonmaanaho et al. 2001).

	Valkea-Kotinen	Hietajärvi
Bulk deposition (mg m ⁻² year ⁻¹)	0.02	0.02
Total deposition (input; mg m ⁻² year ⁻¹)	0.04	0.04
Runoff water (output; mg m ⁻² year ⁻¹)	0.01	0.01
Output/input (%)	18	20
Retention (input-output) mg m ⁻² year ⁻¹)	0.03	0.03
Relative retention (input-output; %)	83	80
Deposition to terrestrial area (g year ⁻¹)	12	162
Deposition to lake (g year ⁻¹)	1	17
Terrestrial retention (g year ⁻¹)	10	Not available
Lake retention (g year ⁻¹)	1	Not available
Terrestrial transfer to lake (g year ⁻¹)	2	Not available

total inputs of cadmium to the forest floor (Ukonmaanaho et al. 2001). According to Bergkvist et al. (1989) Cd is held less strongly in the soil by cation exchange compared to other metals and therefore it is relatively easily taken up by tree roots. Foliar leaching was important in the recycling of cadmium.

Ukonmaanaho et al. (1998) have studied levels of cadmium in various aqueous and biotic media in four small forested catchments in the southern, middle and northern (two) boreal zones in Finland. Aqueous media included: bulk (open) precipitation, throughfall, stemflow, soil water, groundwater, and lake and stream waters. The biotic media included: moss (*Pleurozium scroberii*), needles (*Pinus sylvestris*), litterfall, humus layer, red wood ants (*Formica aquilonia* and *F. lugubris*), and common shrew (*Sorex araneus*) liver.

The decline in cadmium concentrations as the precipitation passed through the ecosystem indicate that most of the heavy metal load in deposition is retained within the catchments. Lake bottom sediments can also be effective in retaining heavy metals (Ukonmaanaho et al. 1998).

5.1.6 Uptake by plants

It is generally thought that the chemical form of cadmium taken up by plants is the free uncomplexed Cd²⁺ ion present in soil solution. Thus, any treatment or changes in soil conditions which affect the concentration or activity of the Cd²⁺ will

affect the plant accumulation of Cd. Soil factors that increase the uptake of cadmium by plants are low pH, high salinity, high cadmium concentration, low organic matter content, low cation exchange capacity, low clay, Fe and Mn oxides concentration, Zn deficiency and presence of NH_4^+ (Kabata-Pendias and Pendias 1984).

The factors affecting the uptake of cadmium by plants are of various kinds e.g atmospheric factors (dry and wet deposition), plant factors (species, plant part, age of the plant or plant part, root excretes, depth of roots in the soil), soil factors (soil parent material, total amount and solubility of soil Cd, amount of clay and organic matter, soil salinity, soil pH, redox potential, cation exchange capacity, interactions between other elements like Zn, weather and climatological factors, cultivation management practices (e.g. fertilization, liming) (modified from McLaughlin et al. 1996 and Chaney and Hornick 1978).

According to Gerritse et al. (1983) the uptake of cadmium by the plants is highly correlated to cadmium concentration in the soil solution, which is influenced by pH. Besides, the availability of cadmium to plants depends not only on the pH of the soil, but also on the pH of the rhizosphere. The plant roots have ability to acidify their surroundings i.e. rhizosphere in order to solubilize elements for enhancing uptake. Plant species differ in their ability to acidify the rhizosphere (Youssef and Chino 1991). Dicotyledonous plants generally take up metals much more than monocotyledonous plants do (Sauerbeck 1991).

Cadmium contents of the crops mainly depend on the purity of the soils, because the greatest part of Cd in the plants is mostly absorbed through the roots from the soil and only a smaller part of Cd is of air born origin. According to some estimates, 20 to 60%, with an average of about one third, of plant Cd may be airborne falling down as either wet or dry depositions (e.g. Hovmand et al. 1983; Christensen 1983), but of course, its proportion varies greatly from one location to another. Thus, about two thirds of plant Cd is normally taken up through the roots from the soil.

5.1.7 Bioaccumulation

Elemental metals and solid phase inorganic metal compounds are generally not bioavailable as such and therefore, the bioaccumulation of inorganic metal compounds is not a useful parameter for their hazard identification. However, it is their constituent soluble metal cations that undergo a biological uptake (Technical workshop 1996).

Bioaccumulation of cadmium is exceptionally intensive by some plants from the soil as compared to many other trace elements. Plant species and plant parts differ in their Cd contents (e.g. see table 2). Older plants or plant parts contain more Cd than younger ones (Kabata-Pendias & Pendias 1984).

Cadmium is generally considered a non-essential element for both plants and animals. Its importance lies in its toxicity. Many plants can accumulate relatively large concentrations of Cd without adverse effect on their growth. Thus, concern is not only for the effect of Cd on plant health, but particularly plant Cd as a source of Cd for herbivores and humans. Consequently, differences in the adsorption rate of cadmium between the plant species are important from both an environmental and health standpoint.

Accumulation of cadmium in plants varies significantly depending on e.g. species, part of species and sites where plants are growing. E.g. blueberries have been noticed to accumulate heavy metals in the following order: berries<leaves<stems<roots (studies refered in Nilsson & Eriksson 1998).

Although metals do bioaccumulate in terrestrial food-chains, their BAFs are generally low. Field-based BAF for cadmium in plant and plant-frugivore food-chains was less than one (Hunter & Johnson 1982, ref. in ICME 1995). In another field study, the BAF was 0.06 for the cadmium in kidneys of a herbivore (Pascoe et al. 1994, ref. in ICME 1995). However, in another study, insect herbivores, detritivores and predators bioaccumulated cadmium at factors 1.1 to 5.4 times higher than their food items (Hunter & Johnson 1982, ref. in ICME 1995). According to the draft EU risk assessment report of cad-

mium oxide (2001) the minimum, maximum and median BAF values of earthworms (dry weight basis) were 1.6, 151.4 and 15.5, respectively. Most important factors affecting the bioaccumulation of cadmium by earthworms are the cadmium concentration of the soil, soil type, pH, soil organic matter and CEC.

5.1.9 PEC in mineral and peat soils

PEC (predicted environmental concentration) should preferably be derived from extractable concentrations of cadmium, because the easily mobilizable cadmium fraction has been considered to represent better the bioavailable cadmium fraction than total cadmium. However, the problems in deriving bioavailable PEC are obvious, and consequently it has not been done. There is not enough information available about the bioavailable concentrations of cadmium in forest soil. In addition, the results of the few studies on extractable cadmium concentrations are contradictory. Due to the great heterogeneity of the forest soils, difficulties in sampling and ash spreading, the results of the studies have to be considered carefully and no definite conclusions can be drawn.

5.2 Effect assessment

5.2.1 Toxicity studies

5.2.1.1 Toxicity to microorganisms

According to Vanhala et al. (1998) EC_{20} value (20 % inhibition of soil respiration) of soil respiration for cadmium was 100-1070 mg/kg in the four weeks laboratory incubation experiment. Samples collected from four coniferous forest plots located in the Finnish Integrated Monitoring programme area were treated with $CdCl_2$ to achieve final Cd concentration of 200, 400, 1000, 2000, 4000, 8000 and 16 000 mg/kg dw of humus layer. The EC_{20} value was lower in the spruce-dominated area than in the pine-dominated area. In four study sites cadmium content, pH, cation exchange capacity (CEC) and base saturation (BS) varies <0.5-0.9, 3.6-3.9, 258-258 and 74-80, respec-

tively. Organic matter content of the samples was high, varying from 63 to 96 %.

In CEPA (1994) eight studies were identified on the effects of cadmium on soil metabolic processes. A level of 2.9 mg Cd/l (cadmium compound not specified) caused a 60% reduction in nitrification (soil pH = 6.4, clay content = 7.7 %) over 60 days (Kobus and Kurek 1990, ref. in CEPA 1994).

According to Bååth (1989) the lowest cadmium concentration yielding an effect on microbial processes in forest humus varied 1.5 to 20 000 mg/kg dw. The most sensitive microbiological processes seemed to be N-transformations. The great variation of the toxicity of cadmium was partly due to the fact that the soils used in studies reviewed have different properties, which affect active metal concentration. Besides, there were methodological differences between different studies in sampling strategy, and intensity, measurement standardisation etc.

According to Bååth (1989) the most important factors affecting metal toxicity to microorganisms are the cation exchange capacity (CEC) and soil pH. Soils with high CEC (organic and clay soils) are usually less sensitive to heavy metals than sandy soils low in organic matter content. Besides, the effects of pH are various: the extent of complexation of metal with organic and inorganic constituents of the environment is affected by pH. Such complexes are generally less toxic than the free metal ions; pH affects the chemical speciation of metal ions and different form may have different toxicity; the metabolic state of microorganisms is affected by changes in pH and the rate of different soil processes is affected by pH *per se*.

Data reviewed by Ros & Slooff (1988) show that soil microbial process may be inhibited: carbon transformation at ≥ 7 mg Cd/kg of soil, nitrogen transformation at ≥ 50 mg Cd/kg of soil, and the activity of sensitive enzymes at ≥ 4 mg/kg of soil. Bewley & Stotzky (1983, ref. in WHO 1992) investigated the effect of cadmium (100 and 1000 mg/kg soil) on carbon mineralization and

on the mycoflora in glucose-supplemented soils amended with clays (kaolinite or montmorillonite) at 9%. Cadmium had no significant effect on the length of the lag period, carbon dioxide evolution or on the amount of carbon mineralized.

Naidu & Reddy (1988, ref. in WHO 1992) incubated cotton soil (0.8% organic carbon, 55% clay) for up to 8 weeks in the presence of CdCl₂ at concentrations of between 10 and 500 mg Cd/kg. The ammonium nitrogen (NH₄-N) concentration increased for the first week at all treatment levels and then decreased at the concentrations of 50 mg/kg or less. The rise in NH₄-N levels led to an increase in nitrate nitrogen (NO₃-N) levels. At all cadmium concentrations there was a significant accumulation of nitrite nitrogen (NO₂-N) in every sample time, suggesting, according to the writers, that cadmium might be toxic to soil nitrification. At all exposure levels cadmium significantly depressed both bacterial and fungal populations. Concentrations of 10 or 50 mg Cd/kg had no effect on soil actinomycetes, but both 100 and 500 mg/kg significantly reduced the population.

Levels of cadmium in soil (CdCl₂) of 2.0 mg Cd/kg dw and 5.0 mg/kg dw inhibited colonization of ectomycorrhizae on white pine (*Picea*

glauca) roots by 62% and 87%, respectively (Dixon & Buschena 1988, ref. in CEPA 1994).

According to the draft EU risk assessment of cadmium oxide (2001) the lowest NOECs found in microbes were at the level of 3 mg/kg. N₂-fixation seemed to be the most sensitive soil microbial process.

5.2.1.2 Toxicity to invertebrates

The toxicity of cadmium to invertebrates is summarized in Table 12.

The lowest NOECs for earthworms have varied from 5 mg/kg dw (*Eisenia fetida*) in the study of Spurgeon et al. (1994, ref. in EU Risk Assessment of cadmium oxide) to 10 mg/kg (*Dendrobaena rubida*) in the study of Begtsson et al. (1986 ref. in EU Risk Assessment of cadmium oxide).

5.2.1.3 Toxicity to plants

Cadmium has been shown to have adverse effects on plant growth and yield in laboratory experiments. However, plants grown in soil are generally insensitive to the effects of cadmium except at high doses. Effects are only seen when cadmium is given nutrient solutions rather than in soil, where

Table 12. Toxicity of cadmium to terrestrial invertebrates.

Organism	Toxic effect	Reference
Grasshopper (<i>Aiolopus thalassinus</i>)	LOEL 1.23 mg/kg (15 % reduction in egg hatching)	Schmidt et al. 1991
Nematode (<i>Aphelenchus avenae</i>)	22-d NOEC 1 mg/kg feed (exposed via fungi)	Doelman et al. 1984 (ref. in WHO 1992)
Collembola (<i>Orchesella cincta</i>)	9-week LC ₅₀ 179.8 mg/kg NOEC 4.7 mg/kg	Van Straalen et al. 1989 (ref. in WHO 1992)
Collembola (<i>Platynothrus peltifer</i>)	9-week LC ₅₀ 817.2 mg/kg NOEC 2.9 mg/kg	Van Straalen et al. 1989 (ref. in WHO 1992)
Snail (subadult) (<i>Helix aspersa</i>)	30-d NOEC 10 mg/kg diet	Russell et al. 1981
Earthworm	NOEC 10 mg/kg dw soil	Ros & Slooff 1988
Springtail	NOEC 4.5 mg/kg feed*	Ros & Slooff 1988
Woodlice	NOEC 2.0 mg/kg feed*	Ros & Slooff 1988

* According to the writers, this Cd level in leafy materials may be reached at ≥ 0.5 mg Cd/kg dw soil.

the cadmium is bound and is therefore less available to the plants (WHO 1992).

Toxicity studies on plants are related mainly to effects on growth and yield and on some physiological parameters. Most of the studies are carried out on agricultural crops.

According to Burton et al. (1984, ref. in EU risk assessment of cadmium oxide 2001) the NOEC for spruce (*Picea sitchensis*) was as low as 1.8 mg/kg.

5.2.1.4 Toxicity to birds

In WHO (1992) data were reviewed on the subacute toxicity of cadmium salts to four species on birds (summarized in table 13). Dosing for 5 days, followed by 3 days of clean diet, resulted in LC₅₀ values ranging from 767 to > 5000 mg/kg diet.

Altered kidney morphology or function are considered to be the most widely accepted endpoints of toxicity in both wild birds and mammals. According to CEPA (1994) a renal concentration of 100 mg of Cd/kg (fw) is the best estimate of threshold toxicity in wild birds. Wood ducks (*Aix sponsa*) fed cadmium in their diet for 3 months showed widespread renal pathological changes at an average renal concentration of 132

mg of Cd/kg, but not at 62 mg/kg (Mayack et al. 1981, ref. in CEPA 1994).

Captive mallard ducks exposed to cadmium in their diet exhibited moderate to severe tubular degeneration over a renal cadmium concentration range of 88 to 134 mg of Cd/kg (White et al. 1978, ref. in CEPA 1994).

Nicholson and Osborn (1983, ref. in CEPA 1994) detected necrosis of renal proximal tubule cells in free-living seabirds from Britain and experimentally in starlings (*Sturnus vulgaris*) at kidney concentrations of 10 to 70 mg Cd/kg (fw). However, Elliott et al. (1992, ref. in CEPA 1994) examined several species of seabirds collected on the Atlantic Coast of Canada and found no renal lesions in birds up to 83 mg Cd/kg (fw) in the kidney.

5.2.1.5 Conclusions of the effect assessment

The toxicity of cadmium to terrestrial organism shows a variable pattern. Plants grown in soil are generally considered insensitive to the effects of cadmium, although some exceptions do exist. Cadmium exhibits moderate and low toxicity to avian species in subacute exposure. Microorganisms and terrestrial invertebrates show moderate or high sensitivity to cadmium.

Table 13. The toxicity of cadmium salts to birds (WHO 1992).

Species	Age (days)	Salt	Duration	LC ₅₀ (mg Cd/kg diet)	Reference
Japanese quail (<i>Coturnix coturnix japonica</i>)	14	Cadmium chloride	5 + 3 days	2440	Hill & Camardese 1986
	14	Cadmium succinate	5 + 3 days	2052	
Pheasant (<i>Phasianus colchicus</i>)	10	Cadmium chloride	5 + 3 days	767	Hill et al. 1975
	14	Cadmium succinate	5 + 3 days	1411	
Bobwhite quail (<i>Colinus virginianus</i>)	14	Cadmium succinate	5 + 3 days	1728	Hill et al. 1975
Mallard duck (<i>Anas platyrhynchos</i>)	10	Cadmium chloride	5 + 3 days	> 5000	Hill et al. 1975
	10	Cadmium succinate	5 + 3 days	> 5000	
Leghorn chicken	2 week	Cadmium chloride	20 days	565	Pritzl et al. 1974
Mallard duck (<i>Anas platyrhynchos</i>)	1 adult	Cadmium chloride	12 weeks	NOEC 10	Cain et al. 1983 White et al. 1978
		Cadmium chloride	?	NOEC 20	

Toxicity of cadmium to aquatic organisms has not considered in this report.

5.2.2 Ash fertilization studies

5.2.2.1 Effects on soil microbes

According to the two months laboratory incubation study by Fritze et al. (2000) wood ash spiked with cadmium at levels that exceed the natural concentrations by 100-fold, did not result in a change in the biological variables, e.g. microbial activity, colony forming units, microbial community structure, appearance of cadmium resistance. However, the same amount of cadmium in pumice without ash decreased soil respiration and changed microbial community structure (the phospholipid fatty acid, PLFA, pattern). The ash thus counteracted the toxic effect of cadmium. In samples treated with pumice, soil respiration rate was reduced by 20 % when humus contained cadmium 196 mg/kg dw.

In a laboratory microcosm study wood ash and pumice were spiked with CdO or CdCl₂ in order to give final cadmium concentrations of 400 and 1000 mg/kg. 60 microcosms (12 cm diameter pots) filled with forest humus were fertilized by spiked ash and pumice at the level of 5000 kg/ha. As the pH of pumice is close to that of humus, pumice eliminates the ash-induced increase in soil pH but at the same time ensures the even dispersion of cadmium over the surface of the humus. In pumice samples pH of humus remained 4.0 compared to pH of 7.0 and 3.0 in ash and untreated samples, respectively. The different form of cadmium had no effect on the soil respiration rate (Fritze et al. 2000).

In the same laboratory microcosmos study as described above Fritze et al. (2001) studied effects of cadmium and ash on fungal community composition and cadmium bioavailability of the humus layer of boreal coniferous forests. Ash fertilization altered the humus layer fungal community, which was analysed from extracted total DNA by using polymerase chain reaction (PCR) and denaturing gradient gel electrophoreses (DGGE). However, the level and form of additional cadmium in the ash had no influence

because it was not bioavailable. The bioavailability of cadmium was measured with bacterial biosensor (*Bacillus subtilis* BR 151/pT0024) emitting light in the presence of cadmium. Humus layer water extracts showed that the cadmium added with the pumice was in a bioavailable form. No luminescence was detected when the cadmium was added with the ash.

According to Fritze et al. (2001) when combining the results from the two studies described above, microcosmos approach could show that only 4.7 to 11 % of the cadmium added without ash was bioavailable. The amount of bioavailable cadmium kg⁻¹ humus has to be over 20 mg before reducing the microbial activity (soil respiration) and changing the bacterial community structure (PLFA pattern) whilst still having no effect on the structure of the fungal community (PCR-DGGE).

According to Fritze & Perkiömäki (1999) the microbial activity (CO₂ production of bacteria and fungus) increased and microbial community changed 1-1.5 years after ash fertilization. The reason for the increased activity of bacterial community has considered to be caused by larger amounts of easily mineralized carbon compounds dissolved in the soil water in increased pH-value. The pH of humus increased in all study areas; dust ash increased pH 1.5 units and hardened ash 0.5 unit.

Dust and hardened wood ash was spread at the levels of 3000 and 9000 kg/ha on dry mineral (ECT, *Empetrum-Calluna* -type) and fresh mineral soil types(VMT, *Vaccinium-Myrtillus* -type). The average cadmium content of ash was 15 mg/kg dw and consequently the load of cadmium on forest soil was 45 and 135 g/ha, respectively depending on fertilization level. With the highest fertilization level (135g/ha) the cadmium content in humus is 9 mg/kg dw (when assuming that the thickness of humus layer is 1.5 cm, the density of humus 0.1 g/cm³dw and consequently the amount of humus 15 000 kg/ha). In addition tolerance of bacterial community to cadmium was tested by adding cadmium (CdO) to one ash sample (3000 kg/ha) to achieve cadmium content of ash 400 mg/kg. Consequently cadmium load on forest

was 1200 g/ha and calculated cadmium content in humus approximately 80 mg/kg. Cadmium resistance of bacterial community was not noticed to develop during one year study period (Fritze & Perkiömäki 1999). According to Pennanen et al. (1996) bacterial community of forest soil develops resistance to heavy metals in high heavy metal concentrations.

In two years experiment by Fritze et al. (1995) the effect of cadmium addition on the respiration rate of forest humus having received wood ash was studied in Central Finland. Wood ash containing cadmium on average of 3.67 mg/kg dw was spread on dry *Vaccinium*-site type forest humus with levels of 1000, 2500 and 5000 kg/ha. In the laboratory cadmium was added to the samples as CdCl₂ to give final cadmium levels of 200, 400, 1000, 2000 and 4000 mg/kg dw of soil.

Wood ash fertilization increased the soil respiration rate at all three fertilization levels. However, addition of cadmium to soil samples decreased the soil respiration rate. The control and first level wood ash fertilized humus (1000 mg kg/ha) had practically the same EC₅₀ value, whereas the higher level wood ash fertilized humus samples reached their EC₅₀ at much higher cadmium concentrations than did the untreated control samples. It has judged that coniferous forest soils treated with a single dose of wood ash withstand cadmium additions to the soil ecosystem, when interpreted on a soil respiration basis, as good or better than control soils. With the higher level wood ash treated soils, the decrease toxicity of cadmium correlates with the treatment dose-dependent rise of pH of these soils. Wood ash with cadmium content of 3.67 mg/kg used 1000-5000 kg/ha on coniferous forest humus did not negatively influence the mineralization rate of the soil nutrients. This was seen from the EC₅₀ values and that the cadmium concentrations of 400 mg/kg soil dw were needed to decrease the soil respiration rate of wood ash treated plots to uncontaminated control treatment levels (Fritze et al 1995).

According to Fritze et al. (1994) ash fertilization did not alter the soil microbial biomass (soil microbial biomass C determined by the fumi-

gation-extraction method and fungal ergosterol, which is an indicator of fungal biomass) when wood ash of 1000, 2500 and 5000 kg/ha was applied in a Scots pine (*Pinus sylvestris* L.) stand. However, the ash application increased the soil respiration rate. Thus wood ash fertilization in a dry *Vaccinium* sp. type site in a pine stand seems to increase the turnover of nutrients without immobilization into the microbial biomass.

The decomposition rate of needle litter was increased and the cycle rate of nutrients fastened in the surface peat (0-20 cm) four months after wood ash fertilization of 16000 kg/ha (Silfverberg and Huikari 1985). According to Silfverberg and Hotanen (1989) the nutrient cycling was improved both quantitatively and qualitatively after ash fertilization. Ash fertilization raised the nutrient content of the needle litter and made the conditions in the soil more favourable for litter decomposition. The decomposition of needle litter was faster in areas fertilized with birch wood ash of 8000 and 16000 kg/ha 38 years ago than in untreated areas. Besides, needles collected from former ash fertilized area decomposed faster in untreated area than needles collected from untreated areas. Also according to Ohtonen and Tuohimäki (1999) the pH-value of the soil was increased and the mineralization of nitrogen fastened a year after ash fertilization.

Bååth (1989) has reported decreasing toxicity of heavy metals in soils with high organic matter contents. Humus can serve as a buffer against heavy metals in soils with a high organic matter content, and is even more efficient than the clay in mineral soils.

5.2.2.2 Effects on mushrooms

According to Lodenius et al. (2001) cadmium concentrations were significantly higher in one species, *Russula emetica*, at ash treated sites compared to untreated control sites. Also for the other species studied the concentrations were in most cases higher in treated areas although the differences were not statistically significant. In study sites approximately 4800 kg (dw)/ha of wood ash was applied. Ash contained 9.2 mg of cadmium

per kg (dw) giving an average load of 44 g/ha. Fruiting bodies were collected 1.5 –2.5 years after ash treatment.

According to the short term experiments of Moilanen and Issakainen (2000) no clear effect of ash fertilization on mushrooms was noticed. It seemed that the cadmium contents of mushrooms in fertilized areas were a little lower than in control areas. The cadmium content in controls was on average 0.7 mg/kg and in fertilized plots 0.4-0.6 mg/kg. In long term experiments (13-52 years after fertilization) the cadmium content of mushrooms was increase in some study plots and decreased in others (see table 14).

In Swedish ash fertilization study there was only one species, *Cortinarius palaeceus*, where cadmium content was significantly higher in ash treated area than in control area. Variation of cadmium content between different species within the same plot were often larger than between fertilized and control areas. In general, litter-decomposing species have higher contents of heavy metals than mycorrhizal species. A reasonable explanation is that the mycelia of the former grows in the surface layer of the soil where the concentrations of these elements are highest. Ash fertilization altered species composition; the amount of mycorrhizal mushrooms decreased while litter-decomposing mushrooms increased (Rühling 1996).

Table 14. Cadmium content (mg/kg) in different species of mushrooms 13-52 years after ash fertilization (Moilanen & Issakainen 2000).

Species	Years after Fertilization	Cd (mg/kg) Control	Cd (mg/kg) Fertilized area
<i>Lactarius rufus</i>	19	0.8	1.9*
<i>Suillus variegatus</i>	9	1.3	1.5
<i>Suillus variegatus</i>	11	0.7	0.4
<i>Lactarius rufus</i>	12	3.8	2.7
<i>Russula paludosa</i>	18	1.0	1.4
<i>Lactarius trivialis</i>	14	0.2	0.2
"	51	0.7	0.5
"	52	0.3	0.2
<i>Russula paludosa</i>	14	1.2	1.7
<i>Lactarius rufus</i>	19	1.4	0.8*
"	26	2.0	1.4

*=difference between control significant

5.2.2.3 Effects on soil invertebrates

Ash has a gradual and long-lasting negative effects on the soil fauna, probably through the increase of soil pH. Enchytraeid worms did not show any signs of recovery even four years after ash application. The first significant changes in macroarthropods were not recorded until 1.5 years after ash treatment. Nematodes did not react significantly before the second summer. However, earthworms seemed to benefit from the ash treatment. The study was carried out during the years 1979-83 both in field and laboratory experiments. No information was available about the quantity of ash used and the content of cadmium in ash (Huhta 1994).

According to Huhta (1984) bark loose ash of 7000 kg/ha (dw) was shown to give a larger decrease in abundance of *C. Sphagnetorum* four years rather than two years after treatment. According to Hotanen (1986) bark wood ash of 3000 kg/ha reduced enchytraeid numbers in a drained spruce swamp and pine bogwood, but the effects were slight compared to seasonal fluctuations. In addition, short term effects of ash upon worm biomass and respiration rate were similar as those for worm numbers. There were no information about the cadmium content of ash.

According to Haimi et al. (2000) ash fertilization, in general, did not cause any dramatic negative impacts on soil fauna and soil fauna seemed to be quite a resistant to the ash application.

However, enchytraeid worms *Cognettia sphagnetorum* responded negatively to the ash treatment of 5000 kg /ha and its numbers dropped first but increased then later. *Cognettia sphagnetorum* which is known to be sensitive, but important species in soil processes of coniferous forest can be regarded as a keystone species, removal (or extinction) of which may lead to changes in the functioning of the whole forest ecosystem. Enchytraeids by biomass dominate the soil fauna in many boreal coniferous forests (Lundkvist 1998). Ash treatment affected moderately soil microarthropoids. In the study 1000 and 5000 kg of ash was

spread on podzolized sandy soil hectare. The cadmium content of the ash was only 1.4 mg/kg (Haimi et al. 2000).

Evidently, a quite thick humus layer buffers the effects of both physical and chemical changes to take place in the soil. That is, soil fauna may find refuge – food resources and shelter for hostile conditions- in the remaining organic soil layer (Haimi et al. 2000, Setälä et al. 2000).

According to Lundkvist (1998) treatment with 8000 kg/ha of a hardened and crushed ash with high content of readily soluble salts caused a downward movement of the enchytraeids (potworms), from the upper 0-1 cm of the soil profile. In addition, at one site the cadmium content increased transitionally in dominating enchytraeids species *C. Sphagnetorum*, which might indicate that it is caused by increased mobility of humus cadmium rather than by an actual release of cadmium from the ash. Such an increased mobility could be explained by short-term acidification following upon the application of wood ash. Although the abundance of enchytraeids after 2.5 months of wood ash treatments was not significantly different from that in untreated controls it cannot be ruled out that ash at a later stage will have more pronounced effects on the enchytraeids. The abundance of earthworms increased after ash treatment due to the increase of soil pH and Ca content. In the study the effects of eight types of wood ash and wood ash + lime at different application rates (2000, 4000, 8000 kg/ha) were studied. The cadmium content of ash varied from 0.1 to 12 mg/kg.

5.2.2.4. Effects on mammals

According to Lodenius et al. (2002) ash fertilization had limited effects on the uptake of cadmium in voles and shrews within a short period of time, even though cadmium concentrations in tissues of common shrews (*Sorex araneus*) were greater 1.5 years after ash treatment in ash treated areas than control areas. Cadmium concentrations in muscle, liver and kidney of bank vole (*Clethrionomys glareolus*) 1.5 years after ash fertilization were slightly but significantly lower in treated areas than untreated areas. The difference in cad-

mium concentrations between herbivorous bank voles and insectivorous shrews has been explained to be caused by different food habits. In addition, the slight increase of cadmium concentrations of bank voles in autumn was assumed to be related to the increasing consumption of fungi by voles in the autumn, because many mushrooms accumulate cadmium.

Approximately 4800 kg/ha of wood ash (dw) was spread on the forest. The cadmium content of the wood ash was 9.2 mg/kg (dw) and consequently cadmium load on forest soil was 44g/ha (Lodenius et al. 2002).

5.2.2.5 Effects on plants

Ash fertilization has not clearly increased the cadmium content of forest berries, but decreased the yields of the forest berries. In peat soils the cadmium content of cloudberries (*Rubus chamaemorus*) and *Vaccinium uliginosum* seemed to decrease 13-14 months after fertilization. Also after 10-20 years of fertilization the cadmium content in cloudberries was generally lower in fertilized areas than in untreated areas: the cadmium content of cloudberries was an average of 0.55 mg/kg dw in control areas compared to 0.35 mg/kg dw in fertilized areas. It is generally assumed that liming decrease the solubility of cadmium in soil and therefore also slower cadmium uptake by plants (Moilanen and Issakainen 2000, description of the study in the chapter 5.1.3).

According to Levula et al. (2000) ash fertilization of 2000-7000 kg/ha had no effect on cadmium concentrations in the lingonberries (*Vaccinium vitis-idaea*) even seven growing seasons after application. However, the dwarf shrub stand was slightly reduced by the application of 5000 kg ash/ha. The cadmium concentration of the wood ash used in the study was only 1.4 mg/kg dw compared to other studies with higher cadmium content in ash.

Silfverberg and Issakainen (1991, description of the study in the chapter 5.1.3) studied effects of ash fertilization on lingonberries, blueberries (*Vaccinium myrtillus*), cloudberries and *Vaccinium uliginosum* in the North of Finland. Cadmium content was relatively high in cloudberries,

where it was 0.69 mg/kg dw in untreated areas compared to concentration of 0.50 mg/kg dw in areas treated with wood ash and 0.44 mg/kg dw in areas treated with peat ash. However, a slight increase of cadmium content was seen in cloudberries 3-8 years after fertilization; the cadmium content of cloudberries in fertilized areas was 0.45-0.46 mg/kg dw compared to the concentration of 0.36 mg/kg dw in untreated areas. The cadmium concentration in lingon- and blueberries was mostly under the detection limit (250 µg/kg dw). No effects on cadmium content of blueberries was noticed 2-3 months and 2-8 years after ash fertilization. However, ash fertilization seemed to have effects on cadmium content of lingonberries. The detection limit of cadmium was exceeded in lingonberries more in ash fertilized areas than in control areas.

According to Swedish ash fertilization study by Rühling (1996) spreading of ash did not lead to a general increase in the uptake of heavy metals in berries. The risk that berries will contain increased contents of heavy metals during the first season after spreading is small. Cadmium content in the blue- and lingonberries varied between <0.01-0.48 mg/kg dw in controls and 0.01-0.16 mg/kg dw in area treated with ash. The cadmium content of berries were analysed a one year after fertilization of 2000-3000 kg/ha (ash content 5.4-9.7 mg/kg dw) in a short term study and 2-9 years after fertilization of 1500-10 000 kg/ha (dust and granulated ash) in a long-term study.

According to Nilsson & Eriksson (1998) ash fertilization had negligible effects on cadmium contents in blueberries. Cadmium content of blueberries were analysed two months and 13 months after treatment of loose and well-hardened granulated ash of 2000, 4000 and 8000 kg/ha. Cadmium content of ash varied from 0.1 to 12 mg/kg dw.

According to Pihlström et al. (2001; description of the study in the chapter 5.1.3) the natural background concentrations of cadmium differ between different species e.g. aspen (*Populus tremula*) accumulates much cadmium. Cadmium concentrations in leaves and branches of aspen were higher in fertilized area than in controls

about two years after ash fertilization. However, the interpretation of the results is difficult, because concentrations of cadmium in aspen were already lower in the control area before ash treatment. Based on a great natural variation of cadmium in aspen and a small number of samples taken in the experiment, no direct definite conclusion can be drawn about the impacts of ash fertilization on concentrations of cadmium in aspen. Also a slight increase of cadmium concentrations in stems of blueberries was noticed about two years after ash fertilization. In addition, the concentrations of cadmium in rosebay willowherbs (*Epilobium angustifolium*) were increased in one sample area after ash fertilization. According to Bramryd (1985, ref. Moilanen and Issakainen 2000) high doses of ash have been noticed to increase the cadmium content of willows.

Ash fertilization alter the ground vegetation of the forest e.g. *Sphagnum*-species vanish (Silfverberg 1996, Silfverberg and Huikari 1985). According to Silfverberg & Huikari (1985) the increase of pH of the surface peat caused by ash fertilization has converted the forest ground vegetation into a more easily decomposing herb- and grass-rich type (dominating species were *Lycopodium*, *Dryopteris*, *Pyrola*, *Vaccinium vitis-idaea*). Wood ash slightly increases the number of species, but on the other hand it favours some competitively strong and dominant species (*Eriophorum vaginatum*, *Rubus chamaemorus*) (Silfverberg 1996). According to Silfverberg and Issakainen (1991) yield of forest berries can be reduced after ash fertilization when *Deschampsia flexuosa* occupies the growing space at the expense of berry species (indirect damage). Besides, the heavy metals, especially cadmium may hamper the metabolism of mosses, and therefore the growth of mosses decreases and they may die (Foy et al 1978, ref. in Silfverberg & Hotanen 1989).

In the greenhouse experiment the germination percentage of Scots pine seeds was strongly decreased by soaking in wood ash solutions (Silfverberg 1995). This negative effect of ash solution on germination was possibly due to the high concentration of hydroxyl ions (Thomas and Wein 1990, ref. in Silfverberg 1996).

5.2.2.6 Effects on aquatic organisms

Cadmium was not leached or accumulated in aquatic organisms (zooplankton, benthic organisms, fish) about 1 year after ash fertilization. The mean cadmium content of zooplankton was 0.54 µg/g dw. In benthic organisms, the cadmium content was less than 1.0 µg/kg dw in all groups of organisms studied, except oligochaetes, where it was more. Cadmium content in muscles and livers of fish was 0.02-0.03 mg/kg dw and 0.3-0.75 mg/kg dw, respectively. In catchment area of two small humic lakes ash was spread at the level of 6400 kg/ha. The mean content of cadmium in ash was 6.9 mg/kg dw (HNO₃). The load of cadmium on the catchment areas was 42-46 g/ha (Tulonen et al. 2000).

5.2.2.7 Conclusions of the ash fertilization studies

The effects of cadmium in ash on invertebrates and microorganisms are hard to prove and distinguish from the effects of the increased pH in soil. The increase of pH after ash treatment seemed to cause the most prominent effects on biota. Many forest species and microbes in general are very sensitive to the increase of pH due to the hundreds of years of adaptation to acid forest soil.

Ash fertilization seems not to hamper the soil microbial activity. On the contrary, it has increased soil respiration and microbial activity. The microbial community was however changed after ash fertilization. Ash fertilization seems to have adverse effects on soil fauna e.g. to the abundance of enchytraeid worms, although soil fauna has generally been considered to be quite resistant to ash treatment. The temporary increase of cadmium in enchytraeid worms was noticed after ash fertilization.

Based on the studies available no clear trend of increased cadmium content in mushrooms was noticed after ash fertilization. However, the latest study by Lodenius et al. (2000) showed a slight trend of increased concentrations of cadmium after ash fertilization although it was not statistically significant. Very often variation of cadmium content between different species of mushrooms in the same area is larger than between fertilized and untreated areas. The situation is more or less the same with berries. No clear trend of increased con-

centrations of cadmium was seen after ash treatment, but a slight increase of cadmium in lingon- and cloudberry stems of blueberries could be noticed. Yields of berries have decreased due to the changes in vegetation after ash fertilization.

Ash fertilization has clear impacts on vegetation. Some species (e.g. sphagnum) suffer and disappear, while others benefit greatly from the fertilizing effect of ash. The effects of cadmium in ash on plants has mainly been seen as elevated cadmium concentrations of certain plants. In general, the natural variation of accumulation of cadmium between different species is great.

Due to the shortage of comparable and comprehensive long-term ash fertilization studies on berries and mushrooms, no definite conclusions can be drawn about the effects of cadmium in ash on cadmium content of berries and mushrooms. The long-term effects of ash fertilization on soil microbes are not known, although the short-term effects seem to be beneficial.

Impacts of ash fertilization on aquatic ecosystem have not been considered in this report. Some short leaching studies of ash fertilization did not show effects on aquatic organisms. No information was however available about long term impacts of ash fertilization on aquatic organisms and ecosystem.

5.2.3 PNEC for terrestrial species

According to the EU Technical Guidance Document (1996) the PNEC (predicted no-effect concentration) should be calculated on the basis of the lowest effect value measured. A PNEC is regarded as a concentration below which adverse effects will most likely not occur. In practise, the PNEC is calculated by dividing the lowest short-term L(E)C₅₀ or long-term NOEC value by an assessment factor (AF). The assessment factors (10, 50 100, 1000) reflect the degree of uncertainty in extrapolation from laboratory toxicity test data for a limited number of species to the “real” environment. Assessment factors applied for long-term tests are smaller while the uncertainty of extrapolation from laboratory data to the natural environment is reduced. Thus, the idea of choosing certain PNEC derived from toxicity studies of single species is to ensure a certain protection level of the

whole taxon (a taxon can be any group of organisms having natural relations, whatever its rank e.g. phylum, genus, species) and further the whole terrestrial ecosystem. Consequently, it is more a question of protection of the whole ecosystem than of certain species or individuals.

Because no quantitative risk assessment was carried out and uncertainties involved in calculation of PNEC, several PNECs were derived from different species in order to get some general idea about the level of ineffective concentration of cadmium to terrestrial organisms. The most lowest PNEC was derived from a study on grasshoppers (Schmidt et al. 1991), which gave the lowest NOEC -value in terrestrial compartment. According to the Technical Guidance Document a LOEC can be used to derive a NOEC with the following procedure: if the effect percentage of the LOEC is >10 and <20%, NOEC can be calculated as $LOEC/2$. Therefore, NOEC for *Aiolopus thalassinus* would be $1.2/2 \text{ mg/kg} = 0.6 \text{ mg/kg}$. Applying an assessment factor of 10, which can be used when long-term data are available for more than three trophic levels, gives a PNEC of 0.06 mg/kg .

The lowest NOECs for earth worms has varied from 5 mg/kg dw (*Eisenia fetida*) in the study of Spurgeon et al. (1994, ref. in EU Risk Assessment of cadmium oxide) to 10 mg/kg (*Dendrobaena rubida*) in the study of Begtsson et al. (1986 ref. in EU Risk Assessment of cadmium oxide). When the assessment factor of 10 was used as above, the PNECs of 0.5 and 1 mg/kg have been received.

PNEC of 0.18 mg/kg was derived from the lowest NOEC of plants (1.8 mg/kg , spruce, Burton et al. 1984, ref. in EU Risk Assessment of cadmium oxide 2001) with assessment factor 10.

PNEC of 0.3 mg/kg was derived from the lowest NOECs of microbes (EU Risk Assessment of cadmium oxide 2001) with assessment factor 10.

5.3 Risk characterisation

According to the EU Technical Guidance Document (1996) the risk for the environment caused by the chemical should be assessed by comparing

the environmental exposure (expressed as PEC) with the threshold concentration for harmful effect in the environment (expressed as predicted no-effect concentration, PNEC). Thus, an estimate of the environmental risk is the ratio $PEC/PNEC$. If the $PEC/PNEC$ of a chemical is greater than 1, there is a risk for adverse effects in the environmental compartment concerned.

Due to the difficulties in deriving bioavailable PEC (see chapter 5.1.9) no quantitative risk characterisation was carried out. However, some preliminary consideration and comparison of PECs and PNECs were made in order to evaluate the likelihood and possibility that cadmium poses a risk to the terrestrial ecosystem.

Only extractable cadmium concentrations were used despite the uncertainties involved in these concentrations, because bioavailable concentrations are the most important ones when considering toxicity of cadmium to organisms.

Looking at the extractable background concentrations of cadmium in mineral and peat soils and different PNEC-values derived, it can be noticed that the concentrations are very close to each other. The mean background concentrations of cadmium (0.22 mg/kg in mineral soil and 0.57 mg/kg in peat soil) as well as the increased concentrations of cadmium after ash treatment (0.65 mg/kg in mineral soil and 1.11 mg/kg peat soil) are already at a high level compared with the PNECs for different taxonomic groups $0.06 - 1 \text{ mg/kg}$. The margin of safety for terrestrial exposure to cadmium seems to be very narrow, and any increase to the natural background concentrations is likely to present some risk for the terrestrial environment.

No quantitative risk characterisation was made to the aquatic compartment, because of the uncertainties and the lack of information on the fate of cadmium after ash fertilisation. No long-term leaching studies of ash fertilization were available.

Impact of cadmium in fertilizers used in agriculture on aquatic organisms has been described in the report of Louekari et al. (2000).

5.4 Conclusions of the environmental part

The toxicity of cadmium to terrestrial organism shows a variable pattern. Plants grown in soil are generally considered insensitive to the effects of cadmium, although some exceptions do exist. Cadmium exhibits moderate and low toxicity to avian species in subacute exposure. Microorganisms and terrestrial invertebrates show moderate or high sensitivity to cadmium.

The impacts of cadmium in ash on microbes and invertebrates are difficult to distinguish from the effects of increased pH in soil. The increase of pH seemed to cause the most prominent effects on biota. In general, soil microbes seem to benefit from the effects of ash treatments; soil respiration and microbial activity has increased. Microbial communities have however changed. The short-term effects of ash fertilization on soil fauna seem to be adverse, although there are some species which benefit from the increase of soil pH.

No clear trend of increase of cadmium content in mushrooms was noticed, although according to one recent study a slight, not statistically significant, increase of cadmium could be seen in mushrooms. The situation is more or less the same with berries, the general trend of increasing concentrations of cadmium in berries is lacking, although a slight increase of cadmium concentrations in lingon- and cloudberry stems of blueberries after ash treatment could be seen.

It can clearly be seen that the total concentrations of cadmium in peat and mineral soils have increased significantly after ash fertilization. In general, the increase of cadmium concentrations in mineral soils has been lower compared to peat soils, where total cadmium concentration in ombrotrophic mires have even doubled about two years after ash fertilization. The fate and impacts on easily mobile and bioavailable extractable fraction of cadmium are still unclear. The extractable content of cadmium seems to increase at least a couple of years after ash fertilization but no definite direct conclusions can be drawn on the basis of so few studies. Generally speaking the information available about the fate of cadmium (transformation, fractions etc.) in forest soil after ash treatment is limited.

A drastic increase of extractable concentrations of cadmium shown in some studies was quite surprising, because according to the general understanding of the behaviour of cadmium with increasing pH the situation should be the opposite. The humus layer has a large capacity to retain cadmium and bind it in a less bioavailable form, especially if pH increases. Depending on the quantity and quality of ash used pH can increase 1-2 units after ash treatment. In general, the mobility of cadmium tends to decrease and its adsorption on soil increase when pH increases. It is generally known that the soil pH is one of the most important factors determining not only the short-term, but also the long-term variations in the uptake of cadmium by organisms and the vertical and horizontal mobility of cadmium in soil.

In fact, available data on extractable background cadmium concentrations and concentrations after ash fertilization do not enable a quantitative risk assessment to be carried out. Based on the preliminary consideration of extractable background concentrations of cadmium and elevated concentrations after ash treatment and the PNEC-values of different terrestrial species, it can however be noticed that the margin of safety for terrestrial exposure to cadmium is very narrow. The background cadmium concentrations are already at a high level compared with the PNECs.

In order to assess more reliably the effects of cadmium in wood ash used as fertilizers in forestry more comprehensive carefully planned long-term ash fertilization studies are needed, where extractable cadmium concentrations are measured in soil. Up to now most of the ash fertilization studies made are linked to the fertilizing effects on forest stands. Also long-term studies on leaching of cadmium from forest soil are needed. In addition, more long-term studies on the effect of ash fertilization on cadmium content of berries and mushrooms are needed.

Based on the current limited number of available data on extractable cadmium concentrations in forest soil, no direct conclusions of the impact of ash fertilization can be drawn. However, on the basis of the data reported the possible risks to the organism in mineral and peat soils caused by ash fertilization can not be excluded.

6 HUMAN HEALTH

6.1 Introduction

In this review, the recent data on cadmium exposure and evidence of health effects of cadmium are summarised. Since our aim is to assess the possible risks caused by ash fertilisation in forestry, the focus has been on foods obtained from forest. The emphasis is given to those consumer groups, e.g. recreational hunters and farmers, who regularly consume forest berries, mushrooms and liver and kidney of elk and hare.

For the assessment of the health effects caused by cadmium, we have utilised the recent report published by the Ministry of Agriculture and Forestry of Finland on “Cadmium in Fertilizers, Risks to human health and the environment” (Louekari et al. 2000). The critical toxic effect of cadmium in terms of general population are nephrotoxicity and effects on bones. Long-term, low-level exposure may cause these health effects in elderly people.

The overall goal of the risk assessment and management is to ascertain that the actual exposure does not cause adverse health effects. The assessment of exposure should cover all relevant groups of the population, especially those who are exposed to high levels of chemicals (“reasonable worst case”). These principles have been recognised in the Council Regulation (EC) 793/93 on Risk Assessment for Existing Substances and the Technical Guidance Document (TGD) supporting the regulation. According to the Technical Guidance Document (EU 1996), upper estimates/maximum exposure and averages are both needed and “the exposure assessment should be focused on those uses for which the highest exposure is expected to occur on a regular basis”. For this assessment, it is assumed that highest exposures concern farmers and recreational hunters (risk groups), who regularly consume foods obtained from forest.

The critical step in the risk assessment procedure is a comparison of the estimated exposure

level and/or the absorbed dose with the No Observed Adverse Effect Level (NOAEL), which is usually obtained from the animal experiments. Since there is much data on the health effects of cadmium in human, NOAELs from the animal studies are not applied. Instead the critical levels of urinary cadmium, associated with adverse effects in humans, are used for risk characterisation.

6.2 Human exposure to cadmium

6.2.1 General discussion

For cadmium as well as with most other environmental pollutants, there is a considerable variation in the human exposure between individuals as well as between population groups. The factors that cause this variation of exposure level and absorbed dose are numerous; the most important factors are listed below:

INTAKE:

- Food consumption habits
- Local food contamination
- Smoking
- Drinking water
- Ambient air
- Occupation

UPTAKE (absorption):

- Interactions in pulmonary or intestinal absorption
- Nutrient status, e.g. deficiency of iron, calcium

OTHER FACTORS:

- Age
- Gender

In this report the emphasis is given to dietary intake of cadmium. In Finland, the average exposure to cadmium via drinking water and via ambient air are 0.1 and 0.02 µg/day, respectively (Louekari et al. 1989). These are of less impor-

tance as compared with the average dietary intake (9.5 µg/day) and therefore exposure from drinking water and ambient air are not considered in detail in this report.

In Finland, the average dietary intake on cadmium about 9.5 µg/day (Mustaniemi et al. 1994, see table 15). It has been observed, that the maximum values of the long-term dietary intake of cadmium are 2-3 fold when compared with the average intake (WHO 1992), this implies that the maximum long-term dietary intake is 20-30 µg/day. High dietary intake of cadmium are caused by elevated energy demand, which is dependent on age or high consumption of food items which have a high content of cad-

mium, such as durum wheat, crustaceans, liver, kidney and mushroom. Supporting this, some studies (Morgan et al. 1988, Louekari et al. 1989, Coomes et al. 1982) suggest that for about 5 % of the population, the dietary intake of cadmium is at least two-fold as compared with the average intake, i.e. 20 µg/day for Finland.

Until recently, the limit values for foods in Finland were: for potatoes 0.05 mg/kg ww; for other vegetables 0.1; for raw cereals and cereal preparations 0.1; and for bran, embryos and durum wheat 0.15 mg/kg ww (the decision of Ministry of Trade and Industry N:o 134/1996). In addition to this, there were Cd limits for some sea foods too.

Table 15. Mean consumption (g/person/d) and cadmium concentration (µg/kg) of the Finnish foodstuffs and mean cadmium intake (µg/person/d and %), (Mustaniemi et al. 1994).

Food/food group	Mean consumption (g/person/d) (Finriski-92)	Current mean Cd Concentration (µg/kg, ww)	Current Cd Intake (µg/person/d)
Wheat	96	45	4,3
Rye	66	10	0,7
Other cereals	22	20	0,4
Vegetables	108	<10	0,5
Root vegetables	29	21	0,6
Potato	122	<10	0,6
Fruits	183	<1	0,1
Berries	39	10	0,4
Meat	62	1	0,06
Internal organs	3	135 ¹⁾	0,4
Fish	39	12 ²⁾	0,5
Milk	442	<2 ³⁾	0,04
Oils and fats	37	<20	0,4
Alcohol	155	<2 ⁴⁾	0,2
Sugar and sweets	31	<10	0,2
Tea drinks	109	<0,1	<0,01
Coffee drinks	433	<0,2	0,04
Totally			9,5

9,5 µg/person/d = 1,1 µg/kg body weight/week

PTWI (Provisional Tolerable Weekly Intake) = 7 µg/kg body weight/week

¹⁾ Mean concentration of cadmium in bovine and porcine liver and kidney.

²⁾ Mean concentration of cadmium in Baltic herring and rainbow trout.

³⁾ Concentration unit, mg/kg dw.

⁴⁾ Mean concentration of cadmium in wine and beer.

In February 2001, EU Standing Committee for Foodstuffs adopted the following maximum levels µg/kg (ww) of cadmium in foods:

Meat of cattle, sheep, pig and poultry	50
Meat of horse	200
Liver of cattle, sheep, pig and poultry	500
Kidney of cattle, sheep, pig and poultry	1000
Crustaceans, excluding brown meat of crab	200
Bivalve molluscs and cephalopods	1000
Cereals, excluding bran, germ, durum wheat grain	100
Bran, germ and durum wheat grain	200
Soybeans	200
Leafy vegetables, fresh herbs, celeriac and all cultivated mushrooms	200
Stem vegetables, root vegetables and potatoes, excluding celeriac	100
Other vegetables and fruits	50

For wild mushrooms, berries and game meat and inner organs, no maximum levels have been set in the relevant regulations.

Some factors that either cause variation of the cadmium exposure or increase the susceptibility among certain groups of population are presented in Figure 4, page 60. There are population groups attributed with more than one of these factors, but in Finland the level of cadmium exposure or urinary excretion of cadmium in those groups has not been studied. In large population studies, the maximum levels of e.g. urinary Cd or urinary β_2 -microglobulin are probably caused by the fact, that for a part of the population, several risk factors simultaneously apply.

6.2.2 Concentration of cadmium in foods potentially affected by ash fertilisation

Plants and animals used as human food, which could be affected by increased cadmium concentrations in forest soil are berries, mushrooms, elk and hare. In an unpublished study, Pihlström (2001) found no difference of cadmium concentrations in perch samples from uncontaminated lakes and lakes affected (the area around the lake was partly fertilised with ash). The number of

samples was 80 in the years 1997-2000 and the average concentrations in perch meat were 18-38 µg/kg (in dry weight). No other studies elucidating this route of human exposure are available.

The meat of elk and hare contains as low amount of cadmium as meat of pork and cattle (see tables 15 and 18). However, the content of cadmium in liver and kidney of elk and hare is high, and could significantly increase the daily dietary intake of cadmium. Lingonberry, blueberry and cloudberry, mushrooms and liver and kidney of game animals are considered to be the most important food items, which could be affected, when the cadmium content of forest soils increases.

The balance in forest soil: output of Cd with harvested wood and input with ash fertilisation

About 475 m³ of wood is harvested per hectare (Metsäkeskus Tapio 1994). Bark and phloem are 12 % (57 m³) of that, with dry weight of 21 660 kg. The cadmium content of this part is assessed to be 0.55 mg/kg in dry weight (compare with table 2) and thus, the output with bark and phloem is 11.9 g. The same figures concerning the heartwood are 88 %, 418 m³ (845 kg/m³) with dry weight of 176 605 kg. The cadmium content of this part is 0.25 mg/kg in dry weight (see table 2) and thus, the output with heartwood is 44.1 g/hectare. The total output of cadmium per hectare is about 56 g (Korpilahti 2001).

Considering the Cd input with ash fertilizers (see table 16) it is reasonable to assume that 10-80 g/hectare represents a realistic range. Thus, in case that ash fertilization is applied twice during the harvest cycle of 70 years, the input is about 20-160 g/hectare which in some cases, is more than the output with harvested wood i.e. 56 g/hectare. There are, however, other outputs of cadmium from the forest soil. Mobilisation and leaching from the soil erosion and transfer due to food nets contribute to the total output.

Balance of cadmium in the forest soil and the peaks potentially caused by ash fertilisation are not fully understood. Recognising this, it is assessed that the input due to ash fertilization is within the same order of magnitude as the output.

Whether cadmium will accumulate in the forest soil due to ash fertilization depends on other factors/flows which contribute to the balance. In short term, it is more likely that the balance of cadmium in forest soil is disturbed, which may affect the food items of interest.

Berries

In the experiment of Silfverberg and Issakainen (1991), wood ash (10 tons/hectare) and peat ash (20 tons/hectare) were added on forest soil. The cadmium contents were 9 and 31 g/ton in peat and wood ash, respectively. The input of cadmium from the wood ash was 310 g/hectare. When this is compared with the cultivated soils, where the upper limit of cadmium input with fertiliser is 100 g/hectare in 5 years, it can be concluded that if ash fertilisation is applied less frequently than once in 15 year the tolerance set for cultivated soils is not exceeded.

Silfverberg and Issakainen (1991) found that on *mineral soils* within three month after application of ash the soil pH increased from 3.74 to 5.46. However, 2-8 years after application of ash, the soil pH was not significantly different from the reference areas. In *peat soils*, pH was 0.3 unit higher 2-8 after treatment as compared with reference areas. This seems to indicate that a delayed peak of increased cadmium solubility and content could not be expected remarkably later than 8 year after application in mineral soils. Obviously, more studies made on different soil types and with different ashes are needed to confirm this preliminary conclusion. Furthermore, higher inputs of Cd/hectare with ash have not been reported in other fertilisation experiments reviewed below. Therefore the content of cadmium in berries measured in this study is likely to represent the reasonable worst case.

In the *mineral soil*, 2-8 years after ash-fertilisation, cadmium content was somewhat higher as compared with non-treated soils. In *peat soil*, cadmium content was twice as high as reference areas (1.0 vs. 0.5 ppm)

Fertilisation with wood or peat ash did not significantly increase the Cd-content in blueberry (two months after application). Cadmium was

detected in only one of 17 samples from treated areas and in none of the 9 samples from reference areas. Eight years after application, cadmium was detected in 2 of samples from peat soils. The result could be partly explained by the low detection limit (250 µg/kg in dry weight) of the plasmaemissionspectroscopy method for cadmium of in berries. Thus, it is possible that the method was not sensitive enough for detection of elevated Cd-concentration after ash fertilisation.

In lingonberry, an effect of ash fertilisation on cadmium content was seen. Two months after application, detection limit was exceeded in 9/14 samples from treated areas and in only 1/7 samples from control areas (see table 16). After 8 years, the detection limit 250 µg/kg (dw) was exceeded in 3 of 7 samples. Half of the detection limit (i.e. 125 µg/kg dw = 18 µg/kg ww) is assessed to be a “worst case” cadmium concentration in lingonberries on ash fertilized areas (see table 21).

Cadmium content is relatively high in cloudberries, ie. 440-690 µg/kg (dry weight). Treatment with ash did not increase the Cd-content in cloudberries when analysed two months after treatment. However, 3-8 years after application, a slight increase of Cd-content in cloudberries growing on treated areas as compared with control samples was seen; 460 vs 360 µg/kg (dry weight). Since the number of samples is small (12) and there are not other studies on the ash fertilisations and cadmium content in cloudberries, this observation is not used for the calculation of the reasonable worst case scenario.

Moilanen and Issakainen (2000) studied the effect of ash fertilisation on cadmium content in berries growing on mineral and peat soils in Northern Finland. The amount of ash applied per hectare varied between 3 and 15 tons. One year after treatment, no effect on cadmium concentrations of berries was seen. Also 10-20 year after treatment the cadmium levels were similar in control and treated areas.

Levula et al. (2000) studied the effect of ash fertilization and prescribed burning on heavy metal content of lingonberries in pine forest. The amount of ash applied on soil were 1, 2.5 and

Table 16. Content of cadmium in lingonberry, blueberry and cloudberry grown on ash fertilized and normal forest soil (dw=dry weight, ww=wet weight/fresh weight) 1)

Cd input with ash fertilization	Cd-content in berries, average, range and number of samples			Reference
	Lingonberry	Blueberry	Cloudberry	
310 g of Cd/hectare with wood ash and 180 g/hectare with peat ash	Two month after: >250 µg/kg (dw) in 9/14 samples. After 8 years: >250 µg/kg in 3 of 7 samples	Two month after: >250 µg/kg in 1 of 26 samples. After 8 years: Cd was detected in 2 of 8 samples	Two months after: in treated areas 470 µg/kg (dw), in control areas 690 µg/kg. After 7 years: 450 µg/kg in treated areas vs 360 µg/kg in controls.	Silfverberg et al. 1991
1.4-7.0 g of Cd/hectare with bark ash	2 and 7 years after: ash treated and control samples contained 3 µg of Cd/kg (ww). 7 years after prescribed burning, Cd content was 9 µg/kg vs 3 µg/kg in controls			Levula et al. 2000
10-80 Cd g/hectare with wood ash		Two months after: berries contained about 1 µg of Cd/kg (ww). Thirteen months after: about 3 µg/kg in treated areas and 1 µg/kg (ww) in controls (see the respective text).		Nilsson et al. 1998
No treatment, effect of emissions from Russian non-ferrous metal plants was studied	10 µg/kg (dw), 9-45 µg/kg, n=150	24 µg/kg (dw), 9-95 µg/kg, n=204		Laine et al. 1993
No treatment, representative background values	3 µg/kg (ww), 1-10, n=4	2 µg/kg (ww), 1-3, n=3	60 µg/kg (ww), 50-60, n=2	Varo et al. 1980

¹⁾ For conversion of dry weight concentrations to wet weight (see tables 20 and 21) the following factors were used (dw/factor=ww): lingonberry, 6.79; blueberry, 8.44; cloudberry, 6.3 (Laine et al. 1993)

5 tons/hectare, which is remarkably less than in the experiment of Silfverberg et al. (1991). The bark ash added on soils contained 1.4 mg of Cd/kg which is also much less than that reported by Silfverberg et al. (1991). Soil pH increased significantly, i.e. by about 1 and 2 units after the application of 2.5 and 5 tons of ash per hectare, respectively.

Samples were collected and cadmium in lingonberries was analysed 2 and 7 year after treatment with ash. Ash fertilisation had no effect on

cadmium concentration of lingonberries, whereas prescribed burning increased the Cd-content in berries.

Obviously, the results of Levula et al. (2000) can not be applied to all ash fertilization practices. In the experiment of Silfverberg et al. (1991) the amount of cadmium input per hectare was about 45-100 -fold higher than in the study of Levula et al. (2000). Thus, more accurate data on actual Cd-input on forest soils, caused by current fertilisation practices would be valuable.

Nilsson et al. (1998) studied the Cd content in blueberries two and thirteen months after ash fertilization in eastern Sweden, near to Uppsala. The ash was from power plants, in which wood (harvesting residues) and in some cases, 10-20 % of peat was burned. Some lots of the ash were granulated and some lots were mixed with lime. The amount of ash applied varied from 2 to 8 tons per hectare. The detection limit for cadmium in berries was 0.4 µg/kg. The Cd content in ash was about 10 ppm. Two months after treatment, variation of the concentration of cadmium in blueberries was large and no significant difference between different treatments were found. Thirteen months after the treatment, the content of cadmium in blueberries had slightly increased. However, the authors did not consider this effect to be related with the treatment, since the different amounts of Cd input to the forest soils had no “dose-relation” to the Cd content in berries. Furthermore, the highest average Cd levels after thirteen months were analysed in samples from lime treated areas. The author consider that time between treatment and sampling, elevated soil pH level, and formation of complexes between cadmium and organic compounds may explain why no clearer effect on the Cd content in blueberries was seen in this study.

Rühling (1996) studied the effect of ash treatment on cadmium content in lingonberry and blueberry. About 2-3 tons of ash was applied per hectare and the cadmium content in the ash varied between 5 and 10 mg/kg. The analysis of

berries did not suggest that the level of cadmium could be increased by ash fertilisation. In most cases, the Cd content in these berries was below the limit of detection.

Laine et al. (1993) studied the Cd content in blueberry and lingonberry in Lapland. This study gives an indication of background levels since ash fertilization was not applied. The average cadmium concentration in lingonberries and blueberries were 10 and 24 µg/kg in dry weight (see table 16).

In conclusion, using the detection limit, number of positive samples of the study of Silfverberg and Issakainen (1991), the wet weight concentrations of cadmium in lingonberries, blueberries and cloudberries in *non-treated* areas are 3, 3, and 68 µg/kg, respectively (see table 16). These figures are in agreement with analytical results reported by Varo et al 1980 and Levula et al. 2000. Using the results of Silfverberg and Issakainen (1991) it is estimated that in ash treated areas the concentration of cadmium in lingonberries, blueberries and cloudberries are 18, 3, and 68 µg/kg, respectively. The high concentration of Cd in lingonberries can be regarded as “reasonable worst case”, since the concentration of cadmium in the ash and the amount of fertiliser applied in that study are high.

Mushrooms

Kojo & Lodenius (1989) studied the cadmium content in various mushroom species. The highest Cd-content were measured in mushrooms grow-

Table 17. Concentration of cadmium in mushrooms (Kojo & Lodenius 1989).

Groups and some species of mushrooms	Average Cd-content mg/kg dry weight ¹⁾	Range	Number of samples
Mushrooms growing on lawns	11	1-84	21
Mycorrhizal mushrooms growing in forests	4.9	0.09-25	39
Mushrooms growing on wood	2.8	1.1-4.4	3
<i>Agaricus</i> sp. (<i>herkkusienet</i>)	19	1-84	13
<i>Amanita muscaria</i> (<i>punakärpässi</i>)	22	17-25	4
<i>Boletus edulis</i> (<i>herkkutatti</i>)		9.8-15	2
WHOLE MATERIAL	7.5	0.09-84	63

¹⁾ For conversion of dry weight concentrations to wet weight (see tables 20 and 21) the factor of 10.0 was used (dw/factor=ww) for mushrooms (Rastas et al. 1989)

ing on lawns and lowest levels were measured in mushrooms collected from forests (mycorrhizal species). The mean Cd-content of lawn decomposers and mycorrhizal mushrooms were 11 and 4.9 mg/kg (dry weight), respectively. Highest concentration of cadmium were found in *Agaricus* sp.; the average was 19 mg/kg and maximum Cd-content was 84 mg/kg (in dry weight).

In the experiments of Moilanen and Issakainen (2000), 5-15 tons of wood ash/hectare and 3-9 tons of peat ash/hectare was applied. In short term, no clear difference was seen in the Cd-concentration of mushrooms after different levels of ash fertilisation. In fact, it seemed that the cadmium content of mushrooms in fertilised areas (0.6 mg/kg) was lower than in control areas (0.7 mg/kg). In long-term experiments, 13-52 years after ash fertilisation, cadmium content had increased in some study plots, and was decreased in others. It has been suggested that cadmium is absorbed in soil particles in less soluble form for several tens of years and therefore is not available for berries and mushrooms.

Lodenius et al. (2001) analysed the cadmium content of 98 mushrooms samples collected from ash treated and control areas in Evo, Southern Finland. Approximately 4.8 tons of ash/hectare was applied; the ash contained 9.2 mg Cd/kg. Thus, the average cadmium load to forest soils was 44 g/hectare. The average (and range) of cadmium concentrations in mushrooms from control and treated areas were 167 (20-1000) µg/kg and 336 (29-2300) µg/kg (ww), respectively. In one species, *Russula emetica*, (*tulipunahapero*) the concentration was significantly higher in samples from treated sites compared to control sites. Also for the other species studied, the concentrations were on the average 56 % higher in treated areas although the difference were not statistically significant. The number of samples for each mushroom species was rather small, i.e. 2-20. It seems possible, that with higher number of samples, an effect of ash treatment could have been observed also in some other species.

Rühling (1996) studied the effect of ash treatment on cadmium content in mushrooms. About 2-3 tons of ash was applied per hectare and the

cadmium content in the ash varied between 5 and 10 mg/kg. In the treated areas, there were fewer mycorrhiza species, whereas litter-decomposing species, which contain more cadmium were often more abundant. In one species of mushrooms, *Cortinarius paleaceus* (*pelargoniseitikki*) the cadmium concentration has significantly elevated in the treated areas. Variation of cadmium concentration between different species within the same experimental plot was often larger than for a species after different treatments.

Kuusi et al. (1981) studied the cadmium concentrations in 326 mushroom samples from Helsinki and from rural areas. The cadmium content varied between 20 and 10100 µg/kg the average being 295 µg/kg (wet weight). The highest values were found in *Agaricus* species and *Amanita muscaria*,

Varo et al. (1980) found that cadmium content of wild mushrooms varied between 20 and 210 µg/kg wet weight (n=25), the former level being nearer to the average of these results.

In conclusion, the variation of cadmium content in mushrooms is large due to species differences and locations. No consistent and clear effect of ash fertilisation has been observed. Several years after fertilisation, cadmium concentration in some species has been slightly increased. Based on the cadmium levels reported especially the most recent study by Lodenius et al. (2001), it is estimated for this report that the average level in mushrooms in ash fertilised and in non-fertilised forests in Finland is about 300 and 150 µg/kg (wet weight), respectively.

Elk and hare

The meat of elk and hare contains a low level of cadmium (table 18). However, concentration of cadmium in liver and kidney of elk is high, 970 and 5600 µg/kg (wet weight), respectively. It is noteworthy, that the concentration of cadmium in liver of elk (970 µg/kg), is much higher than that in pig (20 µg/kg) and cow (60 µg/kg) (Tahvonen & Kumpulainen 1994).

A meal that contains 150 g of elk kidney would result in intake of 840 µg of cadmium, which is more than the average dietary intake

of cadmium during two months. Obviously, the elk kidney and liver are not regularly consumed due to rather limited supply. Annually about 60 000 elks are shot in Finland and it is considered unlikely that recreational hunters and their family members would annually eat several meals consisting of kidney of elk.

Lodenius et al. (2000) reviewed the Cd-concentration in forest insects and found the high concentrations in ants (about 600-6500 µg/kg wet weight) and bark beetles (1200-9400 µg/kg ww). In moths and butterflies the Cd-content is lower, usually below 200 µg/kg (ww). The probable explanation of the high Cd-content in ants is that they feed on greenflies (*Aphididae*), which feed on the phloem of wood. Bark and phloem of the wood are also the main feed of hare and elk, phloem being more rich of energy. Since phloem contains relatively high concentration of cadmium (see table 2), forest mammals and insects, which depend on it, receive higher body burden of cadmium than other animals.

Venäläinen et al. (2001) have observed a serious increasing trend of cadmium concentration in the liver and kidney of elk. In the year 1980, the Cd-concentration in the liver of elk was about 550 µg/kg, whereas in 1999 the concentration was 970 µg/kg. Similarly, the Cd-content in kidney of elk increased from 3700 to 5600 µg/kg (wet weight) during the years 1980-1999 (see table 18). Since this is based on sampling covering the whole country, the ash fertilisation, which is applied only on limited forest areas, is not a likely explanation to the increasing concentrations. Increased mobi-

lisation of cadmium in forest soils, due to acid precipitation might be an explanation (Venäläinen et al. 2001). Unfortunately, the effect of ash fertilisation on the Cd-content in the liver and kidney of elk has not been studied. So far the reported experiments have covered different berries and mushrooms of the forest. It is possible that species dependent on the nutrients of phloem of trees, including elk and hare, are affected by the ash fertilisation.

For this assessment, while monitoring data on effect of ash fertilisation are lacking, it is assumed that cadmium concentration of liver and kidney of elk is the same in fertilised and non-fertilised forests, i.e. 970 and 5600 µg/kg (ww), respectively.

6.2.3 Consumption of berries, mushroom, elk and hare

Consumption of various food items in Finland has been reported by Tennilä (2000) and by Information Service of Ministry of Agriculture and Forestry (MAF) of Finland (Maa- ja metsätalousministeriön tietopalvelukeskus, 2000). Tennilä has published results of a regular household survey, where households maintain a record/diary of purchased amounts of various consumer goods, including food.

In the Food Balance Sheet published by MAF, the total amount of berries consumed is given ie. 14.17 l/year, which is considerably less than that given by Tennilä (2000) 23.0 l/year. Consumption of berries and mushrooms has increased in 30 years, the annual consumption of berries and mushrooms in 1966 was 11.0 l/a and 1.0 kg/a, respectively, whereas these figures were 23.0

Table 18. Cadmium content in hare and elk (µg/kg wet weight) in Finland.

Species	Muscle	Liver	Kidney	Reference
Mountain hare, <i>Lepus timidus</i>	6	450	11000	Venäläinen et al. 1994
Brown hare, <i>Lepus europeus</i>	3	160	1900	Venäläinen et al. 1994
Elk, <i>Alces alces</i>	<100	360-550	2300-3500	Valtonen et al. 1982
	4 (n=102)	970 (n=105)	5600 (n=109)	Venäläinen et al. 2001

l/a and 1.4 kg/a in 1998 (Tennilä 2000). Increasing consumption of berries has also been observed in Food Balance studies. Decreasing consumption of liver and kidney was seen in Food Balance studies, the average amount consumed fell from 2.7 kg/a to 1.4 kg/a during 1990-1998. As in the household survey, most of the liver is purchased and recorded as liver pate or ready meals and not as fresh liver (0.22 kg/year). Therefore, the figure given by Food Balance Sheet for the year 1998, 1.4 kg/year is considered to be correct.

The average consumption of liver and kidney of elk and hare is much too low to be registered, within these studies. In most households these food items are not consumed at all. In families of recreational hunters, liver and kidney of elk are occasionally eaten. It is estimated, based on oral information, that 1/3 of the liver and kidneys of one animal are eaten by a hunter and his family members. The weight of elks liver and kidneys is 3-4 kg and 300-500 g, respectively. Thus, about 1.2 kg of liver and 400 g of kidney are eaten by family of three members. The average number of farmers household members is 3.14 (Tennilä 2000). Among this group, the average daily consumption of elk liver and kidney is about 1 g and 0.4 g, respectively.

For comparison, the average consumption of liver and kidney of cattle and pigs is 4 g/day. Thus, the consumption of inner organs of elk by recreational hunters and farmers (1.4 g/day) partly but not totally replaces inner organs of farm animals.

In the Northern part of Finland, the consumption of all "forest foods" is higher as that in the whole country (see table 19). For assessment of reasonable worst case exposure, it is assumed that among people living in Northern Finland, there is a group which has two-fold consumption of the food items listed in table 19. The respective amounts consumed daily (g/day) are given in table 20 and 21.

These figures illustrate that the forest foods only represent a minor part in the daily diet in Finland. For some groups, such as recreational hunters and farmers, especially in the Northern Finland, forest foods are more important. The consumption of berries and mushrooms has increased, within the last ten years, which is a concern, if the cadmium content in the forest foods is affected by the ash fertilisation.

Table 19. Consumption of certain foods. Figures used for estimation of dietary intakes are bolded. These figures are multiplied by two and divided by 365 to obtain the daily consumption (g/day) in the reasonable worst case scenario

Food item/group	Household Survey 1998			Food Balance Sheet 1998
	Whole country kg/year or l/year	Northern Finland	Farmers	Whole country kg/year
Meat of elk and hare	0.78	1.52	2.92	1.3
Liver and kidney of all animals	0.22	0.16	0.19	1.40
Deer meat	0.54	2.31	0.50	
Blueberries	3.23	5.48	4.37	
Lingonberries and cranberries	4.51	8.26	9.97	
Cloudberries and other berries of forest	2.09	5.53	2.78	
Strawberries	5.68	6.78	10.14	
Red and black currants and other berries	about 8.0			
Mushrooms	1.4		1.31	

6.2.4 Exposure to cadmium from berries, mushrooms and elk

In the following tables, the representative concentration values of cadmium in foods from ash fertilised and control areas, and the respective food consumption figures are used to calculate the die-

tary intake of cadmium. For this estimation, it is assumed that

- most recreational hunters have roughly similar food habits as the inhabitants of the Northern Finland and the farmers. This is reasonable since most of the recreational hunters are farmers.

Table 20. Dietary intake of cadmium among recreational hunters, who have two-fold consumption of these food items as compared with the average of the Northern Finland. For this estimation, average level of cadmium in berries, mushrooms and liver and kidney of elks has been used.

Food item	Cd-concentration µg/kg (wet weight)	Consumption g/day (fresh weight)	Intake of cadmium µg/day
Lingonberry	3	45	0.1
Blueberry	3	30	0.1
Cloudberry	68 ¹⁾	30	2.0
Mushrooms	150	8	1.2
Liver of elk	970 (see table 18)	1 (assumption: 400 g i.e. three meals/year)	1.0
Kidney of elk	5600 (see table 18)	0.4 (assumption 133 g i.e. one meal/year)	2.2
Foods obtained from forest, totally		114.4	7.5
Other foods (see table 15)			9.0 ²⁾
ALL FOODS			15.6

- 1) For conversion of dry weight concentrations to wet weight the following factors were used: lingonberry, 6.79; blueberry, 8.44; cloudberry, 6.3; mushrooms 10.0 (Laine et al. 1993, Rastas et al. 1989)
- 2) Berries and 25 % of inner organs (liver and kidney) are replaced by the forest foods, and therefore the dietary intake of cadmium from other foods decreases by 0.5.

Table 21. Dietary intake of cadmium among recreational hunters, who have two-fold consumption of these food items as compared with the average of the Northern Finland. For this estimation of the reasonable worst case, it is assumed that lingonberries, cloudberry and mushrooms are affected by ash fertilisation.

Food item	Cd-concentration µg/kg (wet weight)	Consumption g/day (fresh weight)	Intake of cadmium µg/day
Lingonberry	18 ¹⁾	45	0.8
Blueberry	3	30	0.1
Cloudberry	68	30	2.0
Mushrooms	300	8	2.4
Liver of elk	970 (see table 18)	1 (estimate: 400 g i.e. three meals/year)	1.0
Kidney of elk	5600 (see table 18)	0.4 (estimate: 133 g i.e. one meal/ year)	2.2
Foods obtained from forest, totally		114.4	8.7
Other foods (see table 15)			9.0 ²⁾
ALL FOODS			17.4

- 1) For conversion of dry weight concentrations to wet weight the following factors were used: lingonberry, 6.79; blueberry, 8.44; cloudberry, 6.3; mushrooms 10.0 (Laine et al. 1993, Rastas et al. 1989).
- 2) It is estimated that in the diet of many recreational hunters and farmers, berries and 25 % of inner organs (liver and kidney) are replaced by the forest foods, and therefore the dietary intake of cadmium from other foods decreases by 0.5.

- within the group of recreational hunters, there is a group which has two-fold consumption of the forest foods; this is a reasonable worst case assumption and the size of the group probably is rather small.

Thus, a food consumption pattern of recreational hunters, who are also farmers and/or live in Northern part of Finland is formed. This food consumption pattern is characterised by maximum use of forest foods. Therefore it serves as a basis of a reasonable worst case scenario. Amounts expressed in kg/year in the table 19 (for Northern Finland), are multiplied by two and converted to g/day for tables 20 and 21). These figures are much higher than the average amounts (see table 19).

6.2.5 Conclusions: Contribution of various food items to the dietary intake of cadmium and data gaps

The contribution of lingonberries and blueberries to the dietary intake of cadmium, irrespective of ash fertilization, is small, ie. below 1 µg/day. In Northern Finland, consumption of cloudberries is rather high, ie. 30 g/day. With relatively high content of cadmium 68 µg/kg, these berries contribute to the intake by 2.0 µg/day. The concentration level reported by Silfverberg and Issakainen (1991) is the same as reported earlier by Varo et al. (1989). There are only five, non-comparable studies available on the effect of ash fertilization on berries, and therefore the above estimates are preliminary. It seems clear, however, that among the forest berries, only cloudberry could have an effect on the dietary intake of cadmium, whereas the exposure from lingonberry and blueberry is not remarkable in any conditions. Therefore, it would be of interest to repeat the study made by Silfverberg and Issakainen (1991), where a slight increase of the Cd concentration in cloudberries was observed after ash fertilisation.

For this assessment, it was assumed that recreational hunters and their family members consume twice the amount of mushrooms as compared with the average consumer. While the daily consumption of mushrooms is low also in that case (8 g/day) the average Cd-concentration is

high (150-300 µg/kg wet weight). Consequently, the daily intake of cadmium from mushrooms is not negligible (1.2-2.4 µg/day). According to Varo et al. (1989) the Cd-content of mushrooms is lower (about 80 µg/kg). Some of the studies cited above indicate that ash fertilisation could have an effect on mushrooms.

Using the average level of cadmium in the liver and kidney of elk and roughly estimated consumption figures, it was calculated that the dietary intake of cadmium from these food items is 3.2 µg/day. The estimated consumption figures represent a reasonable maximum (worst case scenario), which only applies to recreational hunters and their family members. Altogether the consumption of forest foods could, in worst case, increase the dietary intake of cadmium almost two-fold (from 9.5 to 17.4 µg/day). It is noteworthy that this difference is for the most part caused by food consumption habits and not the ash fertilisation.

6.3 Health effects of cadmium exposure

The present review aims to summarise recent findings on the toxicological effects of cadmium in humans. It is considered that the experimental studies in animals are not of great relevance, since large-scale epidemiological studies are available and are to be preferred for animal studies.

In the following, an overview of the key studies on the health effects of cadmium published 1988-1999 is presented and the main results are tabulated.

6.3.1 Kinetics

Cadmium enters the body mainly by inhalation and by ingestion. Fractional intestinal absorption, which normally is about 5 %, is influenced by dietary factors and increases with dietary cadmium concentration. Pulmonary fractional absorption depends partly on the solubility in vivo of the compound.

Kowal (1988) studied the effect of dietary iron and cadmium on the urinary cadmium and β_2 -microglobulin using the data provided by National Health and Nutritional Examination

Survey II (NHANES II). He found that urinary Cd was negatively and significantly correlated with dietary iron and dietary calcium. This indicates that cadmium absorption is increased in the general population of the United States by the low dietary intake of iron and calcium.

6.3.2 Renal effects

The currently applied critical level of cadmium in renal cortex is 200 mg/kg, which corresponds urinary excretion of about 10 µg/24h. This critical level, however, has been obtained from studies on occupationally exposed men. It has been suggested, that the critical level is lower in the general population (2-4 µg/24h) and that application of the critical level biased by the “healthy worker effect” may lead to the underestimation of the health risk in the general population (Buchet et al. 1990). More recently, Elinder et al. (1998a) have suggested that the critical level of cadmium in the renal cortex is remarkably lower. They consider that 50 mg/kg (ww) in renal cortex causes an excess prevalence of renal tubular damage and corresponds the U-Cd level of 2.5 µg/l and the dietary intake of about 50 µg/day.

In a large-scale population study with 1699 subjects in Belgium (the Cadmibel study), Several urinary parameters, urinary excretion of retinol-binding protein, N-acetyl-b-glucosamidase, β₂-microglobulin, aminoacids and calcium were statistically significantly associated with urinary excretion of cadmium. This suggests the presence of tubular dysfunction caused by cadmium in a part of this population. There was a 10% probability of abnormal values of these renal parameters, when cadmium exceeded 2-4 µg/24h. (Buchet et al. 1990). 10 % of the non-smokers and about 30 % of the whole group of study subjects reached this threshold. However, for some urinary parameters, a dose-response relation was observed also when urinary excretion was below 2 µg/24h. Therefore a no-effect-level of cadmium in terms of renal effects is difficult to determine on the basis of this study.

The findings of the Cadmibel study on renal tubular function have been confirmed by a similar

study in contaminated areas in the Netherlands (Kreiss 1990).

Renal function of people who were not occupationally exposed to cadmium but had varying environmental exposure due to local contamination in Germany (Stolberg, Duisburg and Dusseldorf) were studied by Ewers et al (1985). 65 and 66 year old women, who had lived most of their life in one of these areas were selected for the study. Levels of cadmium in serum and in urine were significantly different, the highest levels were found in Stolberg, where cadmium concentrations of soil and plants were also higher than those in other districts. Serum creatinine levels were significantly higher in the residents of Stolberg as compared with Duisburg and Dusseldorf. Other renal parameters (proteinuria, phosphaturia, aminoaciduria) did not show significant differences between the study populations. The authors consider, that for the Stolberg group a synergism of ageing and cadmium with respect to the decline of glomerular function can not be excluded.

Jung et al. (1993) investigated the following groups of individuals: 1) controls; 2) environmentally exposed, and 3) occupationally exposed to cadmium. The serum creatinine and ribonuclease values, indicators of glomerular effect, did not differ between these groups. In the occupationally exposed group indicators of tubular damage (e.g. retinol binding protein, a1-microglobulin) were increased. In the environmentally exposed group, alanine aminopeptidase, alkaline phosphatase and N-acetyl-beta-D-glucosaminidase (NAG) levels were increased. The a1-microglobulin level in urine was increased in individuals with urinary cadmium excretion of >5 µmol/mol creatinine (corresponding 4 µg Cd/l of urine). This supports the results of the Cadmibel study indicating that changes in markers of renal effects are observed at the urinary level of 2-4 µg Cd/l. In 30% of the individuals in environmentally exposed group, a1-microglobulin or N-acetyl-beta-D-glucosaminidase (NAG) levels exceeded the corresponding upper reference limits. These two analytes were recommended for screening and detection of cadmium-induced renal dysfunction.

Table 22. Conversion factors for Cd concentration in urine used in this report:

1 $\mu\text{mol Cd/mol creatinine}$ = 0.81 $\mu\text{g Cd/g creatinine}$
1 $\mu\text{g Cd/24h}$ = 0.7 $\mu\text{g/g creatinine}$
1 $\mu\text{g Cd/24h}$ = 0.7 $\mu\text{g/l}$
1 $\mu\text{g Cd/l}$ = 1.4 $\mu\text{g/24h}$
1 $\mu\text{g Cd/l}$ = 1 $\mu\text{g/g creatinine}$
1 $\mu\text{g } \beta_2\text{-M/24h}$ = 0.7 $\mu\text{g } \beta_2\text{-M/g creatinine}$
Factors are based on the following figures and estimates: Volume of urine: 1400 ml (600-2500 ml)/24h Excretion of creatinine: 1.4 (1.0-1.8 g)/24h 1 mol Cd=96 g, 1 mol creatinine=118 g

Järup et al. (1995) studied 72 persons living near to cadmium polluting industry in Southern Sweden. Those living within 500 m of the plant had significantly elevated U-Cd (average around 1 $\mu\text{g/g creatinine}$) and also displayed a high prevalence of elevated NAG in urine.

A nine year follow-up study of 3178 persons living in a Japanese cadmium- contaminated area was conducted by Nakagawa et al. (1993). The standardised mortality ratios of the urinary β_2 -microglobulin positive subjects (excreting more than 1 000 $\mu\text{g/g creatinine}$) of both sexes were higher than those of the general Japanese population, whereas the cumulative survival curves were lower than those of the urinary β_2 -microglobulin negative group. A higher mortality rate was observed when the urinary excretion of β_2 -M was above 300 $\mu\text{g/g creatinine}$. Using data reported by Nordberg et al. (1997) this corresponds urinary cadmium level of approximately 4-5 $\mu\text{g/l}$.

These results were confirmed by a 15 years follow-up study by Nishijo, Nakagawa et al. (1995) on 2408 individuals living in the same polluted area (Kakehashi River basin). A significant relationship was seen between urinary excretion of RBP and mortality in both sexes. The observed increases of mortality are due to heart failure and renal diseases. Based on the comparison of urinary β_2 -M values, the environmental exposure to cadmium in this area in Japan seems to be somewhat higher than in the contaminated areas in Europe. Whether increased excretion of RBP could

be caused by factors other than cadmium exposure remains to be evaluated.

Yamanaka et al. (1998) found that among people living in non-polluted area in Japan, total urinary protein, urinary β_2 -M and NAG were associated with urinary cadmium. The authors consider that their results are in agreement with studies of Buchet et al. (1990) and Lauwerys et al. (1994), who proposed 2 $\mu\text{g Cd/l}$ as the maximum tolerable internal dose of Cd for the general population. Buchet et al. (1990) estimated that this urinary concentration corresponds a

renal cadmium concentration of about 50 mg/kg.

According to Nogava (1992), a lifelong intake of about 2 g of cadmium, corresponding average daily intake of 80 μg , would bring about a U-Cd value of 4-5 $\mu\text{g/l}$, which would elicit a significant rise in prevalence of tubular damage. However, several recent studies indicate that the threshold for renal effects is lower, 2-4 $\mu\text{g/l}$, which would correspond a daily intake of 40-80 μg .

Reversibility of the cadmium-induced renal lesions was studied by Iwata et al. (1993). They found that while daily dietary intake was dropped from about 200 μg to 53-106 μg (due to replacement of polluted soil of rice fields) there was no evidence that renal lesions were reversible. On the contrary, the tubular damage had, in most cases, been aggravated. However, it is noteworthy, that the urinary concentration in population was very high, during the follow-up it decreased from 8.5 to 6.0 $\mu\text{g/l}$. In another Japanese study by Kido et al. (1990), in most of the examined subjects, serum creatinine, indicative of more severe glomerular damage, tended to increase.

Müller et al (1989) studied the level of indicator enzymes NAG and alanine aminopeptidase (AAP) in two groups: those with urinary cadmium levels less than 2.0 $\mu\text{g/l}$ and those with Cd-U greater of equal to 2.0 $\mu\text{g/l}$. The mean NAG and AAP levels in urine were significantly higher in the high exposure group. The results indicate that markers indicating sub-clinical renal dysfunction, reveal changes already when urinary cad-

mium level is below 10 µg/l, which has been recommended as an upper limit by the 1980 World Health Organisation Study group. These results suggest, similarly to the observations of several other studies cited above, that the threshold level of renal effects of cadmium is close to 2 µg Cd/l of urine, above which first signs of nephrotoxicity can be measured.

Ishizaki et al (1989) studied the dose-response relation between urinary cadmium and β_2 -microglobulin. 3178 inhabitants over 50 years of age in the Cd-polluted Kakehashi River basin, Japan and a smaller group of inhabitants in non-polluted areas were studied. Urinary Cd and β_2 -microglobulin were significantly higher in the Cd-exposed subjects. Prevalence of β -microglobulinemia increased proportionally with increasing urinary Cd concentration, thus confirming the dose-response relation. Biological threshold values for environmentally exposed people suggested on the basis of these results were 3.8-4.1 µg Cd/g creatinine, corresponding to the urinary cadmium level of 3.8-4.1 µg/l.

Nordberg et al. (1997) studied the urinary cadmium level, urinary β_2 -M and urinary albumin in three areas in China. Urinary cadmium in the high exposed area, the medium exposed areas and control area were 10.7, 1.62 and 0.40 µg/l, respectively. There was a clear increase of the β_2 -M and the urinary albumin in the heavily exposure group as compared with the control group and a slight increase in the medium exposed group. Statistically significant dose-response was found between cadmium in urine and urinary β_2 -M.

Studies on occupational exposure to cadmium and renal effects are not reviewed here in detail. An adequate overview is that dose-response data based on epidemiological studies is confirmed by the occupational evidence of cadmium toxicity. For example results from Swedish battery workers (Järup et al. 1994) indicates that depending on age, the prevalence of β_2 -microglobulinuria was 5 % to 15 % at U-Cd levels above 3 nmol/mmol creatinine. In this study, a 10 % prevalence of tubular proteinuria already at 1.5 nmol Cd/mmol creatinine was found in an older age group. This suggests that elderly people are more susceptible to the adverse renal effects caused by cadmium.

The critical concentration of cadmium in urine and in the kidney cortex

As a risk characterisation based on several studies, Elinder et al (1998a) concluded that in the general population, an average U-Cd level of 2.5 µg/l is related to an excess prevalence of renal tubular damage of about 4 %.

Elinder et al. (1998a) estimated that “in order to prevent renal tubular damage that can proceed to clinical disease and perhaps contribute to early death, cadmium levels in the kidneys and in urine should be kept below 50 mg/kg and 2.5 µg/l, respectively.” Elinder et al (1998b) present a “best guess” of the relation of cadmium in kidney cortex, urinary cadmium and prevalence of the tubular effects in the population. These are simplified in table 23. The relation of these three parameters is obviously not mechanistic/deterministic. Not all who have a given kidney concentration of cadmium will develop renal failure. There are susceptibility factors, for example, age, gender, use of

Table 23. Summary of the “best guess” presented by Elinder et al. (1998b) of prevalence of tubular effects and respective cadmium concentration in kidney cortex and urinary cadmium level.

Cadmium in kidney cortex (mg/kg)	Urinary cadmium (µg/l)	Prevalence of renal effects in the respective group of population
<50	<2.5	0
51-60	2.75	1
91-100	4.75	5
141-150	7.25	14
191-200	9.75	30
>200	>10.25	>35

nephrotoxic drugs, which complicate the mechanism by which the body burden of cadmium leads to renal effects.

It is necessary to discuss here, whether the existing evidence justifies the conclusions drawn by Elinder et al. (1998a). First question is the relation between early signs of renal effects and clinical disease and the second question is whether there is enough evidence of increased mortality caused by high exposures to cadmium. First, our evaluation is that there is some evidence of early onset of renal insufficiency (glomerular damage) associated with urinary cadmium level of about 4 µg/l and manifested e.g. by increased level of creatinine in serum. This seems to be the second phase of the development of renal failure which starts as increased excretion of high-molecular weight proteins, which as such could be considered to be a pre-clinical symptom. It is likely that exposure to cadmium which causes clinical disease (e.g. impaired excretion of creatinine) is higher than the exposure that causes e.g. increases urinary level β_2 -microglobuline and NAG.

Second, two Japanese studies (Nakagawa et al. 1993, Nishijo et al. 1995) suggest that renal effects caused by cadmium are associated with increased mortality due to heart failure and renal disease. These observations are preliminary, and this type of studies should be repeated in contaminated and uncontaminated areas of Europe. The level of exposure in these studies is relatively high (U-Cd about 4-5 µg/l) and probably apply to 1) those living in highly contaminated areas and to 2) smokers, who have increased absorption of cadmium and diet, which is rich of cadmium. The observations of increased mortality are serious, since it was also found that the mortality tended to become higher as the severity of renal dysfunction progressed during the follow-up study (Nakagawa et al. 1993).

6.3.3 Calcium excretion and bone injuries

It has been observed that exposure to cadmium may cause higher urinary excretion of calcium. This was confirmed by the Cadmibel study, where a relatively low level of cadmium body burden increased the urinary level of calcium and caused

calcium wasting. Significantly different calcium excretion/24h were (2.0 and 2.6 mmol of Ca/24h) found between groups which had 0.9-1.4 µg Cd/24h and 1.4-8.0 µg of Cd/24h (corresponding 1.0-5.6 µg/l). Also elevation of serum alkaline phosphatase activity was observed in the subjects of the Cadmibel study. These results suggest that environmental exposure to cadmium may be sufficient to influence calcium homeostasis and bone metabolism (Lauwerys et al. 1991). However, it is also stated by authors of the Cadmibel study that the biological significance of this observation still remains to be elucidated. The authors consider, that further studies are needed to show, whether this effect could exacerbate age-related osteoporotic changes especially in women with low dietary calcium (Buchet et al. 1990).

Also Järup (unpublished data) found in a recent study on women in Stockholm (50-70 years of age), a significantly increased urinary excretion of calcium was found in those, who excreted more than 0.81 µg Cd/l, versus women who had a lower U-Cd. This finding is in accordance with the Belgian results cited above.

Elinder et al. (1998b) summarised that there is probably an important causative link between bone effects of cadmium and toxicity on the kidneys (see figure 2). Notably, vitamin D is activated in the kidney to calcitriol, which functions as a hormone with an important role in the absorption of calcium from the gut and in the calcification of bone.

In a 6.6 years follow-up in Belgium, Roels et al. (1999) found that long-term low-level environmental exposure to Cd may accelerate the demineralisation of the skeleton, especially in postmenopausal women, which in turn may lead to greater bone fragility and an increased risk of fractures. The relative hazard rate associated with a doubling of urinary Cd was 1.73 ($p=0.007$) for fractures in women and 1.60 ($p=0.08$) for stature loss in men. It is noteworthy that 6 of the 10 districts studied bordered on zinc/cadmium smelters, and the exposure levels are higher than in Finland. The urinary levels of cadmium were not sufficiently reported.

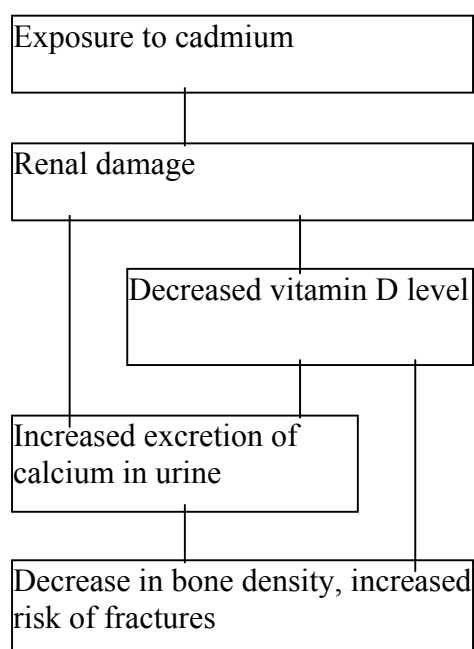


Figure 3. Probable sequences of effects, which could increase the risk of bone fractures, based on Järup (1998), Roels et al. (1999) and Tsuritani et al. (1992)

There is also experimental evidence that cadmium disturbs calcium homeostasis. In long-term exposures, or when repeated doses of Cd-MT are given with short intervals, irreversible changes in the urinary excretion of calcium are seen (Leffler et al. 1996).

Whether a small effect on calcium metabolism may lead to morbidity in the general population remains to be studied. In heavily polluted area in Shipham, Britain, cadmium exposure was not associated with excess mortality from fractures (Inskip et al. 1982). However, bone lesions have been experimentally induced by cadmium in laboratory animals. Combination of the administration of cadmium, and deficiency of vitamin D was particularly adverse (Kjellström 1985). Some epidemiological evidence supports these findings, namely several cases of osteomalacia and osteoporosis have been observed in workers exposed to cadmium and about 150 of the itai-itai patients have developed bone lesions.

Elderly people often suffer from decalcification of bones which can be attributed to ageing or hormonal or nutritional deficiencies. Therefore,

further studies should definitely be undertaken to see whether environmental exposure to cadmium may contribute to osteoporosis and its consequences (Staessen et al. 1996). The significance of the findings of the Cadmibel study in terms of morbidity and mortality are studied in the prospective PheeCad Study in Belgium (Staessen et al. 1996).

Roels et al. (1993) suggest that interference of cadmium body burden with prostanoids observed at the level of 2 µg Cd/g creatinine should be studied further, since it might play a part in the toxicity of Cd in bone. Prostanoids are hormones with many biological activities. It has been suggested, based on a study on cultured osteoblasts like cells, that Cd can stimulate bone resorption via an increased production of prostaglandin E2. If renal synthesis of prostaglandins is affected also in vivo, this observation together with the results of the Cadmibel study, suggests that environmental pollution by cadmium may contribute to bone decalcification and osteoporosis in the general population (Roels et al. 1993).

In a group of workers who had been exposed to cadmium, serum alkaline phosphatase activity increased significantly during the five year follow up period, which may reflect the interference of cadmium with bone metabolism (Roels et al. 1989). Mean urine and blood cadmium levels of the subjects were 18.0 µg/l and 9.7 µg/l, respectively. In comparison, the maximum urinary level observed in the Cadmibel study of people environmentally exposed to cadmium was 8.0 µg/24h (Buchet et al. 1990) which is about 8.0 µg/l.

The quantitative dose response relation for the effects of cadmium on calcium and bone metabolism were elucidated by Staessen et al (1991) in the context of the Cadmibel study; urinary and blood samples of 1987 individuals were studied. The results showed that serum alkaline phosphates activity and urinary excretion of calcium significantly correlated with urinary excretion of cadmium. In men also serum total calcium concentration correlated negatively with the urinary excretion of cadmium. The slopes of these relations showed that whilst U-Cd doubles serum

alkaline phosphatase and urinary calcium rise in both sexes by 3-4 % and 0.25 mmol/24h, respectively, the serum calcium in men failed by 6 μ mol/l. These findings suggest that environmental exposure to cadmium calcium metabolism is gradually affected. The linear regression found between urinary excretion of cadmium and the parameters of calcium metabolism suggest in fact that no threshold exists and that the effects on calcium metabolism develop gradually when cadmium accumulates in the body. The effect may be due to the dysfunction of renal tubules or development of vitamin D resistance (Staessen et al. 1991).

Recent experimental studies in animals support these observations made in humans. The effects of diet that was low in calcium, vitamin D and vitamin E, and added for cadmium on the bone density of the hind legs of mice for experimental period of 29 days - 24 months was investigated by Imai (1995). Using X-rays and a densitometer it was observed that diets deficient of calcium and vitamins D and E promoted the effect of cadmium on the ageing of bone.

6.3.4 Blood pressure and cardiovascular disease

In the Cadmibel study, where the population studied had a wide variation of cadmium body burden due to heavy local contamination by cadmium releases, no statistical association was observed between environmental exposure to cadmium and blood pressure elevation of the prevalence of cardiovascular cases (Lauwerys et al. 1991)

Also in another large scale epidemiological study, the Second National Health and Nutrition Examination Survey (NHANES II) in the USA, no significant correlation between urinary cadmium and blood pressure (Whittemore et al. 1991) was observed after the hypertensive patients were removed from the analysis.

6.3.5 Carcinogenicity

According to the evaluation of the IARC, there is sufficient evidence in humans for the carcinogenicity of cadmium and cadmium compounds. There is sufficient evidence in experimental animals for the carcinogenicity of cadmium com-

pounds. There is limited evidence in experimental animals for the carcinogenicity of cadmium metal. In making the overall evaluation, the Working Group of the IARC took into consideration the evidence that ionic cadmium causes genotoxic effects in a variety of types of eukaryotic cells, including human cells. The overall evaluation is that cadmium and cadmium compounds are carcinogenic to humans (Group 1).

In conclusion, cadmium has been implicated in the development of lung and prostate cancer in exposed workers and in animals under various exposure conditions. However, there is presently no epidemiological and experimental evidence that exposure to cadmium via food may be associated with an increased risk of cancer.

6.3.6 Summary of health effects of cadmium in light of recent epidemiological

Renal effects

The recent studies have not dramatically changed the understanding of the toxicological profile of cadmium. When the health of the general population is considered, renal effects and effects on bones and calcium metabolism still deserve the greatest attention. However, the knowledge on dose-effect relation and thresholds for these effects has improved. Several studies indicate that the safe level, in terms of early renal effects and bone effects of cadmium exposure as expressed in the urinary concentration, is not below 10 μ g of Cd/l urine suggested and applied earlier, but about 2-4 μ g/l (see table 24). There is also evidence that the sub-clinical renal effects might proceed even after cessation of the exposure and may also impair the glomerular function leading to renal insufficiency at an older age.

When the results of the Cadmibel study are considered it should be noted that there was a 10% probability of abnormal values of renal parameters, when cadmium exceeded 2-4 μ g/24h. (Buchet et al. 1990). Among the non-smokers 10 % of the study subjects reached this threshold. However, for some urinary parameters, a dose-response relation was observed when urinary excretion was below 2 μ g/24h. Therefore

a no-effect-level of cadmium in terms of renal effects would be difficult to determine.

Since it has been shown that renal damage caused by cadmium is progressive, it also should be noted that environmental exposure to cadmium, when associated with pre-clinical renal effects (increased urinary excretion of β -microglobulin, NAG, retinol binding protein or albumin) can cause impaired renal function i.e. reduced glomerular filtration rate, at an older age. Due to this effect on the age related change of the renal function, the early pre-clinical renal changes are considered to be adverse by Roels et al. (1989).

Excretion of calcium

It has been observed that exposure to cadmium may cause higher urinary excretion of calcium. This was confirmed by the Cadmibel study (Buchet et al. 1990), where a relatively low level of cadmium body burden increased the urinary level of calcium and caused calcium wasting. Elevation of serum alkaline phosphatase activity was observed in the subjects of the Cadmibel study, and Lauwerys et al. (1991) assessed that environmental exposure to cadmium may be sufficient to influence calcium homeostasis and bone metabolism. Also Järup (unpublished data) found in a recent study on women in Stockholm (50-70 years of age), a significantly increased excretion of urinary calcium in those who excreted more than 0.81 $\mu\text{g/l}$, versus women who had a lower U-Cd. This finding is in accordance with the Belgian results.

The latest and most serious evidence in this respect comes from a Belgian follow-up, made after Cadmibel study. Roels et al. (1999) found that long-term low-level environmental exposure to Cd may accelerate the demineralisation of the skeleton, especially in post-menopausal women, which in turn may lead to greater bone fragility and an increased risk of fractures.

Increased mortality

There is also some evidence that environmental exposure to cadmium observed as increased excretion of β -microglobulin increases mortality among the exposed population (Nakagawa et al. 1993).

The standardised mortality ratios of the urinary β_2 -microglobulin positive subjects (excreting more than 1 000 μg β_2 -M/g creatinine) of both sexes were higher than those of the general Japanese population. Mortality rates increased in proportion to increases in the amount of, β_2 -microglobulin excretion. These results suggest that the prognosis of cadmium exposed subjects with proximal tubular dysfunction is unfavourable. The mortality rate tended to increase as the severity of renal dysfunction progressed. These results were confirmed by a fifteen year follow-up study by Nishijo et al. (1995). The observed increases of mortality are due to heart failure and renal diseases.

In these Japanese studies, higher mortality rate was observed when the urinary excretion of β_2 -M was above 300 $\mu\text{g/g}$ creatinine. Among the environmentally exposed people of the Cadmibel study, urinary β_2 -M of 286 $\mu\text{g/24 h}$ (corresponding 203 $\mu\text{g/g}$ creatinine) was exceeded by 25 % in the high exposure group ($n=331$) (Staessen 1994). This suggests that for a part of the residents of polluted areas in Belgium, the cadmium exposure is at a level associated with increased mortality in the cited Japanese studies.

It remains to be elucidated whether also in contaminated areas and in risk groups in other countries of Europe, cadmium exposure is associated with higher mortality due to renal diseases. It is estimated that U-Cd of 4-5 $\mu\text{g/l}$ is associated with increased mortality. This urinary level cadmium and higher have been reported in the general population (non-contaminated areas, no occupational exposure), from Belgium, Germany, Japan and USA (refs.). The group of population characterised by the high levels of U-Cd is small. Approximates concerning Finland and Sweden are discussed later.

6.3.7 Conclusions on health effects of cadmium

Among the population group having the urinary cadmium of 2-4 $\mu\text{g/l}$, 1-5 % of people will suffer of renal or bone effects caused by cadmium. The renal effects start as increased excretion of high-molecular weight proteins in urine. There is evi-

Table 24. Health effects of cadmium caused by environmental (non-occupational) exposure and the respective urinary level of cadmium (U-Cd).

HEALTH EFFECTS	Critical urinary level of Cd *	Reference
Renal effects/dysfunction		
Increased urinary excretion of RBP, NAG, β_2 -M, AA, Ca	1.4-2.8 $\mu\text{g/l}$	Buchet et al.1990
Increased urinary excretion of albumin, Transferrin, β_2 -M, NAG, prostanoids, sialic acid	5.4 $\mu\text{g/l}$ **	Roels et al. 1993
Age related renal dysfunction, Decline of glomerular filtration rate	10 $\mu\text{g/l}$	Roels et al. 1993
Decrease of creatinine clearance	2.8-7.0 $\mu\text{g/l}$	Staessen et al. 1994
Increase of serum creatinine	1.6 $\mu\text{g/l}$ ***	Ewers et al. 1985
Increase urinary excretion of AAP, Alkaline phosphatase, NAG, α_1 -microglobulin	4.0 $\mu\text{g/l}$	Jung et al. 1993
Increased urinary excretion of NAG	3 $\mu\text{g/l}$	Kawada et al. 1992
Increased urinary excretion of NAG and AAP	2 $\mu\text{g/l}$	Muller et al. 1989
Increased urinary excretion of β_2 -M and albumin	1.62 $\mu\text{g/l}$	Nordberg et al. 1997
Increased urinary excretion of β_2 -M	3.8-4.1 $\mu\text{g/l}$	Ishizaki et al. 1989
Effects on calcium wasting		
Increased urinary excretion of Ca	1.0-5.6 $\mu\text{g/l}$	Buchet et al.1990
Increased urinary excretion of Ca	0.81 $\mu\text{g/l}$	Järup (unpublished data)
Stimulation of bone resorption via increased level of prostaglandin E2	2 $\mu\text{g/l}$	Roels et al. 1993
Decreased level of serum Ca in men	2.8-7.0 $\mu\text{g/l}$	Staessen et al. 1991

RBP=retinol binding protein; NAG=N-acetyl-b-glucosamidase; β_2 -M = urinary β_2 -microglobulin; AA= urinary aminoacids; Ca= urinary calcium; AAP= alanine aminopeptidase

*) These critical levels apply to groups and not to every individual. When the critical level is reached certain significantly increased number of people will suffer from renal effects or increased excretion of calcium.

**) The study group included also workers.

***) geometric mean.

dence that the renal effects are progressive and that renal failure may follow (e.g. increased serum level of creatinine). Furthermore there is some evidence of increased mortality due to renal diseases associated with high exposure to cadmium. This would apply to a part of the elderly population which has a high body burden of cadmium.

There is some evidence that even at the urinary cadmium level of about 1.0 $\mu\text{g/l}$, excretion of calcium will increase, which will decrease the

bone density and increase the risk of fractures. These data should be substantiated, before the U-Cd level of about 1.0 $\mu\text{g/l}$ can be used in the risk characterisation of cadmium. We consider, however, that these data emphasise the need for a conservative risk characterisation.

It is our conclusion that urinary Cd level of 2-4 $\mu\text{g/l}$ is associated with a risk of serious health effects. Although the evidence on the progression of cadmium induced renal effects and evidence of

increased risk of bone fractures is not conclusive, we consider that the recent results have increased the weight of evidence and there is a concern of impairment of public health particularly among the elderly population.

6.4 Risk characterisation

In most epidemiological studies, the health effects have been related to urinary levels of cadmium. Therefore, a comparison of exposure and health effects is made using the urinary level of cadmium (μg of Cd/l of urine).

Urinary Cd-concentration corresponding the average dietary intake in Finland

In the non-occupationally exposed population, according to reports from Sweden and USA, the cadmium concentration in urine is about 0.2-0.6 $\mu\text{g/l}$ (Kowal et al. 1979, Järup, Persson, Elinder 1995). In Sweden and in the USA, the level of dietary intake of cadmium is likely to be close to that of Finland (10 $\mu\text{g/day}$). In Finland, Sweden and USA contamination of agricultural soils by cadmium is not at the same level as in some European countries, where the average dietary intake is elevated. Limited number of urine samples from non-occupationally exposed non-smokers have normally contained less than 0.5 μg Cd/l in Finland (Kiilunen unpublished data). It is assumed for this evaluation that the average urinary level of cadmium in Finland is 0.4 $\mu\text{g/l}$. This is a basis for a conservative risk assessment, which needs to be confirmed or refuted by an adequate analytical study with sufficient number of non-occupationally exposed subjects.

In this assessment, it was found that the dietary intake of cadmium among recreational hunters, farmers and members of their families could be 15.6-17.4 $\mu\text{g/day}$ (see tables 20 and 21). This estimate does not apply to all farmer and recreational hunters, but only those having a high consumption of berries, mushroom and elk liver and kidney and those, who obtain some of their food from ash fertilized areas. The high dietary intake of this consumer group corresponds to 0.8 $\mu\text{g/l}$ of urinary concentration of cadmium (see table 25).

The number of farmers and their family members in 1998 in Finland was 157 362 (Tilastokeskus, Vuoden 1998 kulutustutkimus). Most of the recreational hunters are also farmers; recreational hunters (in rural areas) could be regarded as a sub-population of farmers. Using the exposure-distribution data presented by Louekari et al. (1989) it is assumed that 5 %, ie. about 8000 individuals of this sub-population may have the diet summarised in tables 20 and 21.

Increased absorption of cadmium

Flanagan et al. (1978) showed that women with low body iron stores had on average twofold higher gastrointestinal absorption (10 %) of cadmium as compared with the control group. The highest individual absorption rate was about 20 %. In experimental animals, Friberg et al. (1975) observed a three-fold increase in absorption of cadmium due to low levels of dietary calcium and protein. Kowal (1988) also found in a large nutritional survey (NHANES II) that urinary Cd was negatively and significantly correlated with dietary iron and dietary calcium. Also Berglund et al. (1994) found that reduced body iron stores (serum ferritin) were highly associated with higher B-Cd concentrations. Bäcklund et al. (1996) found that women 50-55 years of age had higher B-Cd levels (0.5 $\mu\text{g/l}$) than men of the same age (0.3 $\mu\text{g/l}$). The difference is probably caused by increased absorption of dietary cadmium in women with low iron status before menopause. Berglund et al. (1998) has assessed that 175 000-700 000 women in Sweden would have empty iron stores and consequently increased B-Cd levels, by about factor of 2. Furthermore, they estimated that, in Sweden about 250 000 smoking women with low iron stores are likely to have 4-6 times the kidney cadmium concentration as compared with non-smokers with adequate iron stores.

Accordingly, it is assumed that for the iron-deficient female sub-population the absorbed amount of cadmium is two-fold higher when compared with the average. For, the urinary level of cadmium of those having a high dietary intake

and increased absorption would be 1.6 µg/l. At present, it is not possible to accurately estimate the numbers of women among farmers, recreational hunters and their family members, who have the dietary habits described above and who are also iron deficient. It was suggested earlier (Louekari et al. 2000) that 2-8 % of the Finnish population would be iron deficient, which, applied to 10 000 people, would mean that 200-800 people (recreational hunters and their family members) are attributed by two of the risk factors, high dietary intake of cadmium and increased gastro-intestinal absorption. At this level, the numerical estimates are uncertain and, at the best, indicative of the magnitude of the groups.

Smoking

Heavy smoking increases the U-Cd remarkably. In Sweden it has been observed that the Cd-concentration in kidneys reflecting the long-term exposure is about 2-3 fold higher for smokers than for non-smokers (Elinder et al. 1976, Nilsson et al. 1995). Luoma et al. found that blood cadmium

level of smokers was three times higher than in non-smokers. Based on the above data and review on blood and urinary cadmium levels by Berglund et al. (1998) it is estimated that U-Cd of heavy smokers is about 2.5-fold as compared non-smokers with average dietary intake of cadmium. This implies that U-Cd of heavy smokers is about 1.0 µg/l. For heavy smokers, who have a high dietary intake of cadmium the urinary level of cadmium would be about 1.4 µg/l.

Total exposure and the respective urinary level of cadmium

Considering all the three risk factors, elevated dietary intake of cadmium in this sub-population of farmers and recreational hunters, increased absorption and smoking, it is estimated that the respective urinary level of cadmium is about 2.2 µg/l. This urinary cadmium concentration exceeds many of the critical concentrations specified in table 24. In fact there are more than three risk factors, as shown in figure 4. Some of the risk factors are either not well characterise (diabetes) or

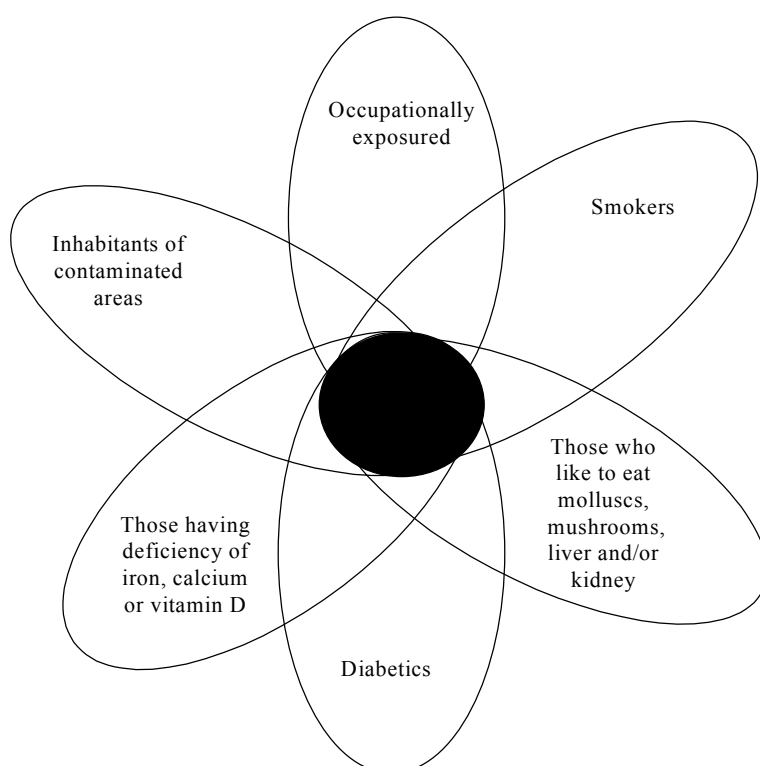


Figure 4. Risk groups. The size of the groups of populations attributed with several of these “risk factors” has not been studied.

not relevant for the present assessment (occupational exposure).

It is not reasonable to try and accurately estimate the number of people affected by all the three risk factors. Obviously, the number of heavy smokers among the 200-800 individuals, who have high intake and increased absorption of cadmium, is very small. As shown in the figure 4, the intersection of the risk groups is much smaller than the separate risk groups.

It was estimated earlier by Louekari et al. (2000) that in some population groups in Finland, the urinary Cd-level is about 2-3 µg/l. The size of risk groups identified in that study, however, was much larger than that presented in table 25 of the present report. For example, it was estimated earlier that there are 250 000 individuals in the Finnish population, who have a high dietary intake of cadmium (corresponding the urinary

concentration of 0.8-1.2 µg/l). For the present assessment it was calculated that approximately 10 000 recreational hunters and their family members living in rural areas have a high dietary intake of cadmium. Furthermore the number of people characterised by two or three of the specified risk factors is not known but is smaller than 200 individuals (see table 25).

Conclusions: Additional exposure and risk caused by foods obtained from forests

The consumption of forest berries, mushrooms and liver and kidney of elk by **an average Finnish consumer** is low. The intake of cadmium from berries and elk liver and kidney is considered negligible. The intake of cadmium from forest mushrooms by average consumer is approximately 1 µg/day.

Table 25 Comparison of estimated urinary levels of cadmium in Finland with the critical urinary concentrations in the middle-aged and elderly population.

Risk Group/ Exposure	Corresponding urinary Cd-concentration (µg/l)	Size of (sub-)population in Finland	Increased risk of health effects Specified below
Recreational hunters, and members of their families, who have a high dietary intake of cadmium	0.8	Approximately 10 000	None
High dietary intake + increased absorption (200 µg/day with two- fold absorption)	1.6	200-800	None
High dietary intake + increased absorption + smoking	2.2	?	<ul style="list-style-type: none"> ▪ Increased urinary excretion of RBP, NAG, β₂-M, AA, Ca ▪ Decrease of creatinine clearance ▪ Increased urinary excretion of AAP, Alkaline phosphatase, NAG, a1-microglobulin ▪ Increased urinary excretion of β₂-M ▪ Stimulation of bone resorption via increased level of prostaglandin E2 ▪ Decreased level of serum Ca in men

RBP=urinary excretion of retinol binding protein; NAG=urinary excretion of N-acetyl-b-glucosamidase, β₂-M=urinary β₂-microglobulin, AA=urinary aminoacids, Ca=urinary calcium, AAP=alanine aminopeptidase;

*) these critical levels often apply to groups and not directly to individuals, since the results have been gained by testing the significance of a difference between two or more groups with certain levels of urinary cadmium.

For the normal scenario for recreational hunters (in the Northern Finland), it is assumed that these hunters and members of their families eat a few meals containing liver or kidney of elk. They are also assumed to eat twice as much forest mushrooms as the average consumer and twice as much forest berries as the average inhabitant of Northern Finland. Justification for these assumptions is given in the chapters above. The dietary intake of cadmium is clearly higher among this consumer group (about 15.6 µg/day) as compared

with an average Finnish consumer (9.5 µg/day). As such this intake is considered to be safe. However, in case recreational hunters or their family members are also heavy smokers and have iron deficiency, which increases the absorption of cadmium, their body burden of cadmium may reach critical level and cause adverse health effects. However, this risk group is very small.

For the reasonable worst case scenario, it is assumed that **recreational hunters and members of their families** have the same food consumption

Table 26. Factors, which determine the health effects of ash fertilisation in specific risk groups.

Group of factors	Factor	Remarks
FERTILISATION PRACTICE	Frequency of ash fertilisation	Once in 20-30 years ?
	Amount of ash applied per treatment	1-20 tons (in published experiments)
	Concentration of Cd in ash	1.4-31 mg/kg (in published experiments)
SOIL	pH and buffer capacity	Greatly affects to the Cd-content of the soil solution.
	Organic matter	Retains cadmium in the upper soil layer.
UPTAKE BY PLANTS	Concentration of Cd in soil	Increases after ash fertilisation
	Species specific uptake of trace elements	Not well characterised
	Interactions with other trace elements	Not well characterised
	Amount of precipitation	Not well characterised
TENDENCY OF INCREASED CONCENTRATIONS OF CADMIUM AFTER FERTILISATION	Berries	Slight increase of Cd content in lingonberries, cloudberries and blueberries not affected
	Mushrooms	Depends on species, a great species-variation of the Cd-content is seen in several studies. In the most recent study, a clear increase of Cd concentration associated with the ash fertilisation was seen.
	Liver and kidney of elk	Not known. Concentration may elevate, since the feed of elk and hare (phloem of young trees) have high Cd concentration
CONSUMPTION OF FOOD ITEMS AFFECTED	Age-, sex-, and area specific food preferences	This factor is significant. Recreationla hunters and their family members consume more "forest foods" as the average consumer.
	Intake/need of calories	May be relevant for some consumer groups.
INCREASED GASTRO-INTESTINAL ABSORPTION OF CADMIUM	Deficiency of iron	Increases the absorption of cadmium and the risk significantly
	Deficiency of vitamin D and other nutrient deficiencies	Not well characterised
SMOKING		Increases the exposure to cadmium and the risk significantly
RELATION OF ACTUAL CD-UPTAKE AND CRITICAL/ADVERSE LEVELS IN THE RISK GROUP	Measured/estimated uptake	Estimated urinary Cd-concentration in risk group is 2-3 µg/l whereas the critical level associated with adverse health effects is 2-4 µg/l.
SIZE OF THE RISK GROUP		Can not be estimated accurately, is probably rather small.

habits as listed in previous scenario. In addition, it is assumed that berries, mushrooms, liver and kidney come from **ash fertilized areas**. For this small group of people, the dietary intake of cadmium is 17.4 µg/day, which is slightly higher than in the previous scenario. Also this level of exposure only causes a risk, if these people are smokers and iron deficient as well.

The dietary intake of cadmium by some recreational hunters and farmers is about two-fold as compared with the average Finnish consumer. On the basis of current data, ash fertilization does not remarkably increase the cadmium exposure of this population group. There is a need for more data on the effect of ash fertilization on the Cd-content of mushrooms and liver and kidney of elk to confirm or refute the preliminary estimates presented in this report.

Factors, which determine the health effects of cadmium in forest fertilizers, are summarized in the table 26. Several of these factors are not sufficiently characterised. Therefore, the possible long-term accumulation of cadmium in forest ecosystem and consequent adverse effects should be studied and minimised, before the ash fertilisation becomes a broadly applied practice.

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ABBREVIATIONS AND DEFINITIONS

AA	Aminoacids
AAP	Alanine aminopeptidase
Acute toxicity	The adverse effect occurring within a short time following the administration of a single dose or multiple doses given within this short time period
Adsorption	The adhesion of molecules to the surfaces of solids
Alkalinity	The acid-neutralizing (i.e. proton-accepting) capacity of water; the quality and quantity of constituents in water which shift the pH towards the alkaline side of neutrality
BCF	Bioconcentration factor: the ratio of the test substance concentration in the test organism (e.g. fish, plant) to the concentration in a medium (e.g. water, soil) at steady-state conditions
Bioaccumulation	The net result of the uptake, distribution, and elimination of a substance due to all routes of exposure, i.e. exposure to air, water, soil/sediment and food
Bioconcentration	The net result of the uptake, distribution and elimination of a substance due to water-borne exposure
Biomagnification	The accumulation and transfer of chemicals via the food web (e.g. algae -invertebrate-fish-mammal) due to ingestion, resulting in an increase of the internal concentration in organisms at the succeeding trophic levels
BAF	Bioaccumulation factor is the ratio between the measured test substance concentration in the organism and that in the soil in a steady-state condition
Cadmibel	A large epidemiological study on health effects of cadmium on the general population in Belgium, reported in various journals in 1990-1996
CEC	Cation exchange capacity
Chronic toxicity	Extended or long-term exposure to a stressor. Long-term effects related to the changes e.g. in metabolism, growth, reproduction, or ability to survive. Exposure concentrations are usually low
DOC	Dissolved organic carbon
dw	Dry weight

EC₅₀	Median effective concentration: 1. the concentration resulting in a 50% change in a parameter (e.g. algal growth) relative to the control, 2. the concentration at which a particular effect (e.g. daphnia immobilization) is observed in 50% of the organism population relative to the control
fw	Fresh weight
LC₅₀	Median lethal concentration: a statistically derived concentration that can be expected to cause death in 50% of animals exposed for a specified time
LOEC(L)	Lowest observed effect concentration (level). The lowest concentration of a material used in a toxicity test that has a statistically significant adverse effect on the exposed population of a test organism compared with the control
NAG	N-acetyl-b-glucosamidase
NHANES II	U.S. National Health and Nutritional Examination Survey II
NOAEL	No observed adverse effect level
NOEC	No observed effect concentration. The highest concentration of a test substance to which organisms are exposed that does not cause any observed and statistically significant adverse effects on the organism compared with the control
PEC	Predicted environmental concentration: the expected concentration in an environmental compartment. The PEC can be based on either measured or calculated data
PNEC	Predicted no effect concentration: environmental concentration which is regarded as a level below which the balance of probability is that an unacceptable effect will not occur
PTWI	Provisional tolerable weekly intake
Safety factor	A factor applied to an observed or estimated toxic concentration or dose to arrive at a criterion or standard that is considered safe. Safety factor, assessment factor and uncertainty factor (UF) are often used synonymously.
ww	Wet weight

ANNEX 1

1 Background cadmium concentrations

1.1. In biota

In order to give some general ideas about the background concentrations in biota in Finland some studies are here referred to.

1.1.2 Cadmium concentration in berries

Cadmium concentrations of forest berries are generally low, < 1 mg/kg dw (Table 1). The Cd concentration of lingonberries (*Vaccinium vitis-idaea*) have varied between 0.004 to 0.3 mg/kg dw which is of the same magnitude or slightly higher than those in blueberry (*Vaccinium myrtillus* L.), but clearly lower than those in cloudberry (*Rubus chamaemorus* L.) (Silfverberg and

Issakainen 1991). According to Silfverberg and Issakainen (1991) the cadmium concentration in cloudberry and *Vaccinium uliginosum* were 0.36 - 0.69 and 0.36 mg/kg dw, respectively.

In Lapland the average cadmium concentration in lingon- and blue berries was 0.010 and 0.024 mg/kg dw, respectively (Laine et al. 1993).

1.1.3 Cadmium concentrations in mushrooms

Mushrooms have clearly higher Cadmium concentrations than berries (Table 2). Variation of cadmium concentration between different species and group of mushrooms is great. Generally, most of the mycorrhizal species typical for Finnish forest ecosystems have concentrations below 1 mg/kg dw (Kojo & Lodenius 1989).

Table 1. Cadmium concentrations (mg/kg dw) in forest berries.

	Lingonberry	Blueberry	Cloudberry	Vaccinium uliginosum	Place	References
Average concentration Sample number			0.36-0.69 4	0.10-0.14 11	Oulu district	Silfverberg and Issakainen 1991
Average concentration Range Sample number	0.01 0.009-0.045 150	0.02 0.009-0.095 204			North of Finland	Laine et al. 1993
Average concentration Range Sample number	0.02 0.009-0.086 8				Kuola	Laine et al. 1993
Average concentration Range Sample number	0.020 0.007-0.068 4	0.017 0.008-0.025 3			Fresh and frozen berries on the market	Varo et al. 1980
Average concentration Range Sample number	<0.014 4	0.025 0.008-0.084 7				Varo et al. 1980
Average concentration Range Sample number	<0.011 <0.007-0.029 6	<0.008 <0.008 2			North of Finland	Lapin läänin-hallitus 1988
Average concentration Range Sample number	<0.014 <0.014 2	<0.02 <0.02 3			East of Lapland	Lapin läänin-hallitus 1989
Average concentration Range Sample number	0.04 0.00-0.23 31	0.08 0.00-0.30 37			All over the Finland	Hårdh 1977
Average concentration Range Sample number	0.054 0.003-0.02 37	0.07 0.04-0.17 22			Study of food stuffs	Piepponen 1988
Average concentration Range Sample number	0.0032 0.0008-0.007 3	0.001 0.0-0.003 5			Berries on the market	Tahvonen & Kumpulainen 1991

According to Eurola et al. (1996) the cadmium contents of different mushrooms species varied considerably. The average concentration of the seven commercially important mushroom species was 0.79 ± 0.98 mg/kg dw (0.07 ± 0.09 mg/kg fw). The level of cadmium was in general below the maximum permitted levels established in the Finnish Food legislation. However, the average cadmium content of *Boletus* and *Leccinum* species and *Rozites caperata* were above the permitted level (0.1 mg/kg fw) due to the strong ability of these species to accumulate cadmium.

1.1.4 Cadmium concentration in lichens and moss

According to the nation wide sampling network which systematically covers the country as a whole (788 samples) the average cadmium concentration

in mosses, lichens and bark is 0.38, 0.69 and 0.31 mg/kg dw, respectively (Lippo et al. 1995).

According to Kubin (1990) the mean cadmium content of lichen (*Hypogymnia physodes*) is 0.70 mg/kg dw, with a range of 0.12-4.25 mg/kg. The fairly broad area of high cadmium concentrations in lichens are found in the western part of the Finland, at the northern tip of Gulf of Bothnia and in Lapland at a latitude at which a substantial mining industry is found across the border in the Russia (Kubin 1990).

In an extensive moss survey by Rühling (1994, ref. in Lodenius et al. 2000) background concentrations of cadmium were less than 0.2 mg/kg in most parts of the Scandinavia with a decreasing trend from south to north.

1.1.5 Cadmium concentration in invertebrates

High concentrations of cadmium (6-10 mg/kg dw) have been noticed in some ant species (Lodenius 1995). According to Ylä-Mononen et al. (1990) cadmium content of different ant species and genus collected in the vicinity of spruces of different degrees of needle-loss varied significantly. In different species of genus *Formica* cadmium content (5.0 - 6.7 mg/kg dw, mean content) was 8-10 times higher than in genus *Myrmica* (0.3 - 0.6 mg/kg dw, mean content). The observed difference between *Myrmica* and *Formica* obviously depends on the fact that *Formica* ants consume large amounts of metalliferous honeydew produced by phloem-feeding cinarid aphids on conifers. *Myrmica* species, on the other hand, consume mostly insects and seeds, and lesser extent of honeydew from herbs and deciduous shrubs.

The body concentration of metals in invertebrates differs between taxonomic groups, species and even individuals within one species. Hunter et al (1987, ref. in

Table 2. Cadmium contents in fungi (mg/kg dw) (Kojo and Lodenius 1989).

Species	N	Cadmium mg/kg dw
Fruiting bodies growing on lawns:	21	11 mean (range 1.0-84)
<i>Agaricus sp.</i>	13	19 mean (range 1.0-84)
<i>Coprinus comatus</i>	1	2.2
<i>C. atramentarius</i>	1	1.3
<i>Lyophyllum connatum</i>	1	5.5
<i>Marasmius oreades</i>	1	1.3
<i>Calvatia excipuliformis</i>	2	2.3-2.6
<i>Bovista nigrescens</i>	1	2.8
<i>Lycoperdon pyriforme</i>	1	3.2
Fruiting bodies growing in forests:	37	4.9 mean (range 0.09-25)
<i>Paxillus involutus</i>	1	0.89
<i>Trichloma album</i>	1	1.3
<i>Lactarius necator</i>	7	1.1 Mean (range 0.4-2.3)
<i>L. rufus</i>	1	0.61
<i>L. torminosus</i>	1	0.51
<i>Russula sp.</i>	6	1.2 Mean (range 0.09-2.5)
<i>Amanita muscaria</i>	4	22 mean (range 17-25)
<i>Chroogomphus rutilus</i>	2	0.35-0.65
<i>Clitocybe sp.</i>	1	1.0
<i>Lepista nebularis</i>	1	1.3
<i>Cantharellula umbonata</i>	1	3.4
<i>Hygrophorus pustulatus</i>	1	2.9
<i>Cantharellus cibarius</i>	1	0.45
<i>C. tubaeformis</i>	1	0.70
<i>Leccinum scabrum</i>	2	0.94-3.5
<i>L. versipelle</i>	1	13
<i>L. vulpinum</i>	1	7.5
<i>Suillus granulatus</i>	1	1.3
<i>Boletus edulis</i>	2	9.8-15
Fruiting bodies growing on trees:	2	2.8 mean (range 1.1-4.4)
<i>Pholiota squarrosa</i>	1	4.4
<i>Mycena galericulata</i>	1	1.1
Total	60	7.5 mean (range 0.09-84)

Bengtsson & Tranvik 1989) ranked groups of invertebrates collected in the vicinity of a copper/cadmium plant on basis of their concentration of cadmium in decreasing order as follows: *Isopoda*, *Oligochaeta*, *Arachnida*, *Collembola*, *Carabidae* and *Chilopoda*.

1.1.6 Cadmium concentration in vertebrates

There is a wide variation in cadmium concentrations among mammals. In terrestrial vertebrates cadmium is usually accumulated in kidneys and, to a lesser extent, in liver (table 3).

According to Heikura et al. (1997) cadmium concentrations in insectivorous common shrews are higher than herbivorous bank voles (table 4). It was assumed that a deposition of cadmium is less in Oulanka than in other study areas, because a part of the cadmium comes with the southerly/southwesterly winds and Oulanka is situated about 200 km farther north than other areas. Consequently, cadmium concentrations of animals in Iso-Palonen study area situated nearest to the mining combine of Kostomuksha, are more close to the cadmium levels found in densely populated industrial areas than in natural forests.

1.1.7 Cadmium concentration in plants

In vascular plants cadmium concentrations vary considerably even though they usually are very low. The concentrations in spruce (*Picea abies*) and May Lily (*Maianthemum bifolium*) are usually below 0.3 mg/kg dw (Kanerva et al. 1988, ref. in Lodenius et al. 2000) while higher concentration can be found from *Salix* species. In coniferous trees the concentrations are highest in the phloem and bark .

Table 4. The mean cadmium concentrations (mg/kg) in bank voles (*Clethrionomys glareolus* Scrb.) and common shrews (*Sorex araneus* L.) in Oulanka national park and Friendship park (Elimys, Juortana, Iso-Palonen). Concentrations were analysed in combined liver and kidney samples (Heikura et al. 1997).

	Bank voles	Common shrews
Oulanka	0.17±0.013	0.95±0.139
Elimys	0.79±0.262	2.93±0.295
Juortana	0.91±0.196	2.28±0.216
Iso-Palonen	1.45±0.320	3.42±0.396

1.2 Cadmium concentrations in lakes, rivers and groundwater

Deposition of cadmium in headwater lakes, streams, and groundwater show large regional differences, reflecting differences in bedrock geochemistry and catchment characteristics. The background concentrations of cadmium in Finnish lakes is generally low. According to NIVA (1999) a median concentration of cadmium in Finnish lakes located throughout Finland and selected at random is 0.01 µg/l. The 90-percentile value for cadmium in surface waters is 0.03 µg/l. Elevated cadmium concentrations are found in north of and in west of Finland. Cadmium concentration in Finnish rivers is typically between 0.01 - 0.04 µg/l (Tarvainen et al. 1997).

According to Tarvainen et al. (2001) (submitted manuscript) the mean cadmium concentration (n=739) in wells, springs and springwells is 0.0436 µg/l, with a range of <0.02-1.27 µg/l. In drill wells (n=263) the mean value is below the detection limit (<0.02 µg/l) and the maximum concentration in 0.56 µg/l.

Table 3. Cadmium concentration (mg/kg ww) in some Finnish mammals (ref. in Lodenius et al. 2000).

Species	Muscle	Liver	Kidney	Reference
Mountain hare (<i>Lepus timidus</i>)	0.006	0.45	11	Venäläinen & Niemi 1994
Brown hare (<i>Lepus europaeus</i>)	0.003	0.16	1.9	
Elk (<i>Alces alces</i>)	<0.1	0.36-0.55	2.3-3.5	Valtonen & Vikberg 1982
Reindeer (<i>Rangifer tarandus</i>)	0.001 (young) 0.003 (adult)	0.27 0.65	0.88 3.5	Rintala et al. 1995
Common shrew (<i>Sorex araneus</i>)	1.3	3.3	6.9	Bergbom unpubl; Nuorteva 1990
Field vole (<i>Microtus agrestis</i>)	0.12	0.34	0.80	
Bank vole (<i>Clethrionomys glareolus</i>)	0.78	0.68	3.2	

