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Element Concentrations in Wild Edible Mushrooms in Finland

Riina Pelkonen,
Georg Alfthan and
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Abbreviations

Table 1. Key to abbreviations used in the study

AAS	atomic absorption spectrometry
Ag	silver
Al	aluminium
As	arsenic
Ca	calcium
Cd	cadmium
Co	cobalt
Cr	chromium
Cu	copper
d.w.	dry weight
EU	European Union
f.w.	fresh weight
Fe	iron
Hg	mercury
ICP-MS	inductively coupled plasma mass spectrometry
JECFA	Joint FAO/WHO Expert Committee on Food Additives
Mg	magnesium
Mn	manganese
Mo	molybdenum
Ni	nickel
NOAEL	no observed adverse effect level
Pb	lead
Pt	platinum
Rb	rubidium
RDA	recommended dietary allowance
Se	selenium
sp.	species
V	vanadium
WHO	World Health Organisation
Zn	zinc

1 Introduction

In Finland wild-growing products such as mushrooms and berries grow in abundance in forests and are traditionally used as a source of food by the Finns. Although the majority of edible mushrooms growing in Finnish forests are not consumed, picking mushrooms is a common activity for a large part of the population. Fungi are widely recognised to have a good nutritional value and in the recent years younger generations in particular seem to have taken a culinary interest in mushrooms.

This report is associated with a more extensive research on four trace elements, Cd, Pb, As and Ni, by the same authors (Pelkonen *et al*. 2006). The previous research provides deeper background knowledge on the accumulation of trace elements in fungi and on the detected correlations between the concentrations of the four elements in mushrooms.

Table 2. The number of samples examined for each mushroom species

Species	Number of samples
Agaricus abruptibulbus	28
Albatrellus ovinus	12
Boletus sp. (B. edulis, B. pinophilus)	21
Cantharellus cibarius	17
Cantharellus tubaeformis	17
Craterellus cornucopioides	8
Gyromitra esculenta	5
Hydnum sp. (H. repandum, H. rufescens)	23
Lactarius sp.(L. deliciosus, L. deterrimus, L. rufus, L. torminosus, L .trivialis)	21
Leccinum sp. (L. aurantiacum, L. versipelle)	25
Macrolepiota procera	4
Suillus variegatus	10
Total of all 12 species	**191**

The concentration of 16 minerals and trace elements, Ag, Al, Ca, Co, Cr, Cu, Fe, Hg, Mg, Mn, Mo, Pt, Rb, Se, V and Zn, were studied for 12 mushroom species (see Table 2). ICP-MS was used for determining the element concentrations apart from Hg, for which cold-vapour AAS was used and Se, which was determined using fluorimetry. Ten of the species included in the research are among species listed by the Ministry of Agriculture and Forestry as commercially sold mushrooms in Finland (see Appendix 1). In addition, *Agaricus abruptibulbus* and *Macrolepiota procera* specimens are included in the study as both species are commonly picked and consumed in Finland. The objective of this report is to update and contribute to the existing data on mushroom element levels as well as to publish the concentrations of elements previously not studied for mushrooms in Finland.

2 Literature Review

2.1
Studies on mushrooms

Collecting wild mushrooms for eating purposes is a popular activity among a considerable part of the Finnish population. Mushrooms are virtually a free source of nutrition and their collection is easy due to the abundance of suitable forest areas and the 'everyman's right' allowing wild products such as mushrooms and berries to be picked practically everywhere in the country without the landowner's permission. Consequently, approximately 90 % of the total amount of mushrooms collected annually in Finland are picked and consumed by private households without intervening commercial retailers (Ministry of Agriculture and Forestry 2002). The annual total of 2–10 million kg of mushrooms collected by private households equals, however, merely 1 % of the average total crop of mushrooms in Finnish forests. It is estimated that 46 % of the population aged between 25 – 65 years pick mushrooms regularly. The average annual consumption of wild mushrooms ranges from 0.5 to 2 kg per person (Ministry of Agriculture and Forestry 2002) – there is, however, considerable variation within the Finnish population and the consumption by many individuals can be assumed to greatly exceed these averages.

The largest part of the fungi organism is the subsurface mycelium, which may spread over areas of several square metres (Byrne & Ravnik 1976). The high growth rate and compressed nature of the mycellia enable fungi to extract elements from the soil very efficiently (Byrne & Ravnik 1976). A broad mycelium cover allows for the fungi to accumulate elements even from soil that has relatively low concentrations of the particular elements (Eurola *et al.* 1996).

In Finland and other Nordic countries the element contents of mushrooms were more actively studied from the late 1970s to early 1980s in both urban (Laaksovirta & Alakuijala 1978, Laaksovirta & Lodenius 1979, Kuusi *et al.* 1981, Lodenius *et al.* 1981a) and rural environments (Hinneri 1975, Movitz 1980, Andersen *et al.* 1982, Nuorteva *et al.* 1986). The concentrations of many of the elements studied here have not been considered in previous research in the Nordic countries. In Finland Eurola *et al*. (1996) have provided the most recent and comprehensive study in the research area by investigating the levels of Cu, Mn, Zn, Cd, Hg and Pb in wild mushrooms in Finland. Their research included six of the species examined in this report.

Many of the other European studies on mushrooms were carried out prior to mid 1980s (Stivje & Roschnik 1974, Seeger *et al.* 1976, Stivje & Besson 1976, Tyler 1980, Tyler 1982, Bargagli & Baldi 1984). Like the Finnish studies, most European fungi research has been carried out on heavy metals along with nutritionally essential elements such as Cu, Zn and Mg. Recent research has largely been concentrated on areas of southern and eastern Europe (Svoboda *et al.* 2000, Demirbaş 2001a & 2001b, Svoboda *et al.* 2002) and often with different species and different environmental conditions to Finland.

Nevertheless, in the recent years Falandysz *et al*. (Falandysz 1997, Falandysz *et al*. 2001) have conducted extensive research on the element concentration of wild mushroom species including *Boletus edulis*, *Cantharellus cibarius*, *Craterellus cornucopioides*, *Lactarius* species, *Leccinum* species, *Macrolepiota procera* and *Suillus variegatus* in Poland. Ten of the elements examined here (Ag, Al, Ca, Cu, Fe, Hg, Mg, Mn, Rb and Zn) were included in these studies.

2.2

Environmental, Biochemical and Nutritional Aspects of the Studied Elements

2.2.1

Essential elements

Ca, Calcium

Calcium is an alkaline earth metal, which exists as a divalent cation forming a single oxidation state, Ca^{+2}. Calcium does not exist as an element in nature, but occurs as limestone ($CaCO_3$), gypsum ($CaSO_4$*$2H_2O$) and fluorite (CaF). Most calcium compounds are insoluble in water, but will solubilise under acidic conditions. Most abundantly (>1000 mg kg^{-1}) calcium occurs in milk products followed by cereals and green leafy vegetables. In Finland very little calcium is provided by drinking water.

Calcium is an essential mineral required for optimal bone formation and skeletal growth. About 25-50 % of dietary calcium is absorbed. For optimal absorption, vitamin D is required. In Finland the daily intake of Ca is approximately 970 mg for females and approximately 1190 mg for males. The mean intake of calcium is clearly higher than the recommended amount. The Nordic recommended dietary allowance (RDA) for both men and women is 800 mg/day. A daily intake of 2500 mg results is considered not to cause adverse health effects but a higher intake may produce gastrointestinal side effects. (Männistö *et al*. 2003, UK Expert Group on Vitamins and Minerals 2003a, Nordic Nutrition Recommendations 2004)

Co, Cobalt

Cobalt is a transition metal that forms oxidation states of +2 and +3. It is widely distributed in the earth's crust. Compounds of biological interest are bivalent. The highest concentrations of cobalt, approximately 0.01 mg kg^{-1}, are found in fish, nuts, green leafy vegetables and cereals. Most of the ingested cobalt is in an inorganic form.

Cobalt is an essential trace element and an integral part of vitamin B12. Despite being an essential element no cobalt deficiency has been reported in humans. Gastrointestinal absorption of small doses of cobalt is nearly complete with the absorption decreasing at higher doses. Most cobalt is eliminated rapidly via urine but a small fraction of Co residues in the body with a slow elimination rate and a half-life of several years. An estimated intake of cobalt from food is 0.012 mg/day and from water 0.02 mg/day. The no observed adverse effect level (NOAEL) for cobalt is estimated to be 1.4 mg/day. A chronic Co intake of 10-23 mg/day may depress the iodine uptake and an even higher intake result in gastrointestinal upset, skin rashes and hot flushes. (UK Expert Group on Vitamins and Minerals 2003c)

Cu, Copper

Copper exists in two oxidation states, Cu^{+1} and Cu^{+2}. In the environment copper may be found as a free metal but mostly it occurs as oxides, carbonates and sulphides in minerals. Cu is also found in a wide variety of soluble salts and organic compounds. Meat, offal, fish and green vegetables are a good source of copper containing more than 1 mg kg^{-1} whereas milk products have a lot smaller Cu content. Very high amounts of copper may be found in whole grain products and nuts.

The biological function of copper is to be an essential component of a number of enzymes involved in energy metabolism, the formation of connective tissue and oxidative defence. Cu is thought to be required for infant growth, host defence mechanisms, bone strength, red and white cell maturation, iron transport as well as cholesterol and glucose metabolism. The signs of human Cu deficiency include anaemia, neutropenia and bone abnormalities. In a normal diet the absorption of copper varies between 35 and 70 %. In the intestine Cu is bound to metallothionein, a protein that is induced by Zn and other trace elements. At high intakes of more 50 mg/day Cu absorption is, however, much lower. In the blood most of Cu is transported bound to caeruloplasmin.

Children are more susceptible than adults to gastrointestinal disturbances which are caused by an excessive chronic copper exposure. A safe upper limit for copper from food varies between 5 to 10 mg/day. The mean dietary intake of Cu ranges from 1 to 2 mg/day. (UK Expert Group on Vitamins and Minerals 2003d, Nordic Nutrition Recommendations 2004)

Fe, Iron

Iron is a transition metal ubiquitous in the environment and biological systems. In the environment iron occurs as a free metal and as iron compounds. It exists in two oxidation states, ferrous Fe^{2+} and ferric Fe^{3+}. Dietary sources rich in iron include liver, meat, nuts, poultry, fish, grains and cereals and dark green leafy vegetables. For the bioavailability of iron only the haem form found in meat, poultry and fish is relevant. The non-haem iron mainly consists of ferric salts, which are much less available for the functional iron in the body.

Iron is an essential trace element for humans due to its necessity in haem proteins such as haemoglobin, myoglobin and cytochromes. Iron deficiency is common and leads to iron-deficiency, anaemia. Approximately 15 % of iron is absorbed from a mixed diet. Very little of the absorbed iron is excreted via the urine. Supplementation with iron at doses of 100-200 mg/day is associated with gastrointestinal disorders. The mean intake of Fe from diet is approximately 12 mg/day. A dose of 17 mg ferric iron is estimated to be the NOAEL for the general public. (UK Expert Group on Vitamins and Minerals 2003e, Nordic Nutrition Recommendations 2004)

Mg, Magnesium

Magnesium is a divalent metallic element, which is very commonly found in the earth's crust. It does not occur as a pure metal in nature but is found in many common minerals. The Nordic RDA for Mg is 280 mg/day for females and 350 mg/day for males whereas the average daily intake in Finland is 309 mg and 405 mg, respectively. High amounts (100-500 mg kg^{-1}) of magnesium are found in green leafy vegetables, legumes and wholegrain cereals while meat and dairy products contain lower levels of Mg (100-300 mg kg-^{1}). Cereal products provide 33 %, potatoes and vegetables 20 %, milk products 15 % and meat and fish 10 % of the total Mg intake.

Mg is an essential mineral element required as a cofactor in many enzyme systems. Magnesium has a multifunctional role in cell metabolism, cell division and in the synthesis of RNA and DNA. Mg is considered essential for the normal functioning of the parathyroid gland and for vitamin D metabolism. Magnesium depletion markedly disturbs calcium homeostasis whereas hypocalcemia is a common manifestation of a moderate to severe Mg deficiency.

The net absorption of Mg from diet is approximately 50 %. High levels of dietary protein as well as dietary fibre from fruit, vegetables and cereals decrease the absorption of Mg. About 5 % of magnesium is excreted in urine.

There are no adverse effects from the ingestion of magnesium from food. The average daily intake of Mg from food is 280 mg. The Nordic RDA for men and women is 400 mg/day and 310 mg/day, respectively. It is estimated that supplemental doses of 400 mg/day do not result in adverse health effects. Excessive dosage of magnesium salts may result in osmotic diarrhoea. (Männistö *et al*. 2003, UK Expert Group on Vitamins and Minerals 2003f, Nordic Nutrition Recommendations 2004)

Mn, Manganese

Manganese is an abundant metallic element that forms a variety of oxidation states. Mn^{2+} and Mn^{3+} are the biologically most important oxidation states. Naturally Mn does not occur in its metallic form but can be found in many minerals as an oxide or a carbonate as well as in iron ores. The highest amounts of Mn are found in bread and cereals (6.8-8 mg kg^{-1}) and in green vegetables (2 mg kg^{-1}) while eggs, milk, fruits and meat (<1 mg kg^{-1}) contain much less Mn. Significant amounts of Mn may also be found in tea.

Mn has a number of important biological functions as a cofactor of enzymes such as arginase, pyruvate carboxylase and mitochondrial superoxide dismutase. It also functions as a specific or unspecific activator for a large number of enzymes participating in the synthesis of e.g. cholesterol. Mn deficiency is rare and has only been demonstrated in experimental conditions. Only a few percent of oral Mn is absorbed. Iron and Mn compete for absorption in the gut. Also many other food components interfere with Mn absorption.

Mn intake from food varies between 2 and 8 mg/day. An acceptable intake resulting in no adverse effects is estimated to be approximately 12 mg/day for the general public. Mn is regarded as the least toxic trace element. Exposure to high intakes of Mn in water has been associated with neurological and behavioural effects. Anaemic individuals may be especially vulnerable to the toxic effects of Mn due to an increased absorption. (UK Expert Group on Vitamins and Minerals 2003g, Nordic Nutrition Recommendations 2004)

Se, Selenium

Selenium is a metalloid with similar chemical and physical properties to sulphur. Se exists in 5 oxidation states, -2, 0, +2, +4 and +6. It is ubiquitous in nature but distributed in a highly uneven manner with the highest concentrations found in arid areas with high soil pH. Plants readily take up Se thus synthesising organic selenium compounds. High Se concentrations are also found in sedimentary rocks and sulphide ores.

The Se concentration in both plant and animal food varies widely throughout the world. In Finland sodium selenate has been added to artificial fertilizers since 1985, which has resulted in the Finnish foodstuff containing the highest Se concentration in Europe. Protein rich foods generally contain the highest level of Se: in meat, fish, milk and cereals the range is 0.1-0.5 mg kg^{-1}.

Se is an essential trace element and its biologically active form amino acid selenocysteine. Selenium is an integral part of selenoproteins such as glutathione peroxidises, iodothyronine deiodinases, thioredoxin reductases and selenoprotein P. The gastrointestinal absorption of Se from food is high and ranges between 40 and 90 %. Approximately half of ingested selenium is excreted via urine.

In Finland the mean intake of Se from diet is 0.07 to 0.09 mg/day. About 75 % of the intake is derived from meat, milk and cereals whereas vegetables only contribute to a small proportion of the total intake. A safe upper level for daily consumption is considered to be 0.45 mg/day. Chronic Se toxicity, selenosis, results in pathological changes in nails and hair followed by adverse effects on the nervous system.

Development of selenosis is associated with intakes exceeding an intake level of 0.85 mg/day. (UK Expert Group on Vitamins and Minerals 2003i, Eurola 2005)

Zn, Zinc

Zinc is an abundant metallic element, which occurs in many minerals but not in a metallic form. It forms compounds with the oxidation state +2. Good dietary sources of zinc are meat and sea foods (10-50 mg kg^{-1}), milk (3 mg kg^{-1}) and wholegrain cereals (10-20 mg kg^{-1}). Foods rich in fats and sugar have a low zinc content.

Zinc is an essential trace element and necessary for the function of several hundred metalloenzymes. It plays a key role in the synthesis and stabilization of genetic material and is necessary for cell division. Signs of zinc deficiency include poor prenatal development, growth retardation, mental retardation, reproductive failure, dermatitis and loss of appetite. Zinc and copper are mutually antagonistic, each competing with the gastrointestinal uptake of the other. Also zinc and iron compete for absorption.

Absorption of dietary zinc from food is approximately 20-40 %. The absorption is higher from meat and fish and lower from cereals. Very little zinc is excreted via the urine. The mean dietary intake of zinc is 12 mg/day. Supplemental zinc at doses of approximately 50 mg/day may affect copper and iron uptake. The estimated safe upper level for daily supplementation with zinc is 25 mg. Early signs of a zinc overdose include gastrointestinal discomfort, cramping and nausea. (UK Expert Group on Vitamins and Minerals 2003k, Nordic Nutrition Recommendations 2004)

2.2.2 Toxic elements

Ag, Silver

Silver is a heavy metallic element occurring in oxidation states +1 and +2. It is rarely found in a metallic form but is a relatively common constituent of sulphide minerals. The main ore from which silver is produced is argentite (Ag_2S). No reliable data on silver in foods are available but the intake from diet is estimated to range between 0.02 to 0.08 mg/day.

Intestinal absorption of silver is approximately 10 %. The biological half-life in the whole body is approximately a few days whereas in the skin and liver it is estimated to be a few months. Silver has no biological role and it is considered to be only toxic. Exposure to high doses (estimated as 0.8 mg/day) of colloidal or organic silver may result in argyria, a condition in which the skin suffers permanent blueish-gray discoloration. A safe level of silver in drinking water is reported to be 0.1 mg l^{-1} for humans and 0.2 mg l^{-1} for laboratory animals. Reduced conditioned-reflex activity and immunological activity is reported to occur at Ag levels of 0.4-0.5 mg l^{-1}. (US EPA 1996, US Agency for Toxic Substances and Disease Registry 1999, Health Canada 2006)

Al, Aluminium

Aluminum is a metallic element and the third most abundant element in the earth's crust. In the environment it is rarely found as a free metal but commonly in most rocks, which contain Al as aluminosilicate minerals. The behaviour of Al in the environment depends on the characteristics of the local environment and especially of the pH. Generally Al is not bioaccumulated to a significant extent.

Al intake from foods range between 3.4 to 9 mg/day. Exposure from antacids may be 100-200 mg/day. Al is not required for any biological functions of the body. Although it is relatively non-toxic it can accumulate in the body due to a reduced kidney function. In dialysis cases a high Al exposure can lead to dialysis encephalopathy resulting from Al accumulation in the brain.

Intestinal absorption of Al from food is 0.1-0.4 % but bioavailable compounds of Al may be absorbed up to 5 %. The minimal risk level for chronic aluminium exposure has been set at 1 mg kg^{-1} Al per day, which corresponds to a daily intake of approximately 60 mg for an adult. (WHO 1997, Ysart *et al*. 1999)

Cr, Chromium

Chromium is a metallic trace element that usually exists in the oxidation states 0, +2, +3 and +6. Biologically relevant states are trivalent and hexavalent. Trivalent Cr is ubiquitous in nature but its hexavalent compounds are man-made. Processed meat, fish, wholegrain products, nuts, pulses and spices contain the most Cr, 0.1-0.2 mg kg^{-1}. The absorption of dietary Cr is low, only 0.5-2.5 %.

The exact biological function of Cr is currently unknown. It is suggested that trivalent Cr potentiates insulin action and thereby influences carbohydrate, lipid and protein metabolism. The essentiality of Cr is unsure but deficiency symptoms have been described in patients undergoing total parenteral nutrition: impaired glucose tolerance and glucose utilisation, neuropathy and elevated plasma fatty acid concentrations. Cr interacts with iron and has been shown to impair iron metabolism and storage. The toxicity of trivalent Cr is low and a daily intake of 0.025 mg is estimated to be a safe amount. Supplementation with approximately 1 mg/day of trivalent Cr is reported not to produce adverse effects. Intake of chromium from diet ranges between 0.02 to 0.16 mg/day. (UK Expert Group on Vitamins and Minerals 2003b, Nordic Nutrition Recommendations 2004, Biego *et al*. 1998)

Hg, Mercury

Mercury is a metal which in its metallic state is liquid at room temperature. It exists in oxidation states +1 and +2. In the environment Hg occurs in sulphide ores such as cinnabar. Significant amounts of mercury are released into the atmosphere from volcanic gases, burning of fossil fuels and gold amalgam roasting. In soils Hg is mainly found as inorganic salts but in the aquatic environment organic mercury compounds such as methylmercury and dimethylmercury are the most common Hg species. In food the Hg concentration is generally below 0.02 mg kg^{-1}except for fish and other types of seafood in which the mercury concentration ranges between 0.1 to 0.5 mg kg^{-1}. Some mushroom species may accumulate relatively high amounts of inorganic Hg.

Mercury is a toxic element which accumulates in the human body. It has a great affinity to bind to sulphur and therefore it may disturb the functioning of thiol-containing proteins. Approximately 80 % of elemental mercury is absorbed via the lungs whereas only 6 % of mercury salts are absorbed from the gastrointestinal tract. In fish the most common Hg species is methylmercury of which 90 % is absorbed.

In Finland the mean intake of Hg from an omnivorous diet is approximately 0.006 mg/day. The consumption of moderate amounts of lake fish may increase the intake up to 0.034 mg kg^{-1} per day, which is the NOAEL for methylmercury. The WHO LOAEL of methylmercury ranges between 0.21 and 0.49 mg/day. The half-life of Hg in the body is 70 days. Chronic exposure to methylmercury can cause damage to the nervous system. In adults the earliest signs of toxicity include paraesthesia, ataxia and blurred vision. With respect to neurotoxicity the foetus is the most vulnerable: there is evidence of developmental retardation in children whose mothers were exposed to methylmercury during pregnancy. (WHO 1990, Alfthan *et al*. 1994)

Pt, Platinum

Platinum is a rare noble metal which is found as such in nature but mainly in sulphide ores in which it forms compounds at the oxidation states +2, +4 and +6. It forms many water-soluble salts. Pt can also form coordination complexes (Pt II and IV) with organic compounds and halogens. In addition to its use due to its catalytic properties and its resistance to oxidation and corrosion, it is currently an active component in catalytic converters of cars. Liver, eggs and meat (3-8 µg kg^{-1}) contain the highest Pt followed by cereals (2.5 µg kg^{-1}) and fish (1.6 µg kg^{-1}).

Pt has no biological function. Animal data indicate that less than 1 % of Pt ($PtCl_2$) is absorbed. Metallic Pt is non-toxic and non-allergenic, but the soluble salts are toxic. Chronic industrial exposure is responsible for the development of platinosis, which is characterized by respiratory and cutaneous hypersensitivity. The mean Pt intake from diet is estimated to range from 0.2 µg/day for adults to 5 µg/day for children. The largest contributors to the intake of platinum are meat (33 %) and cereal products (23.6 %). (WHO 1991, Ysart *et al*. 1999, Wittsiepe *et al*. 2003)

2.2.3
Other elements

Mo, Molybdenum
Molybdenum is a transition metal which can exist in five oxidation states, +2, +3, +4, +5 ja +6, of which the predominant states are Mo (IV) and Mo (VI). In nature Mo does not exist in the metallic state but occurs in association with other elements in minerals. The predominant form of Mo in soils and water is molybdate, MoO_4^{-2}. Good sources of Mo in the diet are cereals, legumes, nuts, offal, milk products and eggs in which the Mo levels range between 0.2 and 0.9 mg kg^{-1}.

Mo is important as a cofactor in the molybdoenzymes, e.g. oxidoreductases. Mo deficiency is extremely rare and restricted to total parental nutrition and to a rare inherited metabolic disorder. Soluble compounds of Mo are well absorbed. Up to 80 % of absorbed Mo is excreted via urine. The US RDA for Mo is 0.045 mg/day. Intake from diets range from 0.10 to 0.15 mg/day. The US Tolerable Upper Intake Level is 2 mg/day. Signs of toxicity are joint pains and increased serum uric acid concentrations. (Steele 1966, Biego *et al*. 1998, UK Expert Group on Vitamins and Minerals 2003h, Nordic Nutrition Recommendations 2004)

Rb, Rubidium
Rubidium is an alkali metal, which is widely distributed in very small quantities in the earth's crust. As metal it oxidizes rapidly and ignites in air. It forms salts with the oxidation state +1. Its chemical properties closely resemble potassium. Vegetables and fruits (0.5-6 mg kg^{-1}) contain the highest Rb, meat, liver and eggs (0.5-1.2 mg kg^{-1}) and especially poultry (1.5-2.3 mg kg^{-1}) somewhat less. Also fruit juices and beverages contain significant amounts of Rb.

The biological function of Rb is unknown. Probably a high fraction of Rb is absorbed and most of it is excreted via urine. The biological half-life is 50-60 days. The mean intake of Rb ranges from 1.3 to 2.3 mg/day. Coffee, tea and other beverages account for 40 % of the total intake. Drinking water can significantly contribute to the intake. Currently toxicological data are available for animals but not for humans. The toxicity of Rb is thought to result from its ability to replace potassium. The ratio Rb/K intake above 40 % can lead to the accumulation of Rb in muscles and red blood cells with possible neuromuscular effects. (Meltzer HL 1991, Anke and Angelow 1995)

V, Vanadium
Vanadium forms oxidation states of -1, 0, +2, +3, +4 and +5. In nature metallic (0) vanadium does not occur in a free form but occurs in a multitude of minerals. The predominant forms in biological materials are vanadate (+5, VO_3^-) and vanadyl (+4, VO^{+2}). Vanadium occurs at levels of 0.005-0.03 mg kg^{-1} in whole grains, seafood, meats and dairy products. Low amounts are found in beverages, fats, oils, fresh fruit and

vegetables and high amounts (>0.10 mg kg^{-1}) in spinach, parsley, mushrooms and oysters.

Vanadium has not been proven to be an essential trace element for mammals and thus no recommendations are established for the intake level of V. In humans signs of deficiency are questionable, although it has been suggested that low intakes may be associated with cardiovascular disease. It is possible that vanadium may interfere with the storage and metabolism of iron as vanadium is bound to transferrin in blood. Only a small fraction, less than 5 %, of ingested vanadium is absorbed and it is predominantly excreted via urine.

The toxicity of vanadium compounds increases as the valency increases with V^{5+} being the most toxic. Oral supplementation of humans with vanadyl compounds at doses of 50-125 mg/day may cause cramps, loosened stools and "green tongue". In the UK the mean intake from food is 0.013 mg/day and the estimated maximum daily intake 0.05 mg. (Lagerkvist & Oskarsson 2007, UK Expert Group on Vitamins and Minerals 2003j)

3 Methodology

3.1

Sampling

The samples examined in this research were chosen from a larger set of mushroom samples collected by Georg Alfthan (National Public Health Institute, Finland). The included 191 fungi samples were collected from various locations in southern Finland between the years 1977 and 1999. The 36 collection sites, which are situated within the 15 areas seen in Figure 1, were chosen randomly depending on where suitable mushrooms were observed. The sites cover forest and park areas as well as some road sites in both rural and urban areas.

The research aimed to define the general trace element content of edible mushrooms that people would privately pick and consume. Thus the sampling sites were principally chosen to represent ordinary collection sites and exclude locations in a close vicinity of any large metal-emitting industries or other such specific polluters. The number of samples from each location and for each species was dependent on the availability of mushrooms in a particular year.

The samples, including the cap, sporophore and stalk, were mainly mature specimens though some individuals at other growth stages were also included. To maintain a good level of accuracy, species with less than two specimens were discarded from the analysis.

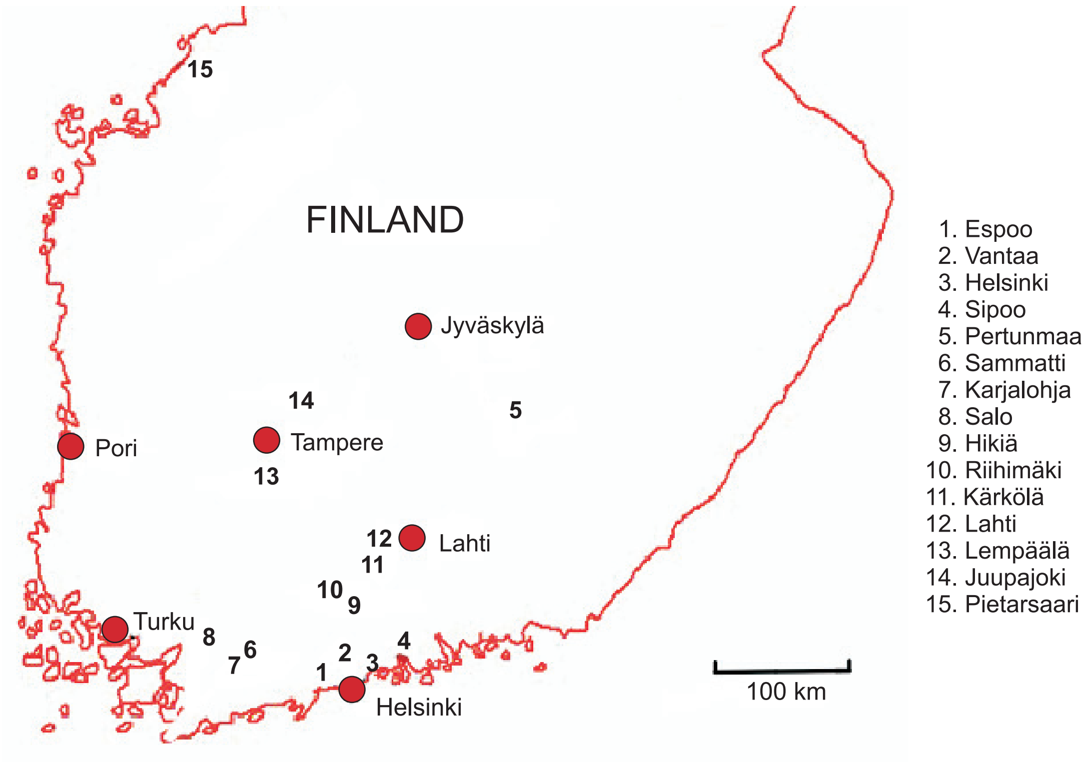

Figure 1. Map showing the collection areas of mushroom samples.

3.2

Sample Preparation and Analyses

Following the collection, the mushroom samples were cleaned carefully using a knife. The sliced fruit bodies were air-dried on filter paper or in a hanging mesh and then further dried at 90°C for 30 minutes. The dried samples were homogenised in an agate mortar and stored at room temperature in glass vials or plastic bags.

The concentrations of some elements may be affected by a long storage period. The dried and homogenised fungi samples were stored in glass or plastic containers at normal room temperature, which is an appropriate technique non-volatile elements such as the ones studied here as well as for Hg. Changes in trace element concentrations from sample storage were therefore not considered significant. Sample contamination was minimised by using an agate mortar in the homogenising procedure and by following the cleaning procedure practices applied at the Finnish Environment Institute Laboratory for non-disposable containers coming in contact with the samples.

Apart from Hg and Se the analysis of the trace element concentrations in the samples was conducted using a computer-controlled Perkin-Elmer Sciex ELAN 6000 inductively coupled plasma mass spectrometry, ICP-MS. For the ICP-MS analysis 50–100 mg of each homogenised sample was weighed and dissolved in 5 ml of 65 % nitric acid (Romil-SpA™ Super Purity Acid) by using an MLS-1200 MEGA microwave unit. The containers used in the microwave unit were 120 ml Teflon® PFA digestion vessels. After the microwave-assisted acid digestion the sample–acid solutions were left to cool for approximately 50 minutes and then diluted to 25 ml with deionised water. These were further diluted into a 1/10 solution. The determination limits were calculated with ten microwave dissolved blank samples:

Determination limit = 10 x standard deviation of blank samples

The determination limits for the studied elements are shown in Table 3.

Table 3. The determination limits for the studied elements

	mg kg^{-1}	
Ag*	0.02	
Al*	2.0	
Co_1*	0.05	
Cr_2*	0.2	
Cu*	0.1	
Hg**	0.01	
Fe*	15	
Mn*	0.1	
Mo*	0.1	
Pt*	0.01	
Rb*	0.2	No determination limit was established for Ca and Mg
Se***	0.01	
V_2*	0.05	
Zn*	2.0	

* Perkin Elmer Sciex ELAN 6000 ICP-MS
** Cold-vapour AAS
*** Diaminonaphthalene-derivative fluorometry
1: A high chloride content in samples may elevate the determination limit
2: A high calcium content in samples may elevate the determination limit

Mercury was determined after a digestion with nitric/sulphuric acids conducted according to a semi-automated cold-vapor atomic absorption spectrometric method (Armstrong & Uthe 1971) and Se after a digestion with nitric/sulphuric/perchloric acids by fluorometry (Alfthan 1984).

The precision between the series was determined by analysis of an in-house reference sample mixture containing several mushroom samples of different species from locations similar to the studied samples. For the ICP-MS, seven fungi samples were processed at a time with one blank and one standard reference material (Certified Reference Material *Cantharellus tubaeformis*, Swedish National Food Administration, Sweden; [see Appendix 2 for element concentrations in the reference material samples] sample). Precision (CV %) between the batches and the accuracy expressed as bias for the reference material samples may be seen in Table 4. No reliable reference values were available for cobalt and chromium.

Table 4. Precision (CV %) between the batches and the accuracy expressed as bias for the reference material samples on ICP-MS

	CV (%)	Bias (%)
Ag	10.2	
Al	9.12	
Ca	13.6	
Cu	2.79	3.96
Fe	17.1	7.76
Mg	3.48	
Mn	8.09	12.2
Mo	143	
Rb	5.33	
V	12.9	
Zn	4.47	4.75

For Hg the precision was 7.3 % and for Se 6.8 %. The accuracy of the method was established by analysing the certified reference materials BCR Pig Kidney CRM 186 for Hg (bias -0.5 %) and Bovine Liver CRM 185 for Se (bias +4.4 %).

In cases where the element concentration of a sample was lower than the determination limit determination limit/2 was used for the calculation of statistical parameters. Since the fungi data is generally quite highly dispersed and some values for the concentrations of individual mushroom samples were found to notably stand out from the major pattern in species concentrations, the median is seen as the most suitable measure of average for comparing and analysing the data. This agrees with the study's aim to define the general element concentrations in fungi.

3.3

Dry and Fresh Weight

The moisture content of fresh mushrooms generally varies between 90 – 95 %. For determining the element amounts in fresh fungi the average dry material contents established in the study by Eurola *et al*. (1996) were used for *Albatrellus ovinus, Boletus* species, *Cantharellus cibarius*, *C. tubaeformis*, *Craterellus cornucopioides* and *Hydnum* species. Values measured by Souci *et al*. (1981) were used for *Leccinum* species. For *Lactarius* species the average of *L. deterrimus* (Souci *et al.* 1981), *L. rufus* and *L. trivialis* (Eurola *et al.* 1996) was used. The dry material contents for each species are displayed in Appendix 3.

4 Results and Discussion

Appendices 4A-D present the average, standard deviation, coefficient of variation, median, range and count values for the element concentrations of each fungi species. The median concentrations of the studied elements are shown in Table 5. For platinum the measured concentrations were uniformly below the determination value of the ICP-MS, 0.01 mg kg^{-1}. In addition to platinum, the median values for cobalt, molybdenum and vanadium were found to be below the ICP-MS determination limits (see Table 3) for some species, which are shown in Table 6. Furthermore, the concentration values of cobalt and iron were not detected for several samples (see Appendices 4A-D).

4.1

Ag, Silver

The median concentration of Ag for all samples was 0.84 mg kg^{-1} dw but it was slightly raised by the very high Ag content of *Agaricus abruptibulbus* (26.90 mg kg^{-1} dw) – with *A. abruptibulbus* excluded, the median value for 11 species was 0.57 mg kg^{-1} dw. A mean value of 35 mg kg^{-1} for *Agaricus campestris* has been reported from Poland (Falandysz *et al*. 1994) and for *Agaricus* species 26 mg kg^{-1} from France (Michelot *et al*. 1998). In this study a high silver concentration was measured also for *Boletus* species (5.09 mg kg^{-1} dw) as well as an elevated concentration for *Macrolepiota procera* (2.55 mg kg^{-1} dw) and *Leccinum* species (1.31 mg kg^{-1} dw), which are comparable with fungi data from Poland (Falandysz *et al*. 1994). For all the other species the Ag levels were 1.31 mg kg^{-1} dw or less with the lowest concentration, 0.07 mg kg^{-1} dw, found in *Craterellus cornucopioides*.

4.2

Al, Aluminium

The highest aluminium content was detected for *Cantharellus cibarius* with 98.0 mg kg^{-1} dw. The median Al concentration for all species was 37.0 mg kg^{-1} dw with a rather uniform distribution between the species. Similar median values of 30 mg kg^{-1} and 53 mg kg^{-1} have been reported for other mushrooms species from southern Sweden (Tyler 1980) and southern Finland (Nuorteva *et al*. 1986), respectively. The median values for most species were below 50 mg kg^{-1} dw. Both *Leccinum* species (11.0 mg kg^{-1} dw) and *Albatrellus ovinus* (14.0 mg kg^{-1} dw) had relatively low aluminium levels.

Table 5. The median concentrations of Ag, Al, Ca, Co, Cr, Cu, Fe, Mg, Mn, Mo, Pt, Rb, V & Zn for each mushroom species (dry weight)

Scientific	Finnish	Swedish	English	No of	**Ag**	**Al**	**Ca**	**Co**	**Cr**	**Cu**	**Fe**	**Hg**	**Mg**	**Mn**	**Mo**	**Pt**	**Rb**	**Se**	**V**	**Zn**
				Samples	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
Agaricus abruptibulbus	Kuusen herkkusieni	Knölfotad snöbolls-champinjon	Champignon	28	26.9	46.5	200	1.02	1.09	197	86.0	2.92	1530	12.5	0.16	< 0.01	28.4	1.71	0.22	175
Albatrellus ovinus	Lampaankääpä	Fårticka	Sheep Polypore	12	0.15	14.0	83.0	0.22	0.83	4.58	18.5	0.12	648	7.60	< 0.10	< 0.01	214	0.36	0.06	39.5
Boletus species	Herkkutatit	Stensoppar	Cep, Boletes	21	5.09	16.0	85.1	< 0.05	1.08	29.9	37.0	0.83	818	8.80	0.10	< 0.01	272	13.2	0.07	130
Cantharellus cibarius	Kanttarelli	Kantarell	Chanterelle	17	0.34	98.0	529	0.47	0.91	46.1	95.0	0.10	1070	29.0	< 0.10	< 0.01	738	0.17	0.33	88.0
Cantharellus tubaeformis	Suppilovahvero	Tratt-kantarell	Trumpet Chanterelle	17	0.09	54.0	255	< 0.05	0.93	38.4	87.0	0.24	584	32.0	< 0.10	< 0.01	456	0.14	0.26	60.0
Craterellus cornucopioides	Musta torvisieni	Svart trumpetsvamp	Horn of Plenty	8	0.07	47.5	492	0.13	1.27	31.0	73.5	0.05	939	34.5	0.11	< 0.01	558	0.15	0.30	120
Gyromitra esculenta	Korvasieni	Stenmurkla	False Morel	5	0.94	35.0	275	0.31	0.93	89.8	92.5	0.08	1050	17.0	0.66	< 0.01	70.4	0.20	0.15	99.0
Hydnum species	Orakkaat	Tagg-svampar	Hedgehog fungus	23	0.66	38.0	217	< 0.05	1.04	23.6	91.5	0.41	976	17.0	< 0.10	< 0.01	1170	0.07	0.20	51.0
Lactarius species	Rouskut	Riskor	Milkcaps	21	0.47	26.0	275	< 0.05	1.05	19.0	49.0	0.27	1090	11.0	< 0.10	< 0.01	374	0.66	0.10	110
Leccinum species	Punikkitatit	Tegel- & aspsoppar	Orange Birch Bolete	25	1.31	11.0	100	0.07	0.96	51.4	42.0	0.43	828	7.90	0.37	< 0.01	168	1.15	< 0.05	100
Macrolepiota procera	Ukonsieni	Stolt fjällskivling	Parasol Mushroom	4	2.55	36.0	134	0.36	1.06	108	74.5	0.88	1300	17.0	0.34	< 0.01	47.6	1.68	0.19	82.5
Suillus variegatus	Kangastatti	Sandsopp	Velvet Bolete	10	0.45	67.0	138	0.14	0.96	20.7	2000	0.24	1000	8.10	0.14	< 0.01	411	1.02	0.09	84.5
Median for all 12 species				191	0.84	37.0	186	0.10	0.99	36.6	75.0	0.31	965	13.0	0.10	< 0.01	300	0.74	0.15	93.0
Source of trivial names in Finnish: Korhonen (1986)																				
Source of trivial names in Swedish: Ryman &Holmåsen (1987)																				
Source of trivial names in English: British Mycological Society (2005)																				

Table 6. The species for which the median element concentration was found to be below the determination limit of the element

Co	Mo	Pt	V
Boletus sp.	*A. ovinus*	ALL sp.	*Leccinum* sp.
C. tubaeformis	*C. cibarius*		
Hydnum sp.	*C. tubaeformis*		
Lactarius sp.	*Hydnum* sp.		
	Lactarius sp.		

4.3

Ca, Calcium

Cantharellus cibarius and *Craterellus cornucopioides* had by far the highest calcium levels of 529 and 492 mg kg^{-1} dw, respectively, while the concentrations of the other species fell within the range of 83.0 – 275 mg kg^{-1} dw. *Cantharellus tubaeformis*, *Gyromitra esculenta* as well as *Hydnum* and *Lactarius* species had somewhat higher than average Ca levels whereas the lowest concentrations were observed in *Albatrellus ovinus* and *Boletus* species. The median including all 12 species was 186 mg kg^{-1} dw. The median values for *Boletus* species and *Leccinum* species were equivalent to Polish data by Falandysz *et al*. (2001). In a French study (Michelot *et al*. 1998) the mean Ca concentrations for several species were, however, nearly ten-fold higher than in this study.

4.4

Co, Cobalt

For cobalt only a number of samples among each species produced reliable results exceeding the Co limit of determination of 0.05 mg kg^{-1} (see Table 3 and Appendix 5A). All median concentrations of cobalt were below 0.47 mg kg^{-1} dw apart from *Agaricus abruptibulbus*, which had the highest median Co concentration of 1.02 mg kg^{-1} dw. The median concentrations of *Hydnum* species (below the determination limit) and *Boletus* species (0.01 mg kg^{-1} dw) represented the lowest cobalt concentrations. Qualitatively the results of this study were similar to those reported for cobalt by Tyler (1980). Here the Co median for all species was 0.10 mg kg^{-1} whereas, possibly due to the different mushrooms species examined, a median value of 0.80 mg kg^{-1} was found by Tyler (1980). Furthermore, Michelot *et al*. (1998) reported a 100-fold higher value for *B. edulis* and 40-fold higher for *Leccinum* species but only three-fold higher values for *Agaricus* species.

4.5

Cr, Chromium

The concentrations of chromium were relatively consistent for all mushroom species. The median Cr concentrations ranged from 0.83 mg kg^{-1} dw (*Albatrellus ovinus*) to 1.27 mg kg^{-1} dw (*Craterellus cornucopioides*). An even distribution of Cr was also reported by Tyler (1980) though he reported a median value of 0.20 mg kg^{-1} for partially different species. For *Boletus* species, *Leccinum* species and *Agaricus* species the concentrations measured in France (Michelot *et al*. 1998) were relatively similar to the levels found here.

4.6
Cu, Copper

The level of copper was clearly elevated for *Agaricus abruptibulbus* (197 mg kg^{-1} dw) as the median concentration for all species was only 36.6 mg kg^{-1} dw. Similarly, the highest Cu concentrations were found among the *Agaricus* species in Sweden (Tyler 1980). In this study somewhat raised Cu levels were also found for *Gyromitra esculenta* and *Macrolepiota procera*. The lowest median Cu concentration was found for *Albatrellus ovinus* with 4.6 mg kg^{-1} dw. For six of the species studied here the element concentrations were similar to the ones established in the study by Eurola *et al*. (1996). Moreover, the data for several commonly analysed mushroom species were similar to the Polish (Falandysz *et al*. 2001) and French results (Michelot *et al*. 1998) for copper.

4.7
Fe, Iron

Apart from the extremely high Fe concentration of 2000 mg kg^{-1} dw found for *Suillus variegatus* the median iron concentrations of wild fungi generally varied between 18.5 and 95.0 mg kg^{-1} dw thus being of the same order as the levels previously published in Finland (Nuorteva *et al*. 1986). A very high mean Fe value of 3600 mg kg^{-1} was also reported for S. *variegatus* in a Polish study (Falandysz *et al*. 2001). The median for all species was 75.0 mg kg^{-1} dw and 72.5 mg kg^{-1} dw without *S. variegatus*. The values are similar compared with those reported from southern Sweden (Tyler 1980) and Poland (Falandysz *et al*. 2001). *Albatrellus ovinus* had the lowest Fe concentration of 18.5 mg kg^{-1} dw only.

4.8
Hg, Mercury

The median Hg concentration for all species was 0.31 mg kg^{-1} dw whereas the mean Hg for all species was found to be 0.94 mg kg^{-1} dw. The highest median value of 2.92 mg kg^{-1} dw was measured for *Agaricus abruptibulbus*. The Hg concentration for *Boletus* species, 0.83 mg kg^{-1} dw, and *Macrolepiota procera*, 0.88 mg kg^{-1} dw, were also clearly higher than the overall median. The highest value measured for an individual specimen was 51.6 mg kg^{-1} dw (*Boletus* species). The Hg concentrations of thirteen *Agaricus* species from different central European countries ranged from 0.7 to 80 mg kg^{-1} (Stijve & Besson 1976). In Finland a mean of 10.8 mg kg^{-1} for *A. abruptibulbus* has been reported by Lodenius (1981b) while in Germany concentrations of 4.5 mg kg^{-1} (Seeger 1976) and in France of 55 mg kg^{-1} (Michelot *et al*. 1998) were measured for different *Agaricus* species. Consistently high values have also been reported for *B. edulis*, 3.2-5.7 mg kg^{-1} by Rauter (1975) and Seeger (1976) as well as for *M. procera*, 1.1-5.8 mg kg^{-1} by Rauter (1975), Seeger (1976) and Falandysz (1997). Besides, an exceptionally high value of 40.6 mg kg^{-1} for *B. edulis* was published in a French study (Michelot *et al*. 1998).

4.9
Mg, Magnesium

The median Mg concentration for all 12 mushroom species was 965 mg kg^{-1} dw and the variation between the species relatively small. Higher than median magnesium levels were measured for *Agaricus abruptibulbus* (1530 mg kg^{-1} dw) and *Macrolepiota procera* (1300 mg kg^{-1} dw) while the other species had concentrations of less than 1100 mg kg^{-1} dw. The lowest median Mg values were found for *Cantharellus tubaeformis* and *Albatrellus ovinus*: 584 and 648 mg kg^{-1} dw respectively. The concentrations for *Boletus* and *Leccinum* species were similar to previously published data by Michelot *et al*. (1998) and Falandysz *et al*. (2001).

4.10
Mn, Manganese

The manganese levels ranged between 7.60 and 34.5 mg kg^{-1} dw with the median for all species being 13.0 mg kg^{-1} dw. These are of the same order as the median values reported in other European studies (Byrne *et al*. 1976, Tyler 1980, Eurola *et al*. 1996). Somewhat elevated Mn concentrations of 29.0-34.5 mg kg^{-1} dw were detected for *Craterellus cornucopioides, Cantharellus tubaeformis* and *Cantharellus cibarius*. *Albatrellus ovinus*, *Leccinum* species, *Suillus variegatus* and *Boletus* species had the lowest concentrations of manganese. Central European data (Falandysz *et al*. 2001, Michelot *et al*. 1998) for the two latter species were similar to the concentrations found here.

4.11
Mo, Molybdenum

The median concentration of Mo for all species was 0.10 mg kg^{-1} dw. With 0.66 mg kg^{-1} dw *Gyromitra esculenta* had clearly the highest content measured for molybdenum whereas the low Mo concentrations of *Lactarius* species, *Hydnum* species and *Cantharellus tubaeformis* ranged between 0.01 and 0.04 mg kg^{-1} dw. Raised Mo levels were also found for *Leccinum* species and *Macrolepiota procera*. The concentrations for *Boletus* and *Leccinum* species were similar to the values measured for the same mushroom species in Poland (Falandysz *et al*. 2001).

4.12
Pt, Platinum

The measured platinum concentrations were uniformly below the ICP-MS determination limit value of 0.01 mg kg^{-1} established for Pt. Platinum concentrations have rarely been established for mushrooms in previous research. However, Djingova *et al*. (2003) have reported a sample of *Vascellum pratense* growing along a motorway in Germany to contain 0.006 mg kg^{-1} of platinum .

4.13
Rb, Rubidium

The concentrations of rubidium fell within a wide range varying from 47.6 mg kg^{-1} dw (*Macrolepiota procera*) to the considerably high level of 1170 mg kg^{-1} dw (*Hydnum* species). For all the other mushroom species Rb concentrations ranged within 168 and 738 mg kg^{-1} dw. The median of Rb for all 12 species was 300 mg kg^{-1} dw and 256 mg kg^{-1} dw for 11 species excluding *Hydnum* species. The results confirm those of Tyler (1980) from southern Sweden that showed *Hydnum* species (1190 mg kg^{-1}, vs. this study: 1170 mg kg^{-1}) and *Cantharellus cibarius* (1070 mg kg^{-1}, vs. this study: 738 mg kg^{-1}) to accumulate Rb to a greater extent than mushrooms in general. The values for *Boletus* species, 272 mg kg^{-1} dw, and for *Leccinum* species, 168 mg kg^{-1} dw, were comparable with the data from Poland, 285 and 333 mg kg^{-1}, respectively (Falandysz *et al*. 2001), and with the value of 130 mg kg^{-1} found for *B. edulis* in Norway (Allen

& Steinnes 1978). Interestingly, the lowest Rb median value in this study was found for A. *abruptibulbus*.

4.14
Se, Selenium

By far the highest median Se concentration was found for *Boletus* species, 13.2 mg kg^{-1} dw. The value is somewhat lower than the mean values published previously in Slovenia, 19.8 mg kg^{-1} (Byrne *et al*. 1976), in Finland, 17 mg kg^{-1} (Piepponen *et al*. 1983) and in France, 23.4 mg kg^{-1} (Michelot *et al*. 1998). The median concentration of Se for all samples was 0.74 mg kg^{-1} dw with *Agaricus abruptibulbus* and *Macrolepiota procera* having clearly increased levels of 1.71 and 1.68 mg kg^{-1} dw, respectively. Previously mean values of 0.8 – 7.8 mg kg^{-1} have been measured for *Agaricus* species in central Europe (Stijve & Besson 1976), 2.7 mg kg^{-1} in Finland (Piepponen *et al*. 1983) and 31 mg kg^{-1} in France (Michelot *et al*. 1998). Somewhat higher Se values for M. *procera* have been found in Slovenia, 2.7 mg kg^{-1}, (Byrne *et al*. 1976) and in Finland, 4.8 mg kg^{-1} (Piepponen *et al*. 1983).

4.15
V, Vanadium

The vanadium concentrations were rather consistent within all species varying between 0.04 and 0.33 mg kg^{-1} dw. The median V content for all mushroom species was 0.15 mg kg^{-1} dw. This value is supported by Byrne *et al*. (1976), who found a mean value of 0.23 mg kg^{-1} but not by Tyler (1980) who reported a median value of 3 mg kg^{-1}. These concentration were, however, measured for different mushroom species than the ones examined in this study. Byrne *et al*. (1976) reported a mean value of 1.94 mg kg^{-1} for *B. edulis* in comparison with the concentration of 0.07 mg kg^{-1} dw found here for *Boletus* species.

4.16
Zn, Zinc

The highest zinc level, 175 mg kg^{-1} dw, was measured for *Agaricus abruptibulbus* while *Albatrellus ovinus* had the lowest zinc concentration of 39.5 mg kg^{-1} dw. The median for all species was 93.0 mg kg^{-1} dw. Slightly elevated levels of Zn were detected for *Lactarius* species, *Craterellus cornucopioides* and *Boletus* species. The median value of all mushroom samples for Zn was identical with the one found in Slovenia, 93 mg kg^{-1} (Byrne *et al*. 1976), and similar to those reported from Sweden, 100 mg kg^{-1} (Tyler 1980), and Finland, 92 mg kg^{-1} (Nuorteva *et al*. 1986). For *A. abruptibulbus* the mean values of 75 mg kg^{-1} (Tyler 1980), 134 mg kg^{-1} (Michelot *et al*. 1998), 138 mg kg^{-1} (Meisch *et al*. 1977) and 210 mg kg^{-1} (Falandysz *et al*. 2001) were similar to the results of this study. The mean Zn concentration of 110 mg kg^{-1} measured for six commercial species in Finland (Eurola *et al*. 1996), of 165 mg kg^{-1} for *Craterellus cornucopioides* in Slovenia (Byrne *et al*. 1976) and of 100 mg kg^{-1} for five species in Poland (Falandysz *et al*. 2001) were also of the same magnitude as the results of this study.

4.17

Possible Health Risks

In general elements accumulate in mushrooms and the implications for health can be seen on a long-term basis. Nevertheless, Michelot *et al*. (1998) suggested that the high accumulation of some elements in fungi may also explain abnormal incidents of poisoning caused by species classified as edible.

The amount of each studied element considered safe for weekly consumption with respect to the current limits and recommendations (see Chapter 2.2) are shown in Table 7. Table 8 presents the median concentrations of the elements for each mushroom species calculated as fresh weight fungi.

Table 7. The weekly intake of the studied elements considered safe according to legal standards or other recommendations

	mg/week	
Ag_{1}	0.56	Average Daily Intake (max.)
Al_{2}	420	Minimal Risk Level for Chronic Exposure
Ca_{3}	6800	Average Daily Intake
Co_{4}	9.80	NOAEL
Cr_{5}	0.18	Safe Daily Intake
Cu_{6}	50	Safe Upper Limit (min & max)
Fe_{7}	119	NOAEL
Hg_{8}	0.24	NOAEL (for methylmercury)
Mg_{9}	2800	NOAEL
Mn_{10}	84	NOAEL
Mo_{11}	14	US Tolerable Upper Intake Level
Pt_{12}	*	Average Daily Intake
Rb_{13}	16	Average Daily Intake (max.)
Se_{14}	3.15	Safe Upper Limit
V_{15}	0.35	Average Daily Intake (max.)
Zn_{16}	180	Safe Upper Limit

* For platinum the safe consumption amount was calculated using the determination limit of the ICP-MS, 0.01 mg kg^{-1}

Table 8. The median concentrations (mg kg^{-1}) of the studied elements in fresh fungi material.

	Ag	Al	Ca	Co	Cr	Cu	Fe	Hg
	mg kg^{-1} fw	mg kg^{-1} fw	mg kg^{-1} fw	mg kg^{-1} fw	mg kg^{-1} fw	mg kg^{-1} fw	mg kg^{-1} fw	mg kg^{-1} fw
Agaricus abruptibulbus	2.69	4.65	20.0	0.10	0.11	19.7	8.60	0.29
Albatrellus ovinus	0.01	1.19	7.06	0.02	0.07	0.39	1.57	0.01
Boletus species	0.51	1.60	8.51	*	0.11	2.99	3.70	0.08
Cantharellus cibarius	0.03	8.82	47.6	0.04	0.08	4.15	8.55	0.01
Cantharellus tubaeformis	0.01	3.51	16.6	*	0.06	2.50	5.66	0.02
Craterellus cornucopioides	0.01	4.47	46.2	0.01	0.12	2.91	6.91	0.00
Gyromitra esculenta	0.09	3.50	27.5	0.03	0.09	8.98	9.25	0.01
Hydnum species	0.05	2.62	15.0	*	0.07	1.63	6.31	0.03
Lactarius species	0.04	2.19	23.2	*	0.09	1.60	4.13	0.02
Leccinum species	0.10	0.85	7.70	0.01	0.07	3.96	3.23	0.03
Macrolepiota procera	0.26	3.60	13.4	0.04	0.11	10.8	7.45	0.09
Suillus variegatus	0.05	6.70	13.8	0.01	0.10	2.07	200	0.02

	Mg	Mn	Mo	Pt	Rb	Se	V	Zn
	mg kg^{-1} fw	mg kg^{-1} fw	mg kg^{-1} fw	mg kg^{-1} fw	mg kg^{-1} fw	mg kg^{-1} fw	mg kg^{-1} fw	mg kg^{-1} fw
Agaricus abruptibulbus	153	1.25	0.02	*	2.84	0.17	0.02	17.5
Albatrellus ovinus	55.0	0.65	*	*	18.1	0.03	0.00	3.36
Boletus species	81.8	0.88	0.01	*	27.2	1.32	0.01	13.0
Cantharellus cibarius	96.3	2.61	*	*	66.4	0.02	0.03	7.92
Cantharellus tubaeformis	38.0	2.08	*	*	29.6	0.01	0.02	3.90
Craterellus cornucopioides	88.2	3.24	0.01	*	52.5	0.01	0.03	11.3
Gyromitra esculenta	105	1.70	0.07	*	7.04	0.02	0.02	9.90
Hydnum species	67.3	1.17	*	*	80.7	0.00	0.01	3.52
Lactarius species	91.9	0.93	*	*	31.5	0.06	0.01	9.28
Leccinum species	63.8	0.61	0.03	*	12.9	0.09	*	7.70
Macrolepiota procera	130	1.70	0.03	*	4.76	0.17	0.02	8.25
Suillus variegatus	100	0.81	0.01	*	41.1	0.10	0.01	8.45

* The dry weight median value for the species is below the determination limit given for the element

The amounts of fresh weight mushroom that may safely be consumed as kilograms per day are presented in Appendices 5A-B. It should be noted that for Ag, Ca, Pt, Rb and V the limiting values used in the calculations are not official or legal standards as such standards are yet to be established for these elements. Therefore the presented amounts may only be used as recommendations for the safe consumption of mushrooms. The recommended amounts of fresh mushrooms calculated to be safe to consume weekly for each element (see Appendices 5A-B and table 9) is maximally 1.4 kg.

The recommended amounts are mostly limited by platinum and rubidium. However, for platinum all concentration values were below the ICP-MS determination limit and thus no safe weekly intake amount could be calculated for platinum. For rubidium the safe amounts are relatively low: for nine of the studied species up to 1.4 kg of mushroom per week may safely be consumed with regard to rubidium. Nevertheless, the toxicity of rubidium is still relatively uncertain and the safe amounts with respect to Rb were calculated based on average daily intake values only, as no safe limits have been established for Rb.

Among the essential elements (see Appendices 5A-B) Fe restricts the consumption of *Suillus variegatus* to 0.59 kg per week. Apart from this, the amounts of fresh fungi considered safe for consumption are higher than 1.4 kg for all mushroom species regarding the essential elements.

In the case of the other elements (see Appendices 5A-B) no health risks are involved regarding their regular consumption: for molybdenum the safe amounts of fresh mushroom range between 212 and 1 400 kg and for vanadium between 11.8 and 74.9 kg per week.

Table 9 presents the amount of fresh mushroom in kilograms per week that is considered safe for consumption with regard to the studied toxic elements. In the case of the toxic elements only 820 g of *Agaricus abruptibulbus* may be consumed per week according to the NOAEL for methylmercury. However, in mushrooms methylmercury makes up only less than 10 % of the total mercury (Stijve & Besson 1976). As inorganic Hg is less toxic than methylmercury, the recommended amount for mushroom consumption with respect to methylmercury may be assumed to be somewhat higher.

Table 9. The amount of fresh fungi (kg/week) considered a safe consumption according to legal standards* or other recommendations* for toxic elements

Toxic elements	Ag 1 kg fw	Al 2 kg fw	Cr 3 kg fw	Hg 4 kg fw
Agaricus abruptibulbus	**0.21**	90.3	1.61	**0.82**
Albatrellus ovinus	45.4	352	2.48	23.3
Boletus species	**1.10**	263	1.62	2.88
Cantharellus cibarius	18.3	47.6	2.14	26.4
Cantharellus tubaeformis	95.7	120	2.89	15.3
Craterellus cornucopioides	85.1	94.1	1.47	56.3
Gyromitra esculenta	5.96	120	1.88	29.8
Hydnum species	12.3	160	2.44	8.41
Lactarius species	14.1	192	1.98	10.5
Leccinum species	5.56	496	2.37	7.19
Macrolepiota procera	2.20	117	1.65	2.70
Suillus variegates	12.4	62.7	1.82	9.92

1 Ag Average Daily Intake (0.56 mg/week)
2 Al Minimal Risk Level for Chronic Exposure (420 mg/week)
3 Cr Safe Daily Intake (0.18 mg/week)
4 Hg NOAEL (for methylmercury, 0.24 mg/week)

* See Table 8.

Furthermore, the consumption of *A. abruptibulbus* is limited to an amount of 210 g per week by the high concentration of silver. The maximum amount for silver was, however, calculated using an average daily intake value as there is no established intake limit for Ag. In our previous report cadmium was found to be the limiting element for *A. abruptibulbus* and the recommended amount for weekly consumption only 140 g (Pelkonen *et al*. 2006). Nonetheless, as *Agaricus* species are not among the commercially sold mushrooms in Finland and some poisonous species similar to *A. abruptibulbus* may easily be mistaken for the edible ones, the species is best left unpicked.

The consumption of Boletus species is limited by silver to an amount of 1.1 kg per week (see Table 9). Therefore some caution should be taken in terms of consuming large amounts of Boletus species regularly. Apart from Boletus species and A. abruptibulbus the consumption of the studied mushroom species is, however, considered safe with regard to the examined toxic elements.

5 Conclusions

In general, the trace element concentrations of fungi in southern Finland were relatively low. Table 10 presents a summary of the maximum weekly amounts of fresh mushrooms that are recommended for consumption according to legal standards and other recommendations. When excluding platinum and rubidium the relevant limiting element among all mushroom species is chromium apart from silver for *Agaricus abruptibulbus* and iron for *Suillus variegatus*. The maximum fungi amounts limited by Cr concentration exceed all, however, 1.4 kg per week, an arbitrary maximal amount estimated to be consumed. Therefore only Ag and Fe are regarded to potentially pose a risk of excessive element intake from mushrooms. Due to the weekly maximum amount of 210 g calculated for *A. abruptibulbus* the species is recommended to be avoided. Moreover, *Suillus variegatus* and *Boletus* species are recommended for consumption in moderate amounts only.

Table 10. The maximum amount of fresh fungi (kg/week) recommended for consumption according to legal standards* or other recommendations*.

	kg/week	Limiting element
Agaricus abruptibulbus	**0.21**	Ag
Albatrellus ovinus	2.48	Cr
Boletus species	**1.10**	Ag
Cantharellus cibarius	2.14	Cr
Cantharellus tubaeformis	2.89	Cr
Craterellus cornucopioides	1.47	Cr
Gyromitra esculenta	1.88	Cr
Hydnum species	2.44	Cr
Lactarius species	1.98	Cr
Leccinum species	2.37	Cr
Macrolepiota procera	1.65	Cr
Suillus variegatus	**0.59**	Fe

Pt and Rb are excluded from the table.
* See Chapter 2.2. for details on legal standards and recommendations

It must be emphasised that for the adverse health effects to occur due to an excessive exposure to minerals and trace elements the consumption of mushrooms must be regular and long-term, that is on a daily basis and for the duration of several months. Such a consumption pattern is not, however, considered to be common. All in all, the presently studied 10 mushroom species sold commercially in Finland are considered safe for moderate consumption with respect to the 16 minerals and trace elements studied here.

The median element concentrations for most mushrooms in the present study are approximately of the same magnitude as those previously published in Finland and southern Europe. The comparison between the studies is, however, not completely accurate as in most of the other research the data are presented as means instead of medians. This tends to exaggerate the differences in element concentrations between the studies. For instance, in this study the mean values were much higher than and the maximum element values over ten-fold higher than the median values for many of the mushroom species. It should also be noted that some discrepancy is possible due to the different analytical techniques used in other studies on mushrooms.

It is important to notice that the mean intake from food and the environment may be considerably large for many elements. According to JECFA the safety margin between the exposure in a normal diet and the level causing adverse health effects may thus be relatively small (Council of Europe 2001).

For this research no distinction was made between the different chemical forms of elements in fungi but only the total concentration of each element was determined. The uptake of different forms and complexes of elements in mushrooms should, however, be considered in more detail as the impacts on health may vary depending on the chemical form of the element ingested. Further investigations should also be focused on the possible accumulation and the synergistic toxic effects of multiple elements in fungi.

When evaluating the toxicity of an element and the risks posed by exceeding a particular exposure level, it is necessary to take notice of the factors influencing the actual effects of a toxic element. For instance, the absorption of zinc and copper is reduced by cadmium (Klaassen 1996). Furthermore, cadmium interferes with enzyme reactions by disturbing the role of zinc in essential body mechanisms (Lahermo *et al.* 1996). High levels of zinc in nutrition are thought to provide protection from the effects of cadmium (Lahermo *et al.* 1996). Moreover, cadmium bioavailability in food has been found to be associated adversely with iron nutrition in human feeding studies and also affected by the presence of elements such as zinc, potassium and calcium as well as phytate, fiber and other food constituents (McLaughlin *et al.* 1999).

This research has increased the knowledge on Al, Ca, Co, Cr, Cu, Fe, Hg, Mg, Mn, Se and Zn levels in several edible fungi species and has established new data for Ag, Mo, Pt, Rb and V, which have not been broadly investigated in previous research on mushrooms. The study also assessed possible health risks involved in the consumption of wild fungi in Finland. Overall, the research has provided recommendations for consumers on choosing and consuming wild mushrooms safely.

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Appendix 1. Mushrooms listed as commercially sold species in Finland.

Albatrellus ovinus
Armillaria mellea group
Boletus edulis, B. pinophilus & B. reticulatus
Cantharellus cibarius
Cantharellus tubaeformis (& C. lutescens)
Craterellus cornucopioides
Cultivated mushrooms
Gyromitra esculenta
Hydnum repandum (& H. rufescens)
Hygrophorus camarophyllus
Lactarius deliciosus & L. deterrimus
Lactarius rufus
Lactarius torminosus
Lactarius trivialis & L. utilis
Leccinum versipelle, L. aurantiacum & L. vulpinum
Morchella species
Rozites caperatus
Russula claroflava
Russula decolorans
Russula paludosa
Russula vinosa
Suillus luteus
Suillus variegatus
Tricholoma matsutake

Source: Ministry of Agriculture and Forestry (2007)

Appendix 2. The Average, Coefficient of Variation (CV %), Certified Values and Bias (%) for Reference Material (Cantharellus tubaeformis) samples on ICP-MS

	Ag mg kg^{-1}	**Al** mg kg^{-1}	**Ca** mg kg^{-1}	**Cu** mg kg^{-1}	**Fe** mg kg^{-1}	**Mg** mg kg^{-1}
Average	0.11 ±0.01	42.7 ±3.90	225 ±30.6	35.8 ±1.00	93.2 ±15.9	615 ±21.4
CV (%)	10.2	9.12	13.6	2.79	17.1	3.48
Certified value			34.4	101		
Bias (%)				3.96	7.76	

	Mn mg kg^{-1}	**Mo** mg kg^{-1}	**Rb** mg kg^{-1}	**V** mg kg^{-1}	**Zn** mg kg^{-1}
Average	43.8 ±3.54	0.03 ±0.04	425 ±22.6	0.14 ±0.02	52.4 ±2.34
CV (%)	8.09	143	5.33	12.9	4.47
Certified value	49.9				55.0
Bias (%)	12.2				4.75

Appendix 3. The dry material contents of the fungi species as a percentage of fresh fungi weight

*	10.0	Agaricus abruptibulbus
	8.5	Albatrellus ovinus
	10.0	Boletus sp. (edulis, pinophilus)
	9.0	Cantharellus cibarius
	6.5	Cantharellus tubaeformis
	9.4	Craterellus cornucopioides
*	10.0	Gyromitra esculenta
	6.9	Hydnum sp. (repandum, rufescens)
**	8.4	Lactarius sp.(deliciosus, deterrimus, rufus, torminosus, trivialis)
	7.7	Leccinum (aurantiacum, versipelle)
*	10.0	Macrolepiota procera
*	10.0	Suillus variegatus

* = general reference value of 10 % dry material used
** = average of L. deterrimus, L. rufus & L. trivialis

Sources: Eurola *et al.* (1996), Souci *et al.* (1981)

Appendix 4A. The statistical values for each mushroom species (dry weight).

A = Average
SD = Standard deviation
CV = Coefficient of variation
Med = Median
MIN = Minimum
MAX = Maximum
R = Range value
n = Number of samples

		Ag	Al	Ca	Co	Cr	Cu	Fe	Hg	Mg	Mn	Mo	Pt	Rb	Se	V	Zn
		mg kg-1	mg kg-1	mg kg-1	mg kg-1	mg kg-1	mg kg-1	mg kg-1	mg kg-1	mg kg-1	mg kg-1	mg kg-1	mg kg-1	mg kg-1	mg kg-1	mg kg-1	mg kg-1
Total 12 species	A	5.80	47.5	249	0.41	1.23	65.8	161	1.13	1000	16.8	0.16	0.00	400	2.70	0.21	107
	SD	12.0	49.6	231	0.83	1.52	88.3	396	4.01	356	12.0	0.20	0.00	396	5.94	0.23	63.4
	CV	2.07	1.04	0.93	2.00	1.24	1.34	2.46	354	0.36	0.72	1.28		0.99	219	1.07	0.59
	Med	0.84	37.0	186	0.10	0.99	36.6	75.0	0.32	965	13.0	0.10	0.00	300	0.74	0.15	93.0
	MIN	0.02	4.20	0.00	0.00	0.18	3.32	16.0	0.03	83.4	3.80	0.00	0.00	5.72	0.02	0.00	28.0
	MAX	61.1	540	1670	5.02	19.6	557	2300	51.6	2310	64.0	1.64	0.00	2280	42.5	1.35	570
	R	61.1	536	1670	5.02	19.4	553	2280	51.5	2230	60.2	1.64	0.00	2270	42.4	1.35	542
	n	191	191	191	79	191	191	92	190	191	191	191	191	191	182	191	191
Agaricus abruptibulbus	A	29.0	51.9	281	1.40	1.31	237	83.6	3.86	1560	14.9	0.15	0.00	35.6	3.90	0.23	191
	SD	16.6	30.9	257	1.37	1.19	125	41.6	3.51	262	7.59	0.06	0.00	30.5	8.24	0.13	86.9
	CV	0.57	0.59	0.92	0.98	0.91	0.53	0.50	90.8	0.17	0.51	0.42		0.86	211	0.56	0.45
	Med	26.9	46.5	200	1.02	1.09	197.0	86.0	2.92	1530	12.5	0.16	0.00	28.4	1.71	0.22	175
	MIN	6.55	8.00	41.9	0.04	0.49	59.6	30.0	1.71	1110	9.50	0.00	0.00	5.72	0.83	0.07	86.0
	MAX	61.1	120	1290	5.02	7.15	557	190	19.9	2310	45.0	0.27	0.00	126	42.5	0.64	570
	R	54.6	112	1250	4.98	6.66	497	160	18.2	1200	35.5	0.27	0.00	120	41.7	0.57	484
	n	28	28	28	17	28	28	19	27	28	28	28	28	28	26.000	28	28
Albatrellus ovinus	A	0.15	14.9	84.8	0.27	0.91	8.11	44.7	0.19	675	7.45	0.06	0.00	258	0.40	0.08	40.6
	SD	0.07	8.39	56.4	0.17	0.57	10.4	43.0	0.19	165	2.91	0.03	0.00	150	0.14	0.07	7.32
	CV	0.45	0.56	0.66	0.64	0.62	1.29	0.96	101	0.24	0.39	0.58		0.58	35.8	0.82	0.18
	Med	0.15	14.0	83.0	0.22	0.83	4.58	18.5	0.12	648	7.60	0.06	0.00	214	0.36	0.06	39.5
	MIN	0.06	4.20	0.00	0.07	0.18	3.32	16.0	0.05	389	3.80	0.00	0.00	99.0	0.19	0.02	31.0
	MAX	0.25	39.0	174	0.53	1.96	40.7	110	0.79	1020	15.0	0.12	0.00	645	0.65	0.25	59.0
	R	0.19	34.8	174	0.46	1.78	37.4	94.0	0.74	631	11.2	0.12	0.00	546	0.46	0.23	28.0
	n	12	12	12	5	12	12	6	15	12	12	12	12	12	13	12	12

Appendix 4B. The statistical values for each mushroom species (dry weight).

		Ag	Al	Ca	Co	Cr	Cu	Fe	Hg	Mg	Mn	Mo	Pt	Rb	Se	V	Zn
		mg kg-1	mg kg-1	mg kg-1	mg kg-1	mg kg-1	mg kg-1	mg kg-1	mg kg-1	mg kg-1	mg kg-1	mg kg-1	mg kg-1	mg kg-1	mg kg-1	mg kg-1	mg kg-1
Boletus species	A	7.56	24.2	133	0.04	1.17	35.2	40.8	3.22	873	9.51	0.11	0.00	271	14.7	0.10	127
	SD	7.22	19.1	121	0.08	0.33	19.4	15.0	10.8	247	4.51	0.07	0.00	109	7.28	0.09	43.1
	CV	0.96	0.79	0.91	2.28	0.28	0.55	0.37	336	0.28	0.47	0.59		0.40	49.4	0.85	0.34
	Med	5.09	16.0	85.1	0.01	1.08	29.9	37.0	0.83	818	8.80	0.10	0.00	272	13.2	0.07	130
	MIN	1.26	4.40	25.9	0.00	0.82	13.3	24.0	0.29	536	4.30	0.00	0.00	102	5.42	0.02	52.0
	MAX	33.3	74.0	591	0.24	1.84	96.0	78.0	51.6	1550	20.0	0.31	0.00	548	32.5	0.38	210
	R	32.0	69.6	565	0.24	1.02	82.7	54.0	51.3	1010	15.7	0.31	0.00	446	27.1	0.36	158
	n	21	21	21	8	21	21	10	22	21	21	21	21	21	22	21	21
Cantharellus cibarius	A	0.71	107	516	0.51	1.09	44.7	90.2	0.12	1030	29.0	0.08	0.00	685	0.18	0.40	94.9
	SD	0.87	34.3	226	0.17	0.64	11.4	27.4	0.08	170	13.3	0.06	0.00	231	0.08	0.32	22.4
	CV	1.23	0.32	0.44	0.33	0.59	0.25	0.30	70.7	0.16	0.46	0.71		0.34	45.2	0.80	0.24
	Med	0.34	98.0	529	0.47	0.91	46.1	95.0	0.10	1070	29.0	0.08	0.00	738	0.17	0.33	88.0
	MIN	0.12	64.0	160	0.33	0.45	26.4	50.0	0.05	684	11.0	0.00	0.00	173	0.05	0.12	65.0
	MAX	2.99	170	895	0.76	3.07	63.3	120	0.41	1260	55.0	0.22	0.00	992	0.36	1.35	130
	R	2.87	106	735	0.43	2.62	36.9	70.0	0.36	576	44.0	0.22	0.00	819	0.31	1.23	65.0
	n	17	17	17	5	17	17	6	17	17	17	17	17	17	17	17	17
Cantharellus tubaeformis	A	0.50	53.2	301	0.05	0.97	38.9	89.3	0.23	611	31.4	0.04	0.00	433	0.14	0.34	60.8
	SD	1.67	18.1	135	0.03	0.27	5.42	19.3	0.07	114	11.6	0.02	0.00	112	0.05	0.22	9.58
	CV	3.36	0.34	0.45	0.54	0.28	0.14	0.22	31.3	0.19	0.37	0.63		0.26	35.8	0.63	0.16
	Med	0.09	54.0	255	0.04	0.93	38.4	87.0	0.24	584	32.0	0.03	0.00	456	0.14	0.26	60.0
	MIN	0.03	24.0	101	0.02	0.53	29.0	60.0	0.10	494	12.0	0.00	0.00	186	0.06	0.06	45.0
	MAX	6.96	87.0	585	0.09	1.48	47.4	120	0.34	975	54.0	0.08	0.00	600	0.23	0.87	79.0
	R	6.93	63.0	484	0.07	0.95	18.4	60.0	0.24	481	42.0	0.08	0.00	414	0.17	0.81	34.0
	n	17	17	17	8	17	17	9	18	17	17	17	17	17	16	17	17
Craterellus cornucopioides	A	2.23	51.6	592	0.12	1.56	33.0	78.3	0.07	999	34.0	0.11	0.00	508	0.14	0.32	116
	SD	5.46	30.1	499	0.03	1.21	9.02	22.9	0.06	229	15.3	0.06	0.00	219	0.08	0.18	19.3
	CV	2.44	0.58	0.84	0.22	0.78	0.27	0.29	82.7	0.23	0.45	0.51		0.43	55.8	0.57	0.17
	Med	0.07	47.5	492	0.13	1.27	31.0	73.5	0.05	939	34.5	0.11	0.00	558	0.15	0.30	120
	MIN	0.02	15.0	148	0.09	0.35	22.4	56.0	0.03	765	16.0	0.00	0.00	146	0.05	0.13	87.0
	MAX	15.7	110	1670	0.14	4.28	50.9	110	0.17	1480	62.0	0.19	0.00	861	0.27	0.57	150
	R	15.7	95.0	1520	0.05	3.93	28.5	54.0	0.14	715	46.0	0.19	0.00	715	0.22	0.44	63.0
	n	8	8	8	3	8	8	4	8	8	8	8	8	8	8	8	8

Appendix 4C. The statistical values for each mushroom species (dry weight).

		Ag	Al	Ca	Co	Cr	Cu	Fe	Hg	Mg	Mn	Mo	Pt	Rb	Se	V	Zn
		mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
Gyromitra esculenta	A	1.11	136	294	0.30	1.28	88.2	206	0.09	1030	19.0	0.65	0.00	85.2	0.39	0.36	99.8
	SD	0.93	226	115	0.05	0.67	20.1	257	0.03	146	9.41	0.14	0.00	33.1	0.45	0.48	6.30
	CV	0.84	1.66	0.39	0.15	0.52	0.23	1.25	33.5	0.14	0.50	0.21		0.39	116	1.32	0.06
	Med	0.94	35.0	275	0.31	0.93	89.8	92.5	0.08	1050	17.0	0.66	0.00	70.4	0.20	0.15	99.0
	MIN	0.18	24.0	129	0.24	0.71	59.4	48.0	0.05	806	10.0	0.49	0.00	56.8	0.15	0.14	93.0
	MAX	2.38	540	434	0.34	2.35	112	590	0.13	1200	32.0	0.79	0.00	122	1.20	1.21	110.0
	R	2.20	516	305	0.10	1.64	52.6	542	0.07	394	22.0	0.30	0.00	65.2	1.05	1.07	17.00
	n	5	5	5	4	5	5	4	6	5	5	5	5	5	5	5	5
Hydnum species	A	1.05	42.1	242	0.00	1.09	23.0	100	0.37	934	18.0	0.16	0.00	1100	0.13	0.22	53.2
	SD	1.24	19.8	161	0.01	0.55	10.5	62.5	0.23	186	7.36	0.36	0.00	577	0.12	0.12	14.3
	CV	1.17	0.47	0.66	1.84	0.50	0.46	0.62	61.2	0.20	0.41	2.20		0.52	95.1	0.55	0.27
	Med	0.66	38.0	217	0.00	1.04	23.6	91.5	0.41	976	17.0	0.04	0.00	1170	0.07	0.20	51.0
	MIN	0.11	7.30	31.4	0.00	0.34	6.13	23.0	0.06	541	5.00	0.00	0.00	339	0.02	0.04	28.0
	MAX	5.89	87.0	555	0.02	2.40	48.2	240	0.74	1290	40.0	1.64	0.00	2280	0.48	0.56	85.0
	R	5.78	79.7	524	0.02	2.06	42.1	217	0.68	749	35.0	1.64	0.00	1940	0.46	0.52	57.0
	n	23	23	23	7	23	23	8	23	23	23	23	23	23	22	23	23
Lactarius species	A	0.61	34.5	259	0.05	1.05	23.1	58.3	0.28	1080	11.4	0.01	0.00	404	0.81	0.17	127
	SD	0.51	20.8	196	0.06	0.39	13.7	30.0	0.16	173	5.12	0.01	0.00	222	0.72	0.28	61.6
	CV	0.83	0.60	0.76	1.09	0.37	0.60	0.51	57.8	0.16	0.45	1.10		0.55	88.5	1.69	0.48
	Med	0.47	26.0	275	0.04	1.05	19.0	49.0	0.27	1090	11.0	0.01	0.00	374	0.66	0.10	110
	MIN	0.11	8.30	39.2	0.00	0.29	5.90	35.0	0.03	796	4.40	0.00	0.00	7.09	0.04	0.02	69.0
	MAX	2.05	86.0	677	0.13	1.81	59.0	100	0.80	1410	24.0	0.05	0.00	911	2.68	1.35	310
	R	1.94	77.7	638	0.13	1.52	53.1	65.0	0.77	614	19.6	0.05	0.00	904	2.64	1.33	241
	n	21	21	21	4	21	21	4	23	21	21	21	21	21	22	21	21
Leccinum species	A	1.41	21.3	104	0.10	1.02	50.6	65.1	0.49	871	8.40	0.38	0.00	193	1.33	0.08	106
	SD	1.00	23.1	85.0	0.11	0.40	13.3	45.3	0.22	340	3.65	0.13	0.00	115	0.64	0.09	35.0
	CV	0.71	1.09	0.81	1.16	0.40	0.26	0.70	44.5	0.39	0.43	0.33		0.60	47.6	1.19	0.33
	Med	1.31	11.0	100	0.07	0.96	51.4	42.0	0.43	828	7.90	0.37	0.00	168	1.15	0.04	100
	MIN	0.44	6.40	0.00	0.00	0.47	31.0	23.0	0.20	460	3.90	0.13	0.00	34.2	0.40	0.00	57.0
	MAX	5.08	87.0	324	0.32	2.25	70.7	150	1.04	1810	19.0	0.62	0.00	531	3.32	0.40	170
	R	4.64	80.6	324	0.32	1.78	39.7	127	0.84	1350	15.1	0.49	0.00	497	2.92	0.40	113
	n	25	25	25	13	25	25	14	27	25	25	25	25	25	26	25	25

Appendix 4D. The statistical values for each mushroom species (dry weight).

		Ag	Al	Ca	Co	Cr	Cu	Fe	Hg	Mg	Mn	Mo	Pt	Rb	Se	V	Zn
		mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
Macrolepiota procera	A	3.55	43.0	139	0.27	1.13	119	82.8	2.08	1270	16.8	0.44	0.00	46.9	3.02	0.42	84.8
	SD	3.70	37.0	77.9	0.24	0.27	39.9	57.2	2.32	231	1.50	0.34	0.00	14.2	2.40	0.54	28.4
	CV	1.04	0.86	0.56	0.89	0.24	0.33	0.69	112	0.18	0.09	0.76		0.30	79.4	1.30	0.34
	Med	2.55	36.0	134	0.36	1.06	108	74.5	0.88	1300	17.0	0.34	0.00	47.6	1.68	0.19	82.5
	MIN	0.59	6.10	48.7	0.00	0.90	88.0	22.0	0.53	994	15.0	0.17	0.00	32.2	1.06	0.08	54.0
	MAX	8.51	94.0	239	0.46	1.51	173	160	6.10	1490	18.0	0.92	0.00	60.3	6.05	1.23	120.0
	R	7.92	87.9	190	0.46	0.61	85.0	138	5.57	496	3.00	0.75	0.00	28.1	4.99	1.15	66.0
	n	4	4	4	3	4	4	4	5	4	4	4	4	4	5	4	4
Suillus variegatus	A	0.54	71.5	156	0.14	3.12	21.8	1950	0.29	963	17.4	0.14	0.00	420.9	1.00	0.13	95.4
	SD	0.27	36.3	118	0.01	5.96	10.5	412	0.16	409	19.0	0.07	0.00	97.1	0.31	0.14	46.3
	CV	0.51	0.51	0.76	0.10	1.91	0.48	0.21	55.1	0.42	1.09	0.49		0.23	31.1	1.04	0.48
	Med	0.45	67.0	138	0.14	0.96	20.7	2000	0.24	1000	8.10	0.14	0.00	411	1.02	0.09	84.5
	MIN	0.22	28.0	17.2	0.13	0.32	12.3	1500	0.18	83.4	4.90	0.04	0.00	253	0.52	0.00	56.0
	MAX	0.99	160	433	0.15	19.6	47.9	2300	0.71	1750	64.0	0.23	0.00	535	1.56	0.40	220
	R	0.77	132	416	0.02	19.3	35.6	800	0.53	1670	59.1	0.19	0.00	282	0.81	0.40	164
	n	10	10	10	2	10	10	4	10	10	10	10	10	10	10	10	10

Appendix 5A. The amount of fresh fungi (kg/week) that may be consumed safely according to legal standards or recommended limits.

	Ag 1	Al 2	Ca 3	Co 4	Cr 5	Cu 6
	kg fw	kg fw	kg fw	kg fw	kg fw	kg fw
Agaricus abruptibulbus	0.21	90.3	340	96.1	1.61	2.54
Albatrellus ovinus	45.4	352	963	524	2.48	128
Boletus species	1.10	263	799	*	1.62	16.7
Cantharellus cibarius	18.3	47.6	143	232	2.14	12.1
Cantharellus tubaeformis	95.7	120	410	*	2.89	20.0
Craterellus cornucopioides	85.1	94.1	147	802	1.47	17.2
Gyromitra esculenta	5.96	120	247	316	1.88	5.57
Hydnum species	12.3	160	454		2.44	30.7
Lactarius species	14.1	192	293	*	1.98	31.2
Leccinum species	5.56	496	883	1820	2.37	12.6
Macrolepiota procera	2.20	117	507	272	1.65	4.63
Suillus variegatus	12.4	62.7	493	700	1.82	24.2

	Fe 7	Hg 8	Mg 9	Mn 10	Mo 11
	kg fw	kg fw	kg fw	kg fw	kg fw
Agaricus abruptibulbus	13.8	0.82	18.4	67.2	903
Albatrellus ovinus	75.7	23.3	50.9	130	*
Boletus species	32.2	2.88	34.2	95.5	1400
Cantharellus cibarius	13.9	26.4	29.1	32.2	*
Cantharellus tubaeformis	21.0	15.3	73.8	40.4	*
Craterellus cornucopioides	17.2	56.3	31.7	25.9	1350
Gyromitra esculenta	12.9	29.8	26.7	49.4	212
Hydnum species	18.8	8.41	41.6	71.6	*
Lactarius species	28.8	10.5	30.5	90.5	*
Leccinum species	36.8	7.19	43.9	138	491
Macrolepiota procera	16.0	2.70	21.5	49.4	412
Suillus variegatus	0.59	9.92	27.9	104	1000

Footnotes:

1	Ag	Average Daily Intake (max.)
2	Al	Minimal Risk Level for Chronic Exposure
3	Ca	Average Daily Intake
4	Co	NOAEL
5	Cr	Safe Daily Intake
6	Cu	Safe Upper Limit (min & max)
7	Fe	NOAEL
8	Hg	NOAEL (for methylmercury)
9	Mg	NOAEL
10	Mn	NOAEL
11	Mo	US Tolerable Upper Intake Level

Appendix 5B. The amount of fresh fungi (kg/week) that may be consumed safely according to legal standards or recommended limits.

	Pt [12]	**Rb** [13]	**Se** [14]	**V** [15]	**Zn** [16]
	kg fw	kg fw	kg fw	kg fw	kg fw
Agaricus abruptibulbus	*	5.67	18.5	16.3	10
Albatrellus ovinus	*	0.89	103	74.9	52.1
Boletus species	*	0.59	2.39	50	13.5
Cantharellus cibarius	*	0.24	206	11.8	22.1
Cantharellus tubaeformis	*	0.54	346	20.7	44.9
Craterellus cornucopioides	*	0.31	223	12.4	15.5
Gyromitra esculenta	*	2.29	158	23.3	17.7
Hydnum species	*	0.20	652	25.4	49.7
Lactarius species	*	0.51	56.6	41.5	18.9
Leccinum species	*	1.24	35.7	*	22.7
Macrolepiota procera	*	3.39	18.8	18.9	21.2
Suillus variegatus	*	0.39	30.9	41.2	20.7

Footnotes:

12	Pt	Average Daily Intake
13	Rb	Average Daily Intake (max.)
14	Se	Safe Upper Limit
15	V	Average Daily Intake (max.)
16	Zn	Safe Upper Limit

* For platinum the safe consumption amount was calculated by using the determination limit of the ICP-MS, 0.01 mg kg^{-1}

DOCUMENTATION PAGE

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Abstract	The aim of the study was to examine the element concentrations of common mushroom species and to evaluate the possible health risks resulting from the consumption of mushrooms. The concentration of Ag, Al, Ca, Co, Cr, Cu, Fe, Hg, Mg, Mn, Mo, Pt, Rb, Se, V and Zn was studied for ten commercially sold mushroom species and two other common edible species in southern Finland. The element concentrations were analysed using AAS for selenium, fluorometry for mercury and ICP-MS for the other 14 elements. The platinum concentration was lower than the detection limit for all mushrooms species (n = 191). The highest aluminium, calcium and vanadium concentration were found in Boletus species. The amounts of mushroom considered safe for consumption were mostly limited by rubidium. When excluding Rb, the maximum amounts of mushroom recommended for consumption were limited by the concentration of chromium in the case of nine of the 12 studied fungi species. Iron was a limiting element for the safe consumption of Suillus variegatus while Agaricus abruptibulbus and Boletus species were limited by silver. In the light of the results the ten commercially sold mushroom species are mainly considered safe to consume. Nevertheless, it is recommended to avoid the consumption of A. abruptibulbus and to consume Boletus species and Suillus variegatus in moderate amounts only.	
Keywords	Fungi, mushrooms, Ag, Al, Ca, Co, Cr, Cu, Fe, Hg, Mg, Mn, Mo, Pt, Rb, Se, V, Zn	
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Julkaisun teema	Ympäristönsuojelu		
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Tiivistelmä	Tutkimuksen tarkoituksena oli tarkastella tavallisten metsäsienten kivennäis- ja hivenainepitoisuuksia sekä selvittää aiheutuuko niiden syönnistä mahdollista terveysriskiä. Tutkimuksessa tarkasteltiin Ag-, Al-, Ca-, Co-, Cr-, Cu-, Fe-, Hg-, Mg-, Mn-, Mo-, Pt-, Rb-, Se-, V- ja Zn- pitoisuuksia kymmenen ruokasienen ja kahden muun syötävän sienilajin osalta Etelä-Suomen alueella. Seleenin analysoinnissa käytettiin AAS:ia, elohopean fluorometriä ja muiden 14 alkuaineen osalta ICP-MS-tekniikkaa. Kaikkien sieninäytteiden (n = 191) platinapitoisuus oli alle määritysarvon. Korkeimmat alumiini-, kalsium- ja vanadiinipitoisuudet tavattiin kanttarellilla (Cantharellus cibarius) ja korkein seleenipitoisuus herkkutateilla (Boletus). Turvalliseksi arvioituja syöntimääriä rajoitti pääasiassa sienten rubidiumpitoisuus. Rubidium pois luettaessa kromipitoisuus rajoitti suositeltavia enimmäissyöntimääriä 12 tutkitusta sienilajista yhdeksän osalta. Rautapitoisuus rajoitti kangastatin (Suillus variegatus) enimmäissyöntimäärää ja kuusen herkkusienen (Agaricus abruptibulbus) ja herkkutattien (Boletus) enimmäissyöntimäärää puolestaan hopeapitoisuus. Tutkimuksen perusteella kymmenen tarkasteltua kauppasienilajia ovat pääasiassa turvallisia syötäväksi. Kuusen herkkusienen syöntiä on kuitenkin suositeltavaa välttää ja herkkutatteja sekä kangastattia syödä vain kohtuullisia määriä.		
Asiasanat	Sienet, Ag, Al, Ca, Co, Cr, Cu, Fe, Hg, Mg, Mn, Mo, Pt, Rb, Se, V, Zn		
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Painopaikka ja -aika	Edita Prima Oy, Helsinki 2008		

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(Mineraler och spårämnen i ätliga svampar i Finland)</td></tr>
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<tr><td>Sammandrag</td><td colspan="4">Studiens mål var att undersöka allmänna ätliga svampars mineral- och spårämneshalter och bedöma om konsumptionen av dessa svampar utgör en hälsorisk. Halten av Al, Ca, Co, Cr, Cu, Fe, Hg, Mg, Mn, Mo, Pt, Rb, Se, V och Zn undersöktes på tio handelssvamparter och två andra arter samlade i södra Finland. Selenhalten mättes med fluorimetri, kvicksilver med AAS och de andra 14 elementen med ICP-MS-teknik.

Platinahalten i alla svampprov (n = 191) var lägre än detektionsgränsen. Cantharellus cibarius innehöll de högsta aluminium-, kalcium- och vanadinhalterna och selenhalten var högst i Boletus arterna. Mängden svamp uppskattad som ofarligt att konsumera var mest begränsad av svampars rubidiumhalter. Kromhalten i nio av 12 svamparter överskred rekommendationen för konsumering. Järnhalten i Suillus variegatus och silverhalten i Agaricus abruptibulbus och Boletus arter överskred också rekommendationen för konsumering. Generellt kan man dock tryggt konsumera dessa tio handelssvamparter. Man bör ändå undvika konsumption av Agaricus abruptibulbus och konsumera endast måttligt Suillus variegatus och Boletus arter.</td></tr>
<tr><td>Nyckelord</td><td colspan="4">Svampar, Ag, Al, Ca, Co, Cr, Cu, Fe, Hg, Mg, Mn, Mo, Pt, Rb, Se, V, Zn</td></tr>
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</table>

The aim of the study was to examine the element concentrations of common mushroom species and to evaluate the possible health risks resulting from the consumption of mushrooms. The concentration of Ag, Al, Ca, Co, Cr, Cu, Fe, Hg, Mg, Mn, Mo, Pt, Rb, Se, V and Zn was studied for ten commercially sold mushroom species and two other common edible species in southern Finland. The element concentrations were analysed using AAS for selenium, fluorometry for mercury and ICP-MS for the other 14 elements.

The platinum concentration was lower than the detection limit for all mushrooms species (n = 191). The highest aluminium, calcium and vanadium concentration were found in Boletus species. The amounts of mushroom considered safe for consumption were mostly limited by rubidium. When excluding Rb, the maximum amounts of mushroom recommended for consumption were limited by the concentration of chromium in the case of nine of the 12 studied fungi species. Iron was a limiting element for the safe consumption of Suillus variegatus while Agaricus abruptibulbus and Boletus species were limited by silver. In the light of the results the ten commercially sold mushroom species are mainly considered safe to consume. Nevertheless, it is recommended to avoid the consumption of A. abruptibulbus and to consume Boletus species and Suillus variegatus in moderate amounts only.

ELEMENT CONCENTRATIONS IN WILD EDIBLE MUSHROOMS IN FINLAND

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