



High tech-metals in the environment and health

Lithium and cobalt

Anne Kousa, Soili Mattila and Maria Nikkarinen



29.5.2013

Arkistoraportti 53/2013





GEOLOGICAL SURVEY OF FINLAND

DOCUMENTATION PAGE

29.5.2013

Authors Anne Kousa Soili Mattila Maria Nikkarinen		Type of report Arkistoraportti	
		Commissioned by GTK/Minera	
Title of report High tech-metals in the environment and health. Lithium and cobalt.			
Abstract Demand for high-tech-metals is increasing because of the rapid expansion of information and communications technology and developments in so called green technology applications over the next few decades. These metals are crucial manufacturing advanced technological products, including circuit boards, semiconductors, coatings, magnets, mobile phones, computers, home electronics, solar panels, wind power plants and electric cars. There is only a limited amount of information available about the potential exposure to natural occurring hi-tech-metals. Therefore the objective of this regularly updated report is to compile the information on high-tech-metals distribution in the environment and in the food chain, human exposure and potential health effects from the literature available. Nowadays high-tech metal exploration and beneficiation form one of the prime subjects of ore research in Finland. The increased amount of processing of these metals justifies highlighting their potential effects on human health. The selection of the high-tech-metals discussed in this report is based on the record of critical and significant metals defined by European Union (EU). This first report covers information about lithium and cobalt.			
Keywords			
Geographical area			
Map sheet			
Other information			
Report serial		Archive code Arkistoraportti 53/2013.	
Total pages 35	Language English	Price	Confidentiality
Unit and section Eastern Finland Office, Land Use and Environment		Project code 2241000/3241000	
Signature/name Jari Hyvärinen Division Manager		Signature/name Anne Kousa Senior Scientist	





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1 INTRODUCTION

Antimony (Sb), beryllium (Be), cobalt (Co), gallium (Ga), germanium (Ge), indium (In), iridium (Ir), lithium (Li), niobium (Nb), platinum (Pt), palladium (Pd), rhodium (Rh), ruthenium (Ru), tantalum (Ta) and certain rare earth elements (REE) among others are examples of hi-tech-metals. Although these metals are needed only in small amounts in the high technology production, they are strategically very important. The economic growth of developed countries is greatly dependent on new technological innovations based on new metallic alloys. Hi-tech-metals are crucial in the production based on a new technology, e.g. tantalum on mobile phone and indium in flat panel television (LCD TV) productions. Tellurium is used in semiconductors and lithium batteries in the electronic industry. Cobalt is used in stainless steel production and aerospace equipments. Lithium and cobalt are also used in pharmaceutical industry. High tech-metals often occur as the by-products of mining. Indium, for example, is available as the by-product in zinc mining.

The health effects of the environmental hi-tech-metals are poorly understood. The scientific publications of the bioavailability of hi-tech-metals from environment to humans is scantily available. Hi-tech-metals are probably not essential trace elements for human health, but vice versa there are indications that most of them are harmful at high concentrations. Human exposure to natural hi-tech-metals can occur through several routes. The general population may get exposed to trace elements by ingestion (drinking water and nutrition) and inhalation of air dust and vapors and in some cases in dermal contact.

Several trace elements essential to humans are essential also to animals (Kabata-Pendias & Mukerjee 2007). However, most of elements that may be harmful to both, humans and animals, are not toxic to plants. Therefore in plants in the food chain humans may get exposed to harmful elements (Kabata-Pendias & Mukerjee 2007, Figure 1).

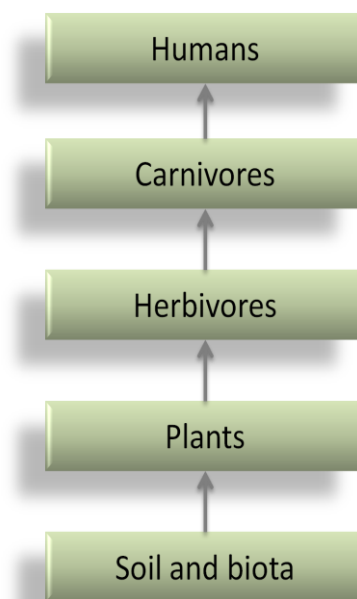


Figure 1. Transferring of chemical elements in terrestrial trophic chain (after Kabata-Pendians & Mukherjee 2007).

2 LITHIUM

2.1 Properties

Lithium was discovered in petalite mineral by the Swedish chemist Johan August Arfvedson (1792-1841) in 1817. The name of lithium is derived from Greek word lithos, meaning stone or rock. Lithium is the 27th most abundant element in nature. It is the lightest naturally occurred metal. It is inflammable and highly reactive as a pure element. Therefore Li is not found naturally as a pure element but it is always present as salts, oxides, or other combined forms (Oregon Health Authority, 2011). Low levels of lithium in drinking water are odorless, colorless and without taste (Oregon Health Authority, 2011). Properties of lithium has been presented in Table 1.

Table 1. Properties of lithium

Symbol	Li
Atomic number	3
Group	1, alkali metals
Period	2
Melting point	180.54°C
Boiling point	1342°C
Density	0.53 g cm ³
Oxidation states	1
Chrystal structure	cubic
Mohs hardness	0.6
Colour	Silver-white
Naturally-occurring stable isotopes	⁶ Li, ⁷ Li

One of a most important use of lithium is in batteries for electronic appliances. Li- batteries are used especially in cameras, mobile phones, laptops, mp3 players etc. Li is also used in lightweight metal alloys together with other metals like magnesium and aluminium in airplane and car industry. Li is used in glass and ceramic production as well as an additive in cement. Chile (64%), USA (17%) and China (17%) are the main countries for lithium production. In the area of EU, the lithium is produced only in Portugal and in Spain (Weber et al. 2011).

Li is a biologically active element. In clinical practice, Li has widely been used in pharmacological doses for the treatment of manic-depressive disorder for decades. Australian psychiatrist John Cade discovered lithium as the treatment of manic depression in 1949 (Cade 1949).

2.2 Distribution in the environment

Lithium is widely distributed in environment. Trace amounts of Li are found in many minerals, nearly all igneous rocks and it is also a component of many mineral springs (Lide DR 2005). Lithium belongs to the group of alkali metals and does not occur as free metal in natural environment (Lide DR 2005). Lithium concentration in the Earth crust is on average 20-25 ppm (Kabata-Pendias & Mukherjee 2007). Li occurs mainly in silicate minerals and associates as accessory element with K-feldspar, biotite, amphibole and clay minerals such as illite. Several pegmatite minerals like spodumene ($\text{LiAlSi}_2\text{O}_6$), lepidolite $\text{K}(\text{Li},\text{Al})_3(\text{Si},\text{Al})_4\text{O}_{10}(\text{F},\text{OH})_2$ and petalite ($\text{LiAlSi}_4\text{O}_{10}$) are compounded of lithium (De Vos et al 2006). During magmatic differentiation Li is enriched in the late pegmatitic stage when micas, certain pyroxenes, and tourmaline crystallize. The Li/Mg ratio increases during magmatic differentiation and Li begins to replace Mg only in the late, pegmatite stage. Together with aluminum, Li has replaced magnesium and iron in crystal lattices (see eg. Koljonen et al. 1992). The most important Li ore, spodumene, contains up to 8.0 w% insoluble Li_2O (Aral & Vecchio-Sadus 2008). While lithium is present in natural environment, it is therefore found in plants, animals, food products and beverages (Oregon Health Authority, 2011). Li is easily absorbed by plants acting as indicator of soil lithium concentrations (Lenntech 2007). The concentrations of lithium in the environment are presented in Table 2.

Table 2. Concentrations of lithium in the environment.

Media	Earth crust mg/kg^{-1}	Igneous rocks mg/kg^{-1}	Soil mg/kg^{-1}	Surface water $\mu\text{g/l}^{-1}$	Sea water $\mu\text{g/l}^{-1}$
Li	20-70 ³	0.5-40 ²	2 – 175 ²	<0.005 – 356 ¹	170 – 200 ²

¹ Salminen et al. 2005

² Kabata-Pendias & Mukherjee 2007

³ Kamienski et al. 1995

2.3 Lithium in waters

Micas and amphiboles are typical host minerals for Li and therefore granites and schists are enriched in Li (Frengstad et al. 2010). Li has no clear solubility ceiling so it is conceivable that Li can be used as an in-

indicator of water-rock interaction (Frengstad et al. 2010). In fresh water and sea water Li occurs as Li^+ (Kjølholt et al. 2003). Li concentrations varied between 1 and 10 $\mu\text{g/l}$ in surface water (Schrauzer 2002, Lennetech 2007) being an average 180 $\mu\text{g/l}$ in sea water (Reiman & Caritat 1998). Li is found in natural brines varying from 20 mg/l in Dead Sea to 1500 mg/l in Salar de Atacama in Chile (Habashi 1997, Moore 2007). The range in river water was 0.16-4.5 $\mu\text{g/l}$ (Gaillardet et al. 2003). Li concentrations in ground water varies between <0.05 to 150 $\mu\text{g/l}$ (Matschullat 1997). Median value of Li in ground water in Southern Norway is 3.6 $\mu\text{g/l}$ (Reiman-Caritat 1998). Very high concentrations in drinking water, over 1000 $\mu\text{g/l}$, have reported from Austria (Kapusta et al. 2011), northern Chile (Zaldivar 1980) and northern Argentina (Concha et al. 2010). In temperate humid zones the Li levels in ground water are lower than in dry, hot regions. Li concentrations, 15000 $\mu\text{g/l}$, have been reported from those hot areas. Using water with Li 5-100 $\mu\text{g/l}$ for irrigation could be harmful to cultivated plants (Kabata-Pendias & Mukherjee 2007).

Median values of Li in Nordic tap water (Norway, Sweden and Finland) and in Nordic bottled water were 0.54 $\mu\text{g/l}$ and 0.64 $\mu\text{g/l}$, respectively (Frengstad et al. 2010). The median value of Li in European bottled waters, 9.94 $\mu\text{g/l}$ (Reimann & Birke 2010) was about 15 times higher than that in Nordic bottled waters. There is no drinking water standard in the EU for Li.

2.4 Soil and plants

Lithium is present in trace amounts in all soil types especially in the clay fraction (Schrauzer 2002). In the terrestrial environment Li is present as lithium carbonate Li_2CO_3 , lithium chloride LiCl or lithium oxide Li_2O (Kjølholt et al. 2003). Estimated mean of world Li concentrations in soil is 20 mg/kg . The concentrations of Li in urban soil and forest soil in humus in Norway is 17.8 mg/l and 0.5 mg/kg , respectively (Reimann & Caritat, 1998). Li is considered easily available to plants. In general, the amount of lithium in plants varies between 0.2 ppm and 30 ppm (Lennetech 2007). It is not required for plants growth but it has been reported to stimulate their growth (Aral & Vecchio-Sadus 2008). On the other hand, there are great differences in the ability of plants to take up Li. Plants in Rosaceae-family have the highest tolerance to Li. Li accumulate to the plant of rose family especially when plants were grown on soil rich in Li (Kabata-Pendias & Mukherjee 2007). Mushrooms seem to be low in Li. The Li concentra-

tions of 17 mushroom taxa varied between 0.064 ppm and 0.609 ppm (Vetter 2005). In moss Li concentrations varied from 0.22 in Norway to 0.34 mg/kg in Germany (Reiman & Caritat 1998). Higher uptake of Li by plants is detected from acidic than alkaline soils (Aral & Vecchio-Sadus 2008). The acidity of soil increases the solubility of some heavy metals like Fe, Ni, Co, Mn and Cu, and also to some extent Al, Pb and Cd. Li concentrations of plants correlated significantly with those elements (Aral & Vecchio-Sadus 2008)

2.5 Air

The occurrence of data on Li in the air is scantily available. Li concentration in air dust is probably associated with its concentrations in fine granulometric fractions in soil (Kabata-Pendia- Mukherjee 2007). The maximum Li concentrations in air varied from 2.3 ng/m³ in world polluted area to 8.9 ng/m³ in world remote area (Reiman & Caritat 1998).

2.6 Distribution of lithium in Finland

Potential Li deposits are found in Kokkola, Kaustinen and Kruunupyy areas in western Finland and Forssa, Tammela and Somero areas in southwestern Finland. Li₂O-concentration is on average 1 % (Tuusjärvi et al. 2009). Lithium concentrations are typically quite low in natural waters being from 1 to 10 µ/l. In rural Finland, median of Li in groundwater is 0.8 µ/l in dug wells and 3.31 µ/l in drilled wells (Tarvainen et al. 2001). The regionally highest Li concentration in the waters pumped from drilled bedrock wells were found in the clay rich western and southern coastal areas of the country. High concentrations were found also in rapakivi areas in south-eastern and south-western Finland (Fig. 2). Li concentrations in ground water in Finland are presented in Table 3.

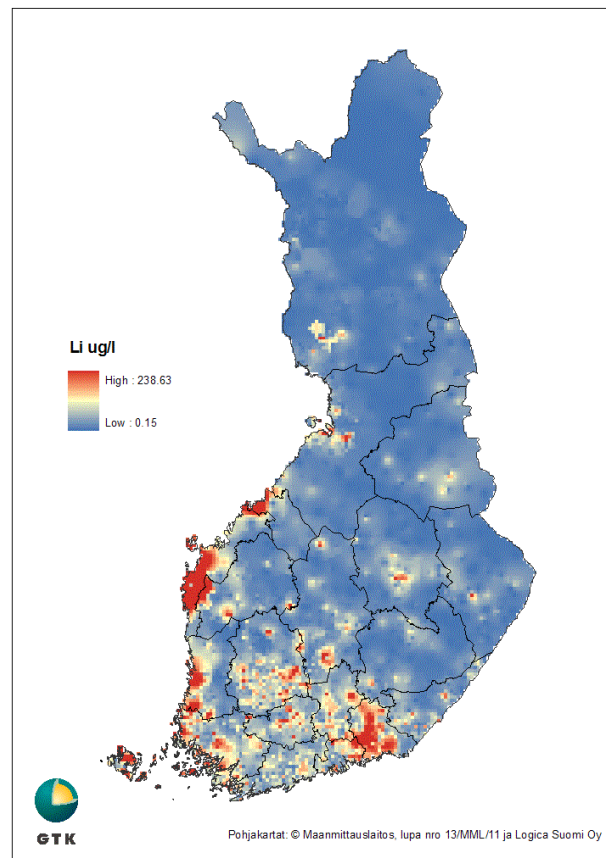


Figure 2. Distribution of Li in ground water in Finland.

Table 3. Li concentrations ($\mu\text{g/l}$) in well water in Finland (Tarvainen et al. 2002)

Well type	N	2 %	Median	Mean	SD	98 %	Max
Dug wells	739	<0.3	0.77	2.79	9.78	17.4	242
Drilled wells	263	<0.3	3.31	6.6	8.5	33.6	47,3

In Finland, the highest Li concentrations in soil were found in glacial till (Fig. 3). Median Li concentration in data of regional geochemical mapping, consisting one sample/ 4 km^2 , was 11.1 ppm (Salminen et al. 1995). In Atlas material, where the sampling density was one sample/ 300 km^3 , the median Li concentration was 14.9 ppm (Koljonen et al. 1992).

The median of total Li concentration in humus was 0.53 mg/kg and the range 0,22- 3,58 mg/kg in old mining area Luikonlahti. The median value of the available fraction of Li was 0.1 mg/kg and the range 0,03-0,53 mg/kg (Nikkarinen & Karlsson 2012). In whole country Li concentration in humus is an average 0.6 mg/kg (Salminen et al. 2003). Li concentrations in soil are presented in Table 4.

Li concentrations in all mushrooms samples taken from old mining area Luikonlahti were under the detection limit (< 0.1 mg/kg) (Makkonen et al. 2013). Li likely originates from the stable silicate minerals and insoluble Li does not end up in food chain via mushrooms.

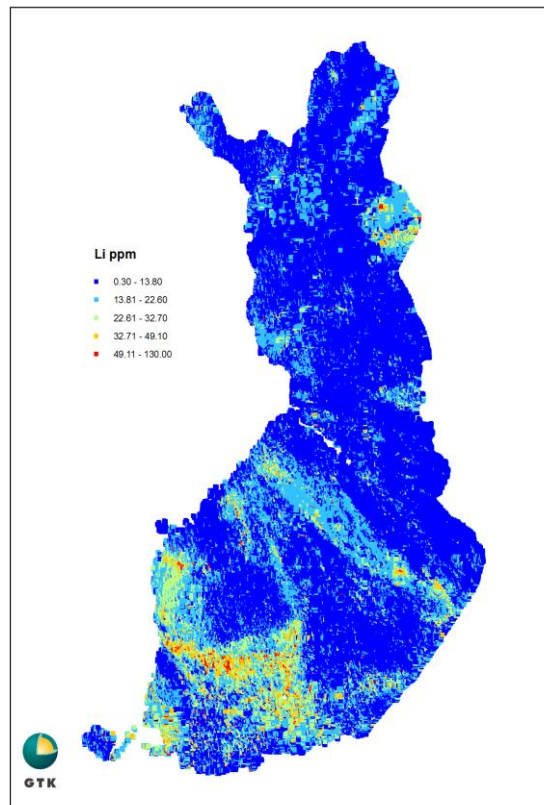


Fig 3. Li concentration in glacial till in Finland (source: GTK).

Table 4. Lithium in soil in Finland (mg/kg)

Material	Median	Range	N
Glacial till	11,1	2,65-183	82062 ¹
Stream sediment	9,5	2,4-32	1050 ²
Humus	0,6 ³	-	-
Humus tot. Li	0.53	0.22-3.58	70 ⁴
Humus available fraction	0.1	0,03- 0,53	70 ⁴

¹ Salminen, 1995, *fraction < 0,06 mm*² Lahermo et al. 1996³ Salminen et al. 2003 (Eastern Baltic Region)⁴ Nikkarinen & Karlsson, 2012. (Luikonlahti)

2.7 Environmental exposure

Li in major ore mineral spodumene is tightly bound to crystal structure and therefore it alone does not cause toxicological problems to humans or animals (Aral & Vecchio-Sadus 2008). However, crushed spodumene generates silica-rich dust which is a health and safety hazard. Occurrence of Li varies geographically and therefore environmental exposure and intake of Li vary in different areas. Lithium is found in various environmental media and therefore the general public could be exposed to small amounts of lithium via inhalation of ambient air, ingestion of food and drinking water (Hazardous Substances Data Bank HSDB 2007). However, inhalation and dermal contact are not likely to be significant routes of exposure to Li (Salocks & Kaley 2003). Metals are virtually poorly absorbed across the skin, so it is not likely that contact with metallic lithium will result in appreciable systemic absorption. Young children may exposure for Li by eating of small scraps of Li foil. Ingestion might be the most significant exposure route especially for children (Salocks & Kaley 2003).

2.8 Intake

General population could get exposed to lithium in food, beverages, air and soil. According to Oregon Health Authority (2011), the ingestion of lithium is usual and it is probably beneficial to health at low doses. The average dietary Li intake is about 2 mg per day (about 0.03 mg/kg/day for a 70 kg man) (Bellile 1994). Grains and vegetables, intake 430-2900 µg/day (Table 5.), are primary dietary sources of Li contributing from 66 % to 90 % of the total Li intake. The remainder of the intake is from the animal derived food stuff (Schrauzer 2002). The U.S. Environmental Protection Agency (EPA) has estimated the daily Li intake range from 650 to 3100 µg in adult person with 70 kg (Saunders 1985). The mean daily Li intake for adults was 8.6 ± 4.6 µg/day in Belgium (range 1.2- 15.2 µg/day) (Van Cauwenbergh et al. 1999).

A daily consumption of 100g fresh mushroom yields 1-6 µg Li intake per person (Vetter 2005). This covers less than 1 % of the daily requirements of Li and therefore mushrooms are not important source of Li in humans. Ingested Li in the form of its soluble salts is absorbed to practically 100% from the small intestine via the Na⁺-channels (Schrauzer 2002) and excreted renally in approximately 24 h (Freeman & Freeman 2006, Oregon Health Authority, 2011).

Table 5. Sources of dietary lithium.

Food Group	Quantity ingested kg food/day	Li Level mg/kg food	Total intake µg/day
Grains and vegetables	0.85	0.5–3.4	430–2900
Dairy products	0.44	0.50	222
Meat	0.21	0.012	2.5
Total			650–3100

Original data: Weiner 1991, adapted from Schrauzer 2002.

2.9 Toxicity and Carcinogenicity

The major mined Li ore spodumene is an aluminium silicate containing up to 8.0 w% Li_2O . This Li is tightly bound to the crystalline structure and therefore it does not pose a toxicological problem (Aral & Vecchio-Sadus 2008). However, during crushing process spodumene generates silica-rich dust causing health and safety hazard.

Metallic lithium is mildly toxic via oral intake but there are differences in physical tolerance between individuals (Aral & Vecchio-Sadus 2008). The central nervous system is the target organ for Li toxicity (Kjølholt et al. 2003). Most of the toxicity information pertains to the pharmaceutical use of lithium carbonate and citrate (Salocks & Kaley 2003). Lithium salts, like lithium carbonate and lithium citrate, are used in treatment of manic depression. In clinical use, the therapeutic window between effective dose and toxic dose is very narrow. In animal experiments in rats, a lethal dose of LiCl at 526-840 mg/kg of body weights has been observed. A dose of 5 g of LiCl can cause fatal poisoning in humans. Li carbonate is applied in psychiatry in doses close to the maximum intake level (Aral & Vecchio-Sadus 2008). Mild lithium poisoning occurs in humans with 10 mg/l Li in blood. 15 mg/l of Li in blood inflict confusion and speech impairment and the concentration of 20 mg/l Li cause a risk of death (Aral & Vecchio-Sadus 2008). Acute poisoning may ensue when a child, for example, ingests lithium accidentally (Timmer & Sands 1999).

The International Agency for Research on Cancer (IARC) does not classify Li as a carcinogenic agent (IARC 2012).

2.10 Ecotoxicological effects

Lithium is mainly found on ion form in the environment and is not expected to bioaccumulate. Lithium is not considered acutely toxic to organisms in aquatic environment at the concentration level found in treated municipal waste water (Kjølholt et al. 2003). The acute environmental toxicity as EC_{50} on *Daphnia magna* was 33-197 mg/L (Table 6) being at least 1000 times higher than the level in natural fresh wa-

ter (Kjølholt et al. 2003). Both lithium chloride and lithium sulphate are highly soluble in water, and the compounds will dissociate in aqueous environment.

Table 6. Test results for environmental toxicity.

Organism	Latin name	Exposure duration	EC ₅₀ (mg/L)	LC ₅₀ (mg/L)	Compound
Mollusc	Dreissena polymorpha (Zebra mussel)	24 hours		185 -232	LiCl
Crustacean	Daphnia magna (water flea)	24 hours	33 - 197		Li ₂ SO ₄
Worms	Tubifex tubifex (Tubificid worm)	24 - 96 hours	9.3 - 44.8		Li ₂ SO ₄
Fish	Pimephales promelas (fathead minnow)	26 days	1 - 6.4	1.2-8.7	LiCl
Fish	Tanichthys albonubes (white cloud mountain minnow)	48 hours		9 - 62	LiCl
Earth worms	Eisenia fetida	7 weeks	10 mmol/kg soil		LiCl

Original data from US. EPA. (2000). Aquatic toxicity information retrieval database (AQUIRE). Modified after Kjølholt et al. 2003 and Aral & Veccio-Sadus 2008.

2.11 Effects in humans

The lithium load is approximately 7 mg in the human body (Lenntech 2007). There is some evidence that Li might be a beneficial trace element for humans (Schrauzer 2002, Adams et al. 2006). Soluble Li compounds are readily absorbed from the gastrointestinal tract (Beliles 1994). Li has been used as a drug

therapy in psychiatry, treatment of bipolar disorder and other psychiatric conditions, for several decades (Cade 1949, Léonard et al. 1995). Li as the drug therapy is well established (see eg. Timmer & Sands, 1999) but there are only few epidemiological studies about intake and potential health effects of Li from natural environmental sources of general population (Figueroa et al. 2012). Zarse et al. (2011) reported that long-term low-dose exposure to Li from tap water may reduce overall mortality in Oita prefecture including 18 municipalities in Japan (Zarse et al. 2011). The inverse association between the lithium concentrations in drinking water and mortality of suicide has been suggested in some ecological studies (Scharauzer et al. 1990, Ohgami et al. 2009, Kapusta et al. 2011, Helbich et al. 2012). In Japanese study, the standardised mortality ratios (SMRs) of suicide in men across 18 municipalities were significantly and inversely associated with lithium levels in drinking water. The authors speculated that very low but very long exposure for lithium could enhance neuroprotective factors and thus decrease the risk of suicide (Ohgami et al. 2009). Lithium concentrations in drinking water varied from 0.7 to 59 µg/l in tap water. In an Austrian study, authors found that 0.01 mg/l increase of lithium concentration in drinking water was associated with a decrease in the suicide rate of 1.4 /100 000 or a 7.2% reduction in the SMR for suicide. (Kapusta et al. 2011). This would correspond to one conventional lithium pill (75 mg) in 7400 l of drinking water (Kapusta et al. 2011). On the contrary, the results of a study from Easter England did not found any association between drinking water lithium and suicide rates (Kabacs et al. 2011).

Harari et al. (2012) studied the transfer of Li from mothers environmentally exposed to Li with up to 700 µg /L in drinking water to fetuses and breast-fed infants in northern Argentina and Chile. Consumption of drinking water high with Li during pregnancy caused exposure to fetus. Li will readily pass through the placenta to the fetus. Infant exposure to lithium through breast milk was markedly lower than the prenatal exposure (Harari et al. 2012).

Broberg et al. 2011 studied the potential health effect of long-term lithium exposure from drinking water on the thyroid in women in the Puna region in the Argentinean Andes. Li concentration of urine was inversely associated with free thyroxine (T4) and positively associated with thyroid-stimulating hormone (TSH) (Broberg et al. 2011).

Li levels in scalp hair was studied in Tokyo prefecture (Schöpfer & Schrauzer 2011). The hair sample reflects the average Li intake during the past 1–3 months. The median values of Li were 0.011 µg/g in men and 0.017 µg/g in women. However, about half of the Li levels were below the detection limit value or below the lower limit value of the laboratory reference ranges (0.05–0.12). The authors suggested that more than half of the subjects would suffer Li deficiency (Schöpfer & Schrauzer 2011).

2.12 Conclusions Li

Altogether, since lithium is successfully used as a therapeutic agent, at relatively large doses, adverse effects may not be expected at low or moderate occupational and environmental exposure when used for other purposes.

3 COBALT

3.1 Properties

Cobalt (Co) is a trace element of group 9 in periodic system. Its melting point is 1495 °C and the atomic mass 58.93. Cobalt is hard ferromagnetic silver white metal and it is mainly used for special alloys. Properties of cobalt are summarised in table 7. Cobalt is essential for humans and most animals as a component of vitamin B₁₂. Co has radioactive isotopes that have been artificially prepared. From these isotopes ⁶⁰Co is most commonly used as a source of gamma rays.

Table 7. Properties of cobalt

Atomic weight	58.93
Atomic number	27
Density	8.9
Melting point	1495 °C

Boiling point	2870 °C
Crystalline form	Silver grey metal, cubic
Main radioactive isotopes	⁵⁷ Co, ⁵⁸ Co, ⁶⁰ Co

3.2 Distribution in the environment

Cobalt, like other metals, is unevenly distributed in the natural environment. Co is a metallic element, which occurs in the nature most frequently in oxidation states +2 and + 3 (Kabata-Pendias 2001). Co rarely forms independent minerals. It occurs in sulphides and silicates in association with Fe and Ni, and in silicates also with Mg. Co is enriched in ultramafic rocks. According to Taylor and McLennan (1985) the average abundance of Co is about 25 ppm in the earth crust, 100 ppm in mafic and ultramafic rocks, 40-50 ppm in mantle type rocks and 1-10 ppm in granites.

Cobalt is usually associated with copper or nickel. About 44% of world production of cobalt comes from nickel ores (WHO 2006). According to U.S. Geological survey (2012) the identified cobalt resources in the world are about 15 million tons. Figure 4 represents the division of cobalt reserves between different countries. Aqueous environment contains also a significant resource of cobalt present in the manganese nodules and concretions of ocean sediments (Glasby 1977). It is assumed that as much as 1 billion tons of cobalt resources may exist in form of manganese nodules and crusts on the ocean floor (U.S. Geological survey, 2012).

The Co concentration in soils depends strongly on the weathered and drifted parent material. A world mean of Co in surface soils varies between 4.5-12 ppm (Kabata-Pendias & Mukherjee 2007). In ground-water and surface waters the concentration of Co range from 0,003 to 10µg l⁻¹ (ATSDR 2004).

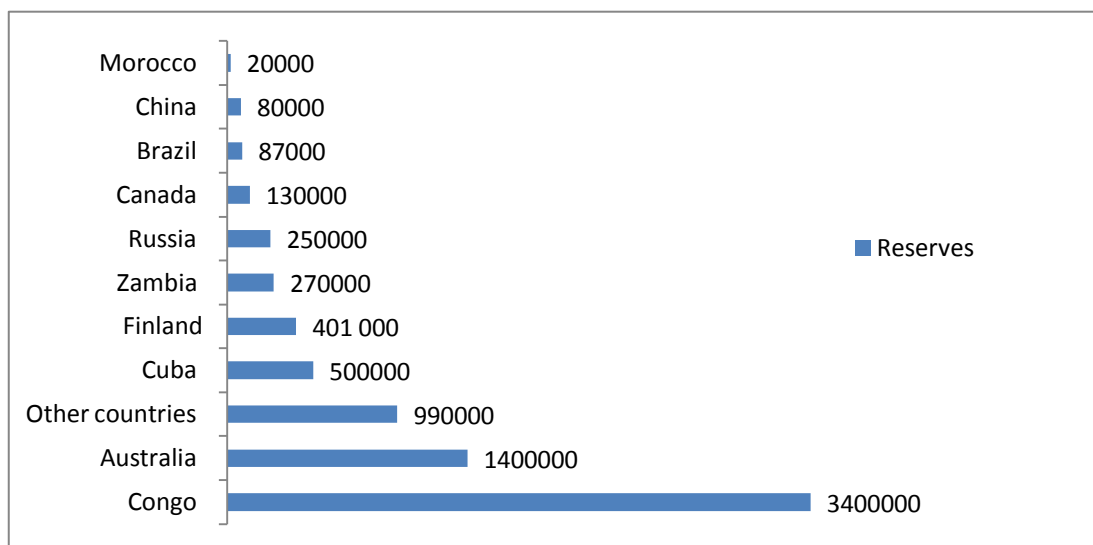


Figure 4. Cobalt reserves (t) in different countries (U.S. Geological Survey 2012, Finland: Rasilainen et al. 2012).

3.3 Cobalt in waters

The mobility of cobalt is determined by clayminerals, organic material and iron- and manganese precipitates, which cobalt is combined to (Turekian 1978). Cobalt also migrates to water with humic matter. According to Reimann and Karitat (1998) the concentration of cobalt in sea waters is 0,0012 µg/l to 0,02 µg/l. Stream water world median value is 0,2 µg /l, when in Finland stream water median is 0,17 µg/l (Reimann & Caritat 1998). Cobalt is highly immobile in natural groundwater conditions. Co content in groundwater is in general below 1 µg/l in pristine areas and 1-10 µg /l in populated areas (Hamilton 1994). Four percent of wells drilled in bedrock in Finland exceeded 1 µg/l cobalt content (Lahermo et al. 2002).

3.4 Soil and plants

A major source of cobalt in soils is inherited from the parent material. Naturally high Co contents are usually observed in soils over serpentine rocks and ore deposits. Also anthropogenic sources as Co fertil-

izers, mining, smelting and industrial processing may cause Co contamination. Mean of the background content of Co on the worldwide scale for sandy soil is $5,5 \text{ mg/kg}^{-1}$ and for loamy soil 10 mg/kg^{-1} . (Kabata-Pendias & Mukherjee 2007).

Due to variable oxidation stages and microbiological activity, Co compounds are complex. Physicochemical properties of soil such as texture, organic matter, Fe/Mn oxides, pH and the presence of complexants, affect to Co circulation and bioavailability. During the weathering process Co is relatively mobile in oxidizing acid environments, but if Fe and Mn oxides as well as clay minerals are present in soil Co stays in solid form (Kabata-Pendias 2001). Soil pH is very important for cobalt uptake by plants. Adsorption of divalent cobalt on soil colloids is high between pH 6 and 7, whereas leaching and plant uptake of cobalt is improved by lower pH.

Co content in plants is controlled by soil properties and ability of plants to absorb Co from the soil. Increase in pH, CEC, organic matter, clay, silt, free iron and total Mn is limiting the soil-to-plant transfer of Co to varying degrees (Dan Luo et al. 2010). The transfer of Co from the soils to edible parts of the plants is lower than that of Zn, Cu and Cd, but higher than that of Pb in the same areas. Sillanpää and Jansson (1992) compared Co content of wheat from 30 countries, and concluded that soil texture is the most important factor of controlling Co content in plants. Plants grown in Co rich soils contains higher amount of Co even if they are not known as Co accumulators (Kabata-Pendias 2001). Solubility of Co in soil is also influenced by liming and using different fertilizers (Klessa et al. 1989). Liming reduces Co content in herbage and this may lead to dangerous Co deficiency for ruminants.

3.5 Air

Atmospheric transport of cobalt seems to be insignificant excluding the industrial effect. Natural sources of cobalt in atmosphere are volcanoes, forest fires, windblown dust, seawater sprays and continental and marine biogenic emissions (Lison 2007). Atmospheric transport of cobalt depends on meteorological conditions, particle size and density. Coarse particles with diameters $>2 \mu\text{m}$ may deposit within 10 km from the start point, while smaller particles may travel longer distances (WHO 2006). Milford and Davidson (1985) found the mass median diameter of atmospheric cobalt to be $2.63 \mu\text{m}$.

3.6 Distribution of cobalt in Finland

The concentration of Co is high in the northern Finland in the areas of volcanogenic greenstones, and in central and southern Finland in areas, where also sulphide ores are found (Koljonen et al. 1992). Cobalt is essential element in Outokumpu type multi-metal sulphide ore association. In Finland Co has been mined and produced in the polymetallic sulphide mines. According to Rasilainen et al. (2012) known cobalt resource in Finland is 401 000 t.

In weathering process cobalt is bound effectively to clay minerals, organic matter and Fe-Mn precipitate. In Finland the highest median contents of Co are found in clay, stream sediment and agricultural soil (Table 8). Co content was in sand 3.9 mg/kg, till 5.8 mg/kg and clay 21 mg/kg in southern Finland (Tartvainen et al. 2011). Co concentration in glacial till in Finland is presented in figure 5. The range of Co concentration in ground water is larger ($<0,02 - 113 \mu\text{g/l}$) than in stream water ($0,02 - 3,87 \mu\text{g/l}$). Regional distribution of Co in stream waters does not reflect to stream sediments (Lahermo et al. 1996). The highest Co concentrations of stream waters are found in the western coastal area of Finland near the city of Vaasa while the highest concentrations of stream sediments are met in the south-western part of the country near the Tampere region.

Table 8. Statistical parameters of aqua regia extractable contents of cobalt in various media

Material	Median	Range	N
Till	7,95 mg/kg	1,58 - 231 mg/kg	82062 ¹⁾
Clay	22,4 mg/kg	3,1 – 35,0 mg/kg	100 ²⁾
Sand/gravel	3,9 mg/kg	1,7 – 9,7 mg/kg	98 ²⁾
Humus	1,4 mg/kg	0,54-23,5 mg/kg	288 ²⁾
Agricultural soil	9,5 mg/kg	...	338 ³⁾
Agricultural soil	17,1 mg/kg		80 ^{3b)}
Stream sediment	10,5 mg/kg	2,4 - 48,5 mg/kg	1050 ⁴⁾
Stream water	0,17 µg/l	0,02 - 3,87 µg/l l	1050 ⁴⁾
Ground water	0,09 µg/l l	<0,02 - 113 µg/l	739 ⁵⁾

¹⁾ Whole Finland, Salminen, 1995, fraction <0,06 mm

²⁾ Pääkaupunkiseudun kehyskunnat, Tarvainen (ed.)2006

³⁾ Finnish fields, Mäkelä-Kurtto et al. 2007

^{3b)} Pääkaupunkiseudun kehyskunnat, Tarvainen (ed.)2006

⁴⁾ Whole Finland, Lahermo et al. 1996

⁵⁾ Whole Finland, Lahermo et al. 2002

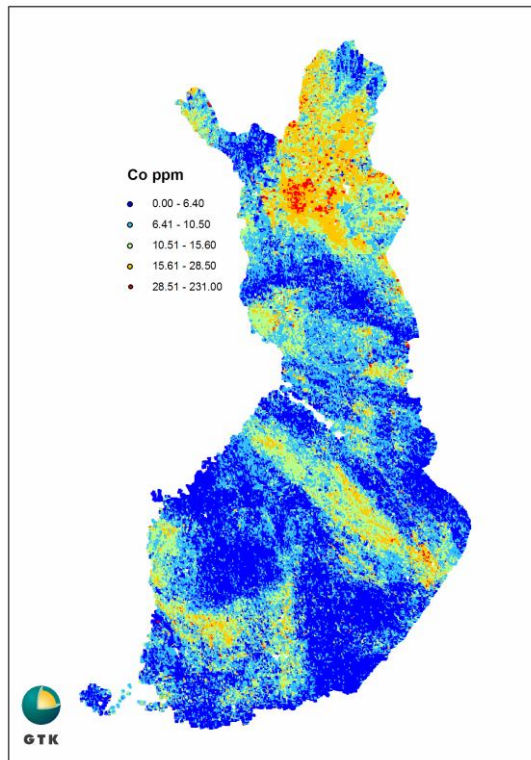


Figure 5. Co concentration in glacial till in Finland (source: GTK).

3.7 Environmental exposure

Cobalt can enter the body in drinking water, nutrition, breathing or dermal contact (ATDSR 2004). The main exposure route for general population is diet. Co content in plants is controlled by soil properties and by plants ability to absorb Co from the soil. The green vegetables and fresh cereals are the richest source of cobalt (0.2–0.6 $\mu\text{g/g}$ dry mass). The poorest sources are dairy products, refined cereals, and sugar (0.01–0.03 $\mu\text{g/g}$ dry mass) (Donaldson et al. 1986). Dabeka and McKenzie (1995) analysed 112 Canadian food items to found Pb, Cd F, Ni and Co levels of these foods. In general, the Co contents were low, but highest level of cobalt was found from waffles and pancakes (0.076 $\mu\text{g/g}$), corn cereal (0.074 $\mu\text{g/g}$) and potato chips (0.07 $\mu\text{g/g}$). Cobalt contents of some plants are presented in Table 9.

Table 9. Cobalt content of some plants (Kabata-Pendias, 2011).

Plant	Dried weight basis µg/g
Cabbage	0.1-0.16
Potato	0.037-0.16
Cucumber	0.087-0.17
Tomato	0.062-0. 2
Orange	0.019-0.045
Sweet corn	0.0081-0.031
Apple	0.019-0.045
Lettuce	0.046-0.21

3.8 Intake

According to Lison (2007) dietary intake of cobalt is highly varied being in general between 5 and 50 µg/day. Although a diet deficient in cobalt may create deficiency of vitamin B₁₂, cobalt is detrimental to health when exposed for it too much. The recommended amount of vitamin B₁₂ is 2.4 µg in a day. This amount contains 0.10 µg cobalt (Lison 2007). When human body is exposed to cobalt, the highest cobalt concentration is found in the liver and kidney (Lison 2007).

The average dietary intake of cobalt among Canadians over all ages and sexes was 11 µg/day (Dabeka & McKenzie 1995). The daily intake of Canadian 1-4 year old children was 7 µg Co and that of the average Canadian male (40-65 years) 15 µg of Co in a day. According to Leblanc et al. (2004) children in France (aged 3 to 14 years) ingested around 7.3 µg of Co per day and adults (over 15 years old) ingested typically about 7,5 µg/day.

Oyoo-Okoth et al. (2012) investigated geologically metal rich areas from the coastal zone of Lake Victoria, Kenya. Children living in this area were exposed to several metals especially through soil and food. The Co concentrations of soil and in some locally produced foods are presented in Table 10. The high body burden of cobalt was found to be a consequence of consuming high amounts of cabbage, cyprinid

fish and maize. Children who were highly exposed to soils were also exposed to cobalt. In the area industrial exposure was insignificant. The conclusion was that geological exposure through soil and consumption of certain local foods lead to high body burden of metals in children. The estimated daily intake of Co from soil, water and some food items by children in the study are presented, respectively, in Table 11.

Table 10. Co concentrations from the four sampling sites at the geologically metal rich coastal zone of Lake Victoria. Water is expressed in $\mu\text{g/l}$, otherwise the units are $\mu\text{g/g}$. (after Oyoo-Okoth et al. 2012).

Compartment	Co $\mu\text{g/g}$
Soil	2.6–15.9
Asian rice	0.32–0.82
Cabbage	0.12–0.42
Zea mays	0.21–0.42
Beef	0.08–0.31
Sweet potato	0.24–0.82
Rastrineobola argentea	0.42–0.61
Water	0.05–0.19 $\mu\text{g/l}$

Table 11. The estimated daily intake of Co from soil, water and some food items by children, who are living in the geologically metal rich coastal zone of Lake Victoria. (Oyoo-Okoth et al. 2012).

Compartment	Co daily intake $\mu\text{g/day}$
Soil	5.14–29.21
Asian rice	15.5–59.61
Cabbage	6.21–20.77
Maize meal	17.37–55.26
Beef	1.16–4.57
Potatoes	15.78–36.20
Fish (Rastrineobola argentea)	34.35–58.06
Water	0.00–0.07

3.9 Toxicity and Carcinogenicity

Cobalt is acutely toxic in large doses. Long-term exposure for cobalt, even at a low level, may cause harmful health effects related to various organs and tissues (see review by Simonson et al. 2012). The inhalation LC₅₀ for cobalt hydrocarbonyl in rats was found to be 165 mg/m³ for a 30-min exposure. Oral LD₅₀ for soluble cobalt compounds have been reported to range from 42.4 to 317 mg/kg body weight, depending on the compound and the species tested. Tricobalt tetra-oxide is reported to have an LD₅₀ of 3672 mg/kg body weight in rats (WHO 2006).

Repeated inhalation exposure has caused inflammation and necrosis in the respiratory tract, thymus necrosis and testicular atrophy in laboratory animals (WHO 2006). Cobalt is cardiotoxic. After oral exposure cobalt has caused increased heart weight and degenerative heart lesions in animals. In some studies cobalt has caused also kidney damage (WHO 2006). Several cobalt compounds are genotoxic in mammals and in mammalian and bacterial test systems in vitro (WHO 2006). In addition, they have caused reprotoxic effects (testicular degeneration, atrophy) in male rats and decreased fertility in males (WHO 2006).

Based on the animal data, the International Agency for Research on Cancer (IARC) has classified cobalt (metal and water soluble salts) possibly carcinogenic to humans (IARC 2006).

3.10 Ecotoxicological effects

Invertebrates are consistently more sensitive to chronic cobalt exposure than fish (Nagpal 2004). Chronic LC50 value established for rainbow trout (*Oncorhynchus mykiss*) was 470 µg/L for 28 day embryo-larval toxicity tests (Birge, 1978) and 520 µg/L (Marr et al. 1998) for a 6 day test using fry. A 21-day LC50 for *Daphnia magna* was 21 µg/L (Biesinger and Christensen 1972). Table 12 summarizes the ranges of toxicity endpoints compiled in the literature (Nagpal 2004).

Table 12. Range of toxicity endpoints for freshwater organisms (adapted from Nagpal 2004).

Class	NOEC (µg/L)	LOEC (µg/L)	EC50 (sublethal) (µg/L)	LC50 (µg/L)
Plants	500-550*	550*	522-23,800	N/A
Fish	132-10,000	225-1,610	not available	470-225,000
Invertebrates	10-600	20 - >50	12*	21-450,000

* based on very limited data; 1 study for LOEC and NOEC for plants and 1 study for EC50 for invertebrates.

3.11 Effects in humans

Knowledge on toxicity of cobalt in humans is based mainly from occupational exposure. Upon occupational exposure (mainly in dust, inhalation exposure) cobalt has caused different lung effects such as asthma, pneumonia, pneumoconiosis, wheezing and allergies (ATDSR 2004). Cobalt may cause contact dermatitis in skin. These symptoms are unlikely upon environmental exposure where people are exposed to cobalt mainly via ingestion. Children may be affected by cobalt by the same way as adults. Cobalt may be transferred from the pregnant mother to the fetus or from the mother to baby in the breast milk (ATDSR 2004).

In the 1960s, lethal cardiomyopathy occurred when people were consuming large quantities of beer with added cobalt sulphate (Morin & Daniel 1967, Kesteloot et al. 1968). Certain brewery added cobalt salts to beer to stabilize the foam. Cobalt exposures leading to death ranged from 0.04 to 0.14 mg/kg/bw/day for several years. This cardiotoxicity is in line with the observations in animal studies.

3.12 Conclusions Co

Altogether, the toxicity of cobalt and adverse effects in man are rather well known. Increased use of cobalt as a high-tech metal does likely not alter exposure patterns, the number of people potentially get exposed occupationally to cobalt will just increase.

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