# Nickel – A Trace Element Hardly Considered

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Abstract— In this paper, occurrence, environmental mobilities and ecological cycling of nickel up to daily intake and allergic reactions of humans is discussed, mainly based on data of the author and others, which are often hidden in multi-element tables, and not available via keywords. Whereas, apart from some hotspots of geology, nickel occurrence in Central Europe is moderate, sources of pollution are mainly smelters and oil production. Oil combustion is likely a main source of nickel pollution in street dust, and after oil spills. Remediation and phytomining may be possible by use of special accumulator plants. Fertilizers do not increase nickel levels in soils. In green plants, nickel levels are much higher than in animal tissues and products of animal origin, and in fungi they are highly variable. From this, vegans have 4-5 times the daily intake compared with mixed diet feeders, which already touches the range of allergic reactions of sensitive persons. Essentiality and toxic effects are also discussed.

Keywords— Nickel – environmental occurrence, feeds, food, daily intake, metabolism, toxicity, allergy.

### PREFACE

A comprehensive review issued by EFSA in 2015 (CASALEGNO ET AL., 2015) concerning nickel in food, feeds and potable water, as well as oral toxicity and dermatitis has urged me to compile values of my own multi-element screenings, within the context of other authors. Because the EFSA-authors have just looked for nickel among the keywords, they missed a lot of data issued in multi-element databases, like mine. Frequently, data of my own department have not been entered into the internal database, because they were not requested for, but measured within the frame of multi-element screening. Among items of human nutrition, only those matrices have been outlined, if sufficient numbers of samples resp. representative sampling has been assured. Compilation of local data from the East of Austria makes sense, because concentration levels might be different to other regions due to climatic conditions, different soils and environmental effects, as well as different varieties grown. Thus in Germany, nickel levels in wheat and rye decline from south to north (BRÜGGEMANN 1999).

Steel abrasion and corrosion of steel during milling, cutting, and sieving can substantially increase nickel levels in green plant samples (SAGER, MITTENDORFER 1997), which necessitates critical views upon the sample preparation method used, in particular in case of papers issued some decades earlier. Increasing awareness of blanks together with improvements in sensivities and specifities of determination methods have hopefully increased the reliabity of data given.

#### GEOLOGY

Mean crust values for nickel given in various sources may vary, but 80 mg.kg-1 seems to be the most plausible (WEDEPOHL 1995).

During the cooling process of the magma, nickel is removed from the silicate melt at an rather early stage by crystallisation of olivines, pyroxenes, and amphiboles. The ion radius of Ni<sup>2+</sup> ranges between Mg<sup>2+</sup> and Fe<sup>3+</sup>. Therefore, some more nickel has been found in basic rocks, clays and flysch (Bodiš and Rapant 1999). In presence of sulfur, Ni is fixed together with Fe in pyrrhotite and pentlandite [(Ni,Fe)<sub>9</sub>S<sub>8</sub>]. Other ore veins contain enrichments of chromium-nickel-cobalt, or NiAs. Sediments sampled in creeks and rivers of Slovakia < 0,125 mm contained a median of 23 mg.kg-1 (25% percentile = 16 / 75% percentile = 31 / 99% percentile = 88 mg.kg<sup>-1</sup>) (BODIŠ, RAPANT 1999). In Austria, very local higher geological abundancies have been found around Rechnitz in serpentinites, as well as near Preg-Kraubath, Trieben and Heiligenblut (PIRKL ET AL., 2015).

Nickel-containing sulfides and silicates are prone to rapid weathering, and the released nickel gets sorbed preferably at Fe-Mn-oxide surfaces, in particular in tropical laterites (BODIŠ, RAPANT 1999; PIRKL ET AL, 2015).

### COAL AND OIL

In coals, nickel has not been enriched with respect to its abundance in rocks and soils. Brown coals used in Austrian power plants (sampled 1985/86) contained nickel at a median concentration of 29 mg.kg<sup>-1</sup> (range 2,1 – 121), and hard coals 15 mg.kg<sup>-1</sup> (range 6,3 – 46). This matches the range found in Chinese coals (9,3 – 18,6 mg.kg<sup>-1</sup>) or US-coals (1,1 – 19 mg.kg<sup>-1</sup>) (SAGER 1999). After combustion in Austrian caloric power plants, slags contained 24-398 mg.kg<sup>-1</sup>, and fly-ashes 22-153 mg.kg<sup>-1</sup>. Similar Ni-levels for fly-ash from coal combustion have been reported from Brazil (range 115–230 mg.kg<sup>-1</sup>) (BELLAGAMBA ET AL., 1993). After combustion, nickel has an affinity towards hematite/magnetite, but not towards CaO/CaSO<sub>4</sub>-partikels and soot, in particular after combustion of finely ground coal with oxygen at 1400°C (CLARKE 1993).

Mineral constituents can be removed from crude coal by dissolution in oil and subsequent pressure filtration at 45°C (ZIEGLER 2012).

In oil, in particular vanadium, but also nickel, have got enriched, they are therefore regarded as markers from oil combustion. Medium and heavy crude oils as well as high boiling fractions contain high amounts of sulfur and metals, like 10–160 mg.kg<sup>-1</sup> Ni, bound to porphyrines. The proportion V/Ni ranges from 10 to 100 and can be used to classify oils and rocks of origin with respect to the period of origin and redox conditions met there, as well as the lithological facies. In oil from Venezuela, crude oils were assigned to 5 groups, and in in each of them, a good correlation between vanadium and nickel could be established (LOPÉZ SALVADOR, MONACO 2017).

In oil, Ni and V are bound to 3 different high molecular fractions. Thermal treatment during oil distillation results in the aggregation of high-molecularweight fractions and thus to enrichment in the residue (DESPREZ ET AL., 2014). During raffination, they remain largely in the residue (asphalt), which contains an average of 336 mg.kg-1 (range 250–500mg.kg<sup>-1</sup>) Ni and >2000 mg.kg<sup>-1</sup> /(range 500–5000 mg.kg<sup>-1</sup>) V. Therefore, asphalt is a main source of Ni in street dust (see chapter ,,atmosphere and dust").

De-sulfurization of oil by reaction with  $H_2$  under pressure and release of the resulting  $H_2S$  in general also removes Na, V and Ni from the oil-made products (ZIEGLER 2012).

In oil-contaminated soils, high degradation rates of nickel- and vanadiumporphyrines could be established at weak acid pH by combined actions of *Bacillus megaterium-Enterobacter cloacae* as well as *Aspergillus unguis- Penicillium griseofulvum* (CORDERO ET AL., 2015).

After the explosion of the oil-drilling platform deepwater horizon, at April 20<sup>th</sup>, 2010 in the Gulf of Mexico, 779 million litres of crude oil dissipated within 87 days, which contaminated an area of 75000 km<sup>2</sup>. Whereas the hydrocarbons could be degraded or burnt, the metals dissolved in the crude oil remained on site (V, Ni, Cr), or formed fine dust particles in the course of carburation, which led to enrichment and biomagnification in whales (see chapter about food of animal origin)(WISE ET AL., 2014).

### SOILS AND FERTILIZERS

In soils derived from clay rocks, higher nickel levels can be expected, whereas soils derived from

carbonaceous rocks usually contain nickel at lower levels. Aqua regia may not release total nickel in all cases, in particular at hotspots. Thus, median nickel for arable topsoils in France has been determined as 21,0 mg.kg<sup>-1</sup> in total (4363 samples), and as 19,1 mg.kg<sup>-1</sup> (5184 samples) in aqua regia (BAIZE ET AL. 2007). In the UK, a median of total Ni was found at 15,8 mg.kg<sup>-1</sup> in arable soils and at 22,0 mg.kg<sup>-1</sup> in urban soils. Nickel was slightly higher in Northern Ireland than in England and Wales, some hotspots of geological origin occurred in Scotland (ROSS ET AL. 2007). In Taiwan, however, soils of the Central mountain range contained just  $13.2 \pm 1.5 \text{ mg.kg}^{-1}$  (KUO ET AL., 2009), possible due to subtropical climate and high precipitation rates, and generally high vertical mobility of nickel in soils (SAGER 2001). In Austria, local enrichments have been found in sedimentites from cretaceous, and above serpentinites (DANNEBERG 1999). The Austrian soil inventory done by aqua regia soil digests found a median abundance of 34 mg.kg<sup>-1</sup> for nickel in arable soils (range of medians of various soil types 25-45 mg.kg<sup>-1</sup>) (DANNEBERG 1999). Soils sampled in Vienna city also contained just  $30.3 \pm 6.3 \text{ mg.kg}^{-1}$ (PLAHL ET AL., 2002).

In Hokkaido (Japan) native green plants contain 20-100 mg.kg<sup>-1</sup> Ni in dry mass due to high nickel and low calcium levels met in local soils, which have been developed upon ultramafic rocks, which is more than Cu, and in some cases also more than Zn and Mn. The hyper accumulator *Thlaspi japonicum* reached top levels of Ni >0,1%, higher than Fe, but without showing toxicity symptoms (HORIE ET AL., 2000).

On behalf of the Council Directive 1999/31/EC on landfill of waste, and §8 of the the Bundesbodenschutzgesetz 1999 (Federal Soil Protection Act), the German government has set thresholds for nickel of 70 mg.kg<sup>-1</sup> for childrens playgrounds, 140 mg.kg<sup>-1</sup> for habitational areas, 350 mg.kg<sup>-1</sup> for sport-and leisure areas, and 900 mg.kg<sup>-1</sup> for industrial areas, each determined for dry soil sieved < 2mm digested by aqua regia. In Austria, each province has issued a soil protection act of its own.

In mine tailings, organic carbon, nutrients or soil bacteria are hardly present. In New Caledonia at a mine tailing of 1,8% Ni, prior to planting grass, nitrogen fixing soil bacteria were isolated from the rhizosphere of endemic plants *Gymnostoma ebbianum* and *Serianthus calycina*, to modify and amplify their especially Nitolerant genes by molecular genetic methods (HÉRY ET AL., 2005).

Whereas lime addition lowers mobilities and phytotoxicities of most metal ions for arable crops, it increased Ni-uptake into accumulator plants of the Alyssum family. Under various soil pH and Ni concentrations tested, *Alyssum murale* accumulated up to 1,1% Ni, and *Allyssum corsicum* up to 0,7% Ni in its dry mass (KUKIER ET AL., 2001; BREWER ET AL., 2001).

Also, after NPK fertilization, *Alyssum bertolonii* accumulated Ni 13400 fold from a Ni-rich substrate, and *Berksheya coddii* 17000 fold (BROOKS ET AL., 1998).

Mixing of de-watered sewage sludge with equal amounts of sawdust as well as lime gradually increased the water-soluble and exchangeable fractions after 3 months, because of lowering of its pH (ŠČANČAR ET AL., 2001).

After mixing the top 15 cm of various soils with nickel-contaminated urban sewage sludge (4625mg.kg<sup>-1</sup> Ni), elution of nickel with carbonaceous simulated river water from respective soil columns increased significantly. Nickel migrated faster in unsaturated columns, except for the carbonaceous soil, in spite of simultaneous pH increase caused by the sewage sludge. Higher retention from carbonate or organic carbon was achieved only at unsaturated conditions (WELCH, LUND 1987).

Sequential leaching procedures revealed high affinities of nickel towards Mn-oxides and Fe-oxide containing phases, depending on the geochemical matrix (SAGER ET AL., 1989; SAGER, VOGEL 1993). About 1/4 or more remained bound to refractory phases, however. In particular at non-contaminated sites, mobility in 0,16M actetic acid and 0,2M oxalate solution remains marginal (SAGER 2016). Amounts readily adsorbed from aqueous solutions are hardly released into neutral or alkaline salt solutions, but almost completely at pH 5 or less, because obviously the hydroxide which gets formed at alkaline surfaces, dissolves (SAGER 1995; ZATKA ET AL., 1992). In acetic acid, tartaric acid or oxalic acid solutions, nickel migrated through clayey barrier layers (Kf about 10<sup>-15</sup> m.s<sup>-1</sup>) quicker the Cd, Cu, and Pb in any case, and frequently even quicker than the acid itself (SAGER 2001).

´mg.kg <sup>-1</sup> in TS	Median	Range	
Arable soil (East of Austria)	34	25 - 45	Danneberg 1999
Ammonium nitrate limes	< 0,5	< 0,5 - 3,7	Sager 2009
Limestones, dolomites	2,1	< 0,5 - 30,5	Sager 2009
NPK-mineral fertilizer	6,5	< 0,5 - 30,5	Sager 2009
PK-mineral fertilizer	11,4	2,2 – 23,4	Sager 2009
Di-ammonium phosphate	16,4	4,0 – 89,5	Sager 2009
Fermented urban biowaste (green	4.12	16 98	Sager 2012
ton)	4,12	1,0 - 9,0	Sager 2012
Garden moulds	7,6	< 0,5 - 32,6	Sager 2009
Manures and dungs	10,1	1,2 – 32,7	Sager 2009
Composts	24,5	10,0 – 37,4	Sager 2009

Table.1: Nickel in fertilizers sold in Austria

Because nickel levels encountered in fertilizers are usually lower than in soils, accumulations from fertilizations need hardly to be considered (table 1). Fertilization of an equivalent equal to 100 kg P.ha<sup>-1</sup> is about equal to the annual atmospheric deposition, and an equivalent of 100 kg N is even less (SAGER 2009).

Also, composts, manures and dungs contain less nickel than arable soils. Thus, urban biowaste of Vienna collected separately within brown tons, contained after pre-selection and sieving an average of 10,46 mg.kg<sup>-1</sup> from the center, 17,12 mg.kg<sup>-1</sup> from the suburbs, and 14,43 mg.kg<sup>-1</sup> from the city border areas, contrary to the urban soils (mainly parks), which had 30,25 mg.kg<sup>-1</sup> (PLAHL ET AL., 2002).

Urban biowaste monthly collected at 4 sites of an Austrian provincial capital city, contained even less nickel than compost samples. In outliers due to faulty inputs (2 out of 44 samples), however, nickel concentrations increased 9-fold, thus necessitating control and site selection measures (SAGER 2012).

### WATER

A threshold for nickel in potable water at 20  $\mu$ g.l<sup>-1</sup> has been implemented by the Council Directive 98/83/EC after respective recommendation of the WHO. This value applies to a sample of water obtained at the tap and taken so as to be representative of a weekly average value ingested by consumers.

In Cornwall, a known metalliferous and arseniferous region, about 500 private wells have been tested, which were not subject to official control. Traditionally, groundwater was filtrated through  $0,45\mu$ m, and tap water was analyzed as such, but differences were only noted in case of Pb and Fe. Only 3% of the samples contained Ni above theshold, and were also high in Mn. Whereas water samples of pH <6 caused Cu-

contaminations from tap tubes, this was not the case for Ni, Cd, and Cr (ANDER ET AL., 2016).

Sampling of rainwater from roofs is prone to contaminations from the roof material, dust input and organic debris, as well as from microbial activities. Pasteurization in black painted glass tubes by heating from sun rays may cope with the latter. Contact of the chloride containing rain water with a steel pot, however, caused corrosions and subsequently an increase of nickel in the processed water samples (DOBROWSKY ET AL., 2015).

In fish ponds in Southern Bohemia, nickel concentrations in aquatic macrophytes raised up to  $6,1 - 28,2 \text{ mg.kg}^{-1}$ , which is equal to the levels in sediments  $(10,1 - 25,5 \text{ mg.kg}^{-1})$ , though in the water just  $3,7-20,4 \mu \text{g.l}^{-1}$  were found (DRBAL 1991). Barks from fir trees adsorbed 58% of nickel from synthetic well water, and desorbed it again within 8-13%. Conditioning the barks with urea, however, raised Ni adsorption to 86%, and decreased desorption to just 3% (KHOKHOTVA, WAARA 2011).

In surface waters, uptake of nickel into algae increased in parallel to the incorporation of C by photosythesis, and correlated non-linearly with the proton flux. In freshwater of pH 7,8 and 12°C, algal nickel uptake was 76% more at light than at dark (GRAY, HILL 1995).

1 g of barley straw can adsorb about 10 mg nickel from aqueous solution, maximum at pH 4,85 (THEVANNAN ET AL., 2010). 1 g of montmorillonite can sorb about 2 mg Ni at pH 5-6, which could be increased by Fe-coatings, but not by Al-coatings (COOPER ET AL., 2002). Aqueous suspensions of lime approach a pH 8-9, resulting in adsorption of Ni, like Pb, Cd, Zn, Cu and Cr(III), at < 90% at the solid. Sorption of Nickel upon finely ground bricks at 80%, and sorption at silicate pebbles at 65% were less effective (AZIZ ET AL., 2008). Fly ash from coal- operated power plants is suitable for the removal of nickel from metal contaminated effluents, e.g. from non-ferrous smelters, which is necessary to save the bacteria of sewage sludge treating processes, which are harmed at Ni > 15 mg.l<sup>-1</sup>. The efficiency of fly ash was better than active carbon, but worse than zeolite. Above pH 8,5-9, complete and largely irreversible adsorption at the solids occurred, but none below pH 4,5 (MAVROS ET AL., 1993).

Samples to check pollution from tap water tubings, which may release in particular Cu, Pb, and Ni, are obtained from 1 liter without discarding directly at the consumer's site (random sampling of the day). If thresholds are surpassed, sequential sampling has to be done (for Austria: Trinkwasserverordnung 2001, resp. update of the food safety act 2017). Metal water supply tubings, particularly from water heating supplies, can release metals into the potable water, which decrease exponentially versus the consumed water volume (informal measurement of the author).

#### ATMOSPHERE AND DUST IMMISSION

Apart from antropogenic emissions, the most important source of atmospheric particulates is the weathering of the continental crust. Antropogenic emissions can be easily traced from enrichments over iron.

In the aerosol sampled above the Atlantic Ocean, only < 0,05 -10 ng.m<sup>-3</sup> nickel have been found, lowest above the Southern part, and maximum in the Channel (VOLKENING, HEUMANN 1990). In Detroit region within 1988-92, atmospheric nickel concentrations in residential areas were determined as 5-16 ng.m<sup>-3</sup>, and in industrial areas 8-32 ng.m<sup>-3</sup>. Antropogenic emission sources like vehicles, fuel and navigation remained constant, whereas emissions from smelting and welding facilities varied due to economic fluctuations (PIRONE ET AL. 1995).

Nickel contents in the fine dust of Santiago de Chile (PM<sub>10</sub>) lowered in winter (July) within the period 1997 – 2003 from 60 ng.m<sup>-3</sup> to 20 ng.m<sup>-3</sup>. Similar concentration decreases appeared also for V, Pb, As, Cu and Cd, which could be traced to lower industrial emissions and lower coal heatings, just Cr increased. Sequential extraction of the dust particles assigned nickel to the group of immobile elements (Ni, Mo, Ca, Mg, Ba, Al) (RICHTER ET AL. 2007). In the Saloniki region, total nickel concentrations in fine dust (PM<sub>7,5</sub>), samples 1997/98 4m above ground, differed between urban sites at  $6,8 \pm 5,6$  ng.m<sup>-3</sup> and sites close to industrial areas at 12,8  $\pm$  6,2 ng.m<sup>-3</sup>. Similar effects were observed for Cd, Mn and Zn (VOUTSA, SAMARA 2002).

At hardly populated sites in Norway, metal deposition tends to decrease from the most southern point at Birkenes towards the north, with seasonal fluctuations, but without marked seasonal trends. This atmospheric nickel deposition was calculated from concentrations met in rainwater samples and annual precipitation, to be 1,2 - 12 g.ha<sup>-1</sup>a<sup>-1</sup> (BERG ET AL. 1994), which can be regarded as background immission.

Higher precipitation rates, in parts also as fog, might cause much more total atmospheric deposition in high mountain areas, far away from emission sources. At 2 stations at the Christlumkopf mountain (1768m, Achenkirch, Tirol) close to woods, nickel deposition of 25,02 g.ha<sup>-1</sup>a<sup>-1</sup> were measured, as the sum of 14,77 g.ha<sup>-1</sup>a<sup>-1</sup> wet deposition, only 0,71 g.ha<sup>-1</sup>a<sup>-1</sup> dry deposition, and 9,54 g.ha<sup>-1</sup>a<sup>-1</sup> g/ha.a from the fog. In some distance downhill, at the Mühleggerköpfl, total nickel deposition amounted only 13,62 g.ha<sup>-1</sup>a<sup>-1</sup>, as the sum of 9,78 g.ha<sup>-1</sup>a<sup>-1</sup> wet, 3,67 g.ha<sup>-1</sup>a<sup>-1</sup> dry, and only 0,17 g.ha<sup>-1</sup>a<sup>-1</sup> from the fog (BAUER ET AL. 2008).

Top levels of atmospheric nickel deposition of 170-240 g.ha<sup>-1</sup>a<sup>-1</sup> have been reported from urban districts in Paris, sampled in 1988 (GRANIER ET AL. 1992). Also, the atmospheric deposition at the sea of Tokyo Bight is strongly influenced from human activities. Samples have been obtained by collection of wet precipitation, and for dry deposition by means of a water surface sampler employing circulating 0,25M HCl. Total Ni deposition was 28- 98 g.ha<sup>-1</sup>a<sup>-1</sup>, and the proportion of dry to wet deposition was 3,7 (SAKATA, TANI, TAKAGI 2008).

Top concentrations in street dusts were found in Tokyo at 540 mg.kg<sup>-1</sup> (2005), whereas in Seoul it was just 62 mg.kg<sup>-1</sup> (2010; range 42-109 mg.kg<sup>-1</sup>), and in Budapest it was 27,5 mg.kg<sup>-1</sup> (2010; range 19,2 – 49,9 mg.kg<sup>-1</sup>) (SAGER ET AL. 2015); the latter is within the range of adjacent soils. Dust, collected in 1m above a highly frequented road in the central mountain range of Taiwan, contained 17,1  $\pm$  12,0 mg.kg<sup>-1</sup>, and the adjacent soil 13,2  $\pm$  1,5 mg.kg<sup>-1</sup> Ni. Principal component analysis revealed assignment of Ni to Cu, but not to the group of Fe, Al, Mn resp. Pb and Zn. Road traffic increased nickel concentration in the fine fraction PM<sub>2,5</sub> from 5,8 to 7,3-16,7 ng.m<sup>-3</sup>, in the medium fraction PM<sub>10-2,5</sub> from 3,76 to 3,9 – 14,4 ng.m<sup>-3</sup>(KUO ET AL. 2009).

Whereas fly-ash of an oil-driven powerplant contained 0,41% Ni, Ni in leaves of trees within 0,7-1,5 km nearby (*Rhus typhina L.*) increased just to 1,2 mg.kg<sup>-1</sup>, which was interpreted as long-distance transport effects of the 210 m high chimney 210m (YOUNGS ET AL. 1993).

Contrary to soils, the easily mobilisable fraction of nickel found in street dusts can be about half and thus rather high, which was measured in Sevilla 1996 (FERNANDEZ ESPINOSA ET AL. 2002).

Urban dust samples from the Saloniki urban region contained about 80% of Ni soluble in 0,1M-HCl, which was regarded as labile, contrary to dust samples from the Saloniki industrial region of about 60% soluble in 0,1M-HCl. The solubility in artificial serum was regarded as bioavailable, which was 46% for the urban dust samples, and 24% for the dust close to the industrial areas. The soluble solid phase is presumably NiSO<sub>4</sub>, and the hardly soluble phase presumably Ni-oxides (VOUTSA, SAMARA 2002).

Completely other particles are encountered in industrial emissions from melters and metal processing, like NiS, NiSe, NiTe, Ni<sub>3</sub>S<sub>2</sub>, NiAs, Ni<sub>11</sub>As<sub>8</sub>, Ni-metal, ferronickel, ferrite and naturally occurring pentlandite  $[(Ni,Fe)_9S_8]$ . Among them, some are highly carcinogenic (NiS, Ni<sub>3</sub>S<sub>2</sub>). They could be discriminated by sequential leaching with 0,1M ammonium citrate ("soluble"), H<sub>2</sub>O<sub>2</sub>-

citrate ("sulfidic"), Br<sub>2</sub> in CH<sub>3</sub>OH ("metallic") and HNO<sub>3</sub>-HClO<sub>4</sub>-HF ("oxidic") (ZATKA ET AL. 1992).

Occupational exposure from nickel containing dusts occurs especially in the air at the working site of smelters and metal processing facilities. Soluble nickel compounds get rapidly adsorbed by the lung tissues, but the top cancerogen is  $Ni_2S_3$ . To the contrary, in nickel mining no statistically significant relationship between lung cancer and nickel exposition could be established, because the dominant mineral pentlandite [(Ni,Fe)<sub>9</sub>S<sub>8</sub>] is non-cancerogenic (SCHAUMLÖFFEL 2012).

Because nickel in coal is bound to sulfides and oxides, fly ash emissions from caloric power plants contain NiSO<sub>4</sub>, NiS and NiS<sub>2</sub>, as well as nickel-containing spinels NiFe<sub>2</sub>O<sub>4</sub>. but not Ni<sub>2</sub>S<sub>3</sub>. High combustion temperatures favour the formation of the oxide, lower temperatures favour the phosphate (SCHAUMLÖFFEL 2012).

Metallic nickel-nanoparticles of 53 nm average diameter, have been obtained by reduction of a NiCl<sub>2</sub>-containing aerosol with H<sub>2</sub> at 950°C with 99% yield. Lowering the temperature to 800°C lowered the yield, as well as the average particle diameter to 31 nm (YONG JAE SUH ET AL. 2004).

In Austria, thresholds have been set for the concentration of inhalable particulate nickel compounds in air, like NiO, NiO<sub>2</sub>, NiS, Ni<sub>2</sub>S<sub>3</sub>, and Ni<sub>2</sub>O<sub>3</sub>. (Grenzwerteverordnung 2006, Bgbl 242/2006, Addendum I and II).

### FUNGI

In general, the composition of soil is of stronger influence upon the contents of mushrooms than upon the composition of green plants, but respective investigations are scarce. In boletus edulis from central Finland, growing upon granitoid rocks, 1,32 mg.kg<sup>-1</sup> (of Ni in dry mass) had been found, and from a region higher in nickel from East of Finland, it was 1,55 mg.kg<sup>-1</sup> (of Ni in dry mass). The difference between these sites was much larger for Lactarius trivialis, i.e. 0,55 mg.kg<sup>-1</sup> resp. 1,95 mg.kg<sup>-1</sup> (NIKKARINEN, MERTANEN 2004).

### FEEDS

Commercially available composite feeds for any kinds of animal contain about 2 mg.kg<sup>-1</sup> of Ni. Slightly lower levels in feeds targeted to calves and cats/dogs probably result from higher proportions of meat and dairy products in the composite. Some more differences appear in commercial supplementary feeds, the median level of which is higher for pigs, sows, and piglets, than for cattle, calves, deer, and poultry (table 2).

In basic feeds for dairy cattle, sampled directly at farms in Lower Austria, nickel levels were lowest in

maize silage, like for most of trace metals, and highest in hay. The lucerne sample (table 2) was used for a round robin test, which had to be ground and milled in 24 different laboratories, and subsequently analyzed at the same site by the same operators and instruments, after dry-ashing of 4g (SAGER, MITTENDORFER 1997). The latter should indicate the precision of the entire analytical procedure.

´mg.kg <sup>-1</sup>		Median	Range	Samples
Composite feeds	Calves	0,26	0,09 - 0,74	12
	Sheep + goats	1,71	0,17 - 3,60	14
	Pigs + sows	1,78	0,88 - 3,86	28
	Piglets	1,78	0,63 - 6,55	58
	Poultry	2,22	1,34 - 3,83	46
	Dogs+cats(d.m.)	1,01	0,61 – 2,82	35
	Fish	2,21	1,41 – 3,36	12
Supplementary feeds	Cattle	3,76	1,54- 12,6	73
	Calves	4,17	1,21 - 8,37	40
	Sheep+goats	1,75	1,04 - 3,18	11
	Horses	2,37	0,85 - 7,12	46
	Pigs	5,95	2,05 - 13,8	169
	Piglets	6,09	1,11 – 15,0	126
	Poultry	3,52	2,00 - 10,1	44
	Dogs+cats(d.m.)	1,19	0,44 - 1,80	7
	Deer	2,86	2,41 - 4,83	5
Basic feed	Hay	3,10	1,09 - 7,98	18
	Grass silage	1,03	0,23 - 4,63	17
	Maize silage	0,25	0,17 - 0,36	8
	Cereals	1,00	0,31 - 1,92	18
Round robin	Lucerne	1,09	0,73 – 2,44	24

Table 2 · Nickel in	foods (SAGE	R 2006 · SAGER	HOREGGER 201	3. SAGER	MITTENDORFER	1997))
Tuble.2. Mickelin	Jeeus (SAGE	$\Lambda 2000, SAGER$	110DEGGER 201	J, SAGER,	MITTENDORFER	177/))

## FOOD OF GREEN PLANT ORIGIN

Based on dry mass, food for human nutrition of green plant origin contain some less nickel than food for domestic animals. Just carrots were rather high in Ni (table 3), which needs to be confirmed, however. High levels met in cocoa are known from other references as well. Further sources of nickel intake of human consumption, like nuts, spinach, or mushrooms, have not been investigated in this work. Tea leaves and coffee beans might contain much nickel, which is largely not transferred to the consumed beverage.

Table 3A. Nickel in f	food of green plant	origin, mg.kg <sup>-1</sup>	dry mass
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´mg.kg <sup>-1</sup>	Median	Range	Samples	
Potatoes	1,08	0,61 – 1,65	40	Spiegel, Sager 2008
Carrots	4,64	3,79 – 10,69	37	Sager, unpublished
Wheat (organic)	0,134	0,043 - 0,242	42	Sager, Erhart 2016
Wheat (round robin)	0,255	0,118 - 0,692	30	Sager, Mittendorfer 1997
barley (round robin)	0,34	0,18 - 1,06	24	Sager, Mittendorfer 1997
Tomatoes + seeds	0,235	0,115 - 0,485	22	Sager 2017
Tomatoes minus seeds	0,235	0,118 - 0,534	21	Sager 2017
apples	0,08	< 0,08 - 0,49	104	Sager 2014
Milk chocolate	0,98	0,52 - 1,43	19	Sager 2012
Dark chocolate	3,07	2,64 - 4,89	9	Sager 2012
Very dark chocolate	4,26	2,57 - 7,93	15	Sager 2012
cocoa	15,33	10,77 – 17,12	3	Sager 2012

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´mg.kg <sup>-1</sup>	Median	Bereich	Anzahl	
Potatoes	0,223	0,165 - 0,317	40	Spiegel, Sager 2008
Carrots	0,445	0,36 - 1,03	37	Sager, unpublished
Tomatoes +seeds	0,018	0,011-0,038	22	Sager 2017
Tomatoes minus seeds	0,015	0,009 - 0,022	21	Sager 2017
Apples	0,011	< 0,003 - 0,035	104	Sager 2014
Soy-,,Milk"	0,59	0,43 - 1,06	5	Sager 2018

Table  $\overline{3B. Nickel in food of green plant origin, mg.kg^{-1} wet weight (FS)}$ 

Contrary to Cd and Pb, traces of Ni are proven to be essential and have a wide range of effects, including plant growth, plant senescence, N metabolism (as a component of urease), and Fe- uptake. In barley (*hordeum vulgare*), Ni deficiency had been observed after grown for three generations in purified nutrient solution <30 ng/l Ni, resulting in a 15% reduction of optimum yield and Ni in the grains of  $90 \pm 10 \text{ µg.kg}^{-1}$  dry weight. Ni deficiency inhibited the development of the embryo soon after the formation of the shoot primordia; the root primordia of Ni-deficient grain were poorly developed or absent at harvest (BROWN ET AL. 1987).

Increase of total nickel in soil from 30 to 50 mg.kg<sup>-1</sup>, resp. addition of 35  $\mu$ g.l<sup>-1</sup> in hydroponic culture, did not effect growth of various crops, like spinach (*spinacea oleracea*), maize (*zea mays*), beans (*phaseolus vulgaris*), cabbage (*brassica oleracea*), rice (*oryza sativa*), or ryegrass (*lolium perenne*). All plants investigated contained higher nickel concentrations in their roots than in their shoots, and Ni-additions went preferably to the roots. In the shoots, highest levels were met in beans and ryegrass, and lowest in maize. Due to low root masses, however, about 80% of total Ni contents in beans, cabbage and spinach were located in the shoots (GUO ET AL., 1995).

Additions of soluble NiSO4 to an alkaline soil (pH=8,0 / 14,3% clay/ 5,5% CaCO<sub>3</sub>) up to 600 mg.kg<sup>-1</sup> Ni did not result in Ni uptake proportional to the added amount. Just barley (hordeum vulgare) decreased growth, but cabbage (brassica juncea), spinach (spinacea oleracea), sorghum (sorghum vulgare), beans (phaseolus vulgaris), tomatoes (solanum lycopersicum) and ricinus (ricinus communis) were not effected. Nickel remained mainly in the roots, just in the brassica the excess was transferred to the shoots. Maximum nickel uptake was noted into spinach leaves, and minimum into tomato plants. Top values in edible parts were 65 mg.kg<sup>-1</sup> in spinach, 21 mg.kg<sup>-1</sup> in beans, 8,1 mg.kg<sup>-1</sup> in tomatoes, and in sorghum and barley just 4 mg.kg<sup>-1</sup>, in dry mass each (GIORDANI ET AL., 2005). In case of sufficient NPK fertilization, no toxicity symptoms in pot experiments developed in carrots, potatoes, and onions up to 250µg.l<sup>-1</sup> nickel in irrigation water (equal to 100 g.ha<sup>-1</sup>), because

sorption of the soil was quicker than plant uptake (STASINOS, ZABETAKIS 2013).

In case of more saline irrigation, however, like in the delta of the Nile, spinach, maize and leeks retain less nickel (and also cadmium) in the roots, resulting in higher transfer to the leaves, which was traceable in the soil saturation extract (HELAL ET AL., 1998).

Lower nickel levels encountered in white bread from Denmark (median 101  $\mu$ g.kg<sup>-1</sup>) compared with the level in Austrian wheat (median 255  $\mu$ g.kg<sup>-1</sup>) can be explained from humidity and the milling fraction of the cereal (LARSEN ET AL., 2002). Similar nickel levels have been found already in 1983 in the FRG, at a median of 228  $\mu$ g.kg<sup>-1</sup> (range 60-1100  $\mu$ g.kg<sup>-1</sup>). After milling, the white flour made 70% of the total grain weight, but contained just 12% of the entire nickel, the rest was bound to the brans (SCHELLER ET AL. 1988). German wholemeal bread contained 166  $\mu$ g.kg<sup>-1</sup>, which was more than double of conventional mixed bread of 69  $\mu$ g.kg<sup>-1</sup>. Abrasion in the bakery additionally increased nickel in wholemeal bread versus nickel in wholemeal flour.

German potatoes contained just 16,5  $\mu$ g.kg<sup>-1</sup> Ni in wet weight, but Danish potatoes had 50  $\mu$ g.kg<sup>-1</sup>, and Danish carrots 51  $\mu$ g.kg<sup>-1</sup> (LARSEN ET AL., 2002).

Because grapes have more than half of their nickel bound to the skin, during wine processing the nickel mainly moves to the residue, and further amounts get adsorbed at the glass bottle. Nickel accumulates preferably in leafy vegetables, cocoa and nuts. Within a compilation from Great Britain about trace elements contents of various food items, maximum nickel was found in nuts to contain 2,5 mg.kg<sup>-1</sup> in wet weight (YSART ET AL., 1999).

Tea leaves also contain rather much of nickel, median values from various tea-cropping regions in Asia ranged 1,2 - 2,6 mg.kg<sup>-1</sup>. But as tea leaves are strong adsorbents, the nickel level in the ready made beverage remains very low (TADAYON, LAHIJI 2011). Also, nickel gets adsorbed on ground coffee within 15 min at 90% in the cold, but just at half at 44°C. For desorption into acid, however, pH 3 is at least needed (SUK, SU 2004).

Though the components for beer brewing contain significant amounts of nickel, like hop with 1,3 mg.kg-1 (range 0,6-2,1 mg.kg<sup>-1</sup>), and malt with 0,11 mg.kg<sup>-1</sup>

(range  $0.08 - 0.50 \text{ mg.kg}^{-1}$ ), nickel was below detection limits in the ready made beer because of filtration (ČEJKA et al., 2011).

#### FOOD OF ANIMAL ORIGIN

Table 4A. Nickel in food of animal origin, mg.kg<sup>-1</sup> in dry mass

´mg.kg <sup>-1</sup>	Median	Range	Samples	
Egg white	< 0,6	< 0,6	77	Sager 2011
Egg yolk	< 0,25	< 0,25	65	Sager 2011
Sausages	0,142	0,017 - 0,304	35	Sager 2010
Chicken (breast)	0,124	0,064 - 0,313	17	Sager et al. 2018
Chicken (leg)	0,182	0,055 0,325	17	Sager et al. 2018
Raw milk	< 0.05	< 0.05 - 0.185	103	Sager, Hobegger 2013
(Lower Austria)	( 0,05	( 0,05 0,105	105	Suger, Hobegger 2010
Whole milk	0,02	< 0,02 - 0,26	30	Sager 2018
Skim milk	< 0,02	< 0,02 - 0,09	6	Sager 2018
Sour cream	< 0,02	< 0.02 - 0.07	6	Sager 2018
Cream	0,036	< 0,02 - 0,10	7	Sager 2018
Honey	0,033	< 0,006 - 0,33	122	Sager 2017

Table 4B. Nickel in food of animal origin, mg.kg<sup>-1</sup> in wet weight

´mg.kg <sup>-1</sup>	Median	Range	Samples	
Egg white	< 0,28	< 0,28	77	Sager 2011
Egg yolk	< 0,23	< 0,23	65	Sager 2011
Sausages	0,054	0,008 - 0,148	35	Sager 2010
Deer	0,020	< 0,005 - 0,042	15	Sager 2005
Raw milk (Lower Austria)	< 0,007	< 0,007 - 0,024	103	Sager, Hobegger 2013
Whole milk	0,003	< 0,002 - 0,041	30	Sager 2018
Skim milk	0,002	< 0,002 - 0,019	6	Sager 2018
Sour cream	< 0,002	< 0,002 - 0,015	6	Sager 2018
Cream	0,015	< 0,002 - 0,045	7	Sager 2018
Hard cheese	0,243	0,024 - 0,406	14	Sager 2012
Semi-hard cheese	0,286	0,063 - 1,062	19	Sager 2012
Soft cheese	0,304	0,126 - 0,446	18	Sager 2012
Fresh cheese (cow)	0,273	0,065 - 0,470	18	Sager 2012
Sheep/goat cheese	0,115	0,036 - 0,259	15	Sager 2012
Honey	0,030	< 0,006 - 0,296	122	Sager 2017

Compared with innards, muscles are low in nickel. Meat products receive their nickel mainly from spices and additives, but not from steel vessels and cans (SCHELLER ET AL. 1988). In pork, pig livers and pig kidneys, as well as beef, and beef liver from Sweden, nickel was found below the detection limit of 0,010 mg.kg<sup>-1</sup> wet weight. Most beef kidneys had about 0,014 mg.kg<sup>-1</sup>, only a few of them were higher (JORHEM ET AL., 1989).In France, commercially available fish contained just 0,056 mg.kg<sup>-1</sup> Ni in wet weight (range 0,032–0,161), and no accumulation was noted in predators. Nickel in other seafood was slightly higher at 0,123 mg.kg<sup>-1</sup> (GUÉRIN ET AL. 2011).

To simulate corrosion of nickel-plated Cu riflebullets, they were inserted into meat juice for 7 days, and released up to 0,093 mg Ni, which did not result in a significant increase of nickel concentrations around the shot wound of the game meat. Average Ni release of a Niplated bullet during roasting of pork was 0,0028 mg (maximum 0,0043 mg) (PAULSEN, SAGER 2017).

In whales, higher nickel levels than in domestic animals and fish have been encountered. Nickel in innards from pot whales of the North Sea ranged about 2,5 mg.kg<sup>-1</sup> in dry weight till lower detection limit. The skin of pot whales from 17 non-contaminated areas, sampled as biopsies of obviously healthy free swimming individuals, had 2,4 mg.kg<sup>-1</sup> in wet weight. Contrary to this, the skin of finbacks and pot whales from the Gulf of Mexico contained an average nickel of 15,9 mg.kg<sup>-1</sup> (range 1,7-94,6 mg.kg<sup>-1</sup>) in 2010, sampled soon after the large oilspill of the drilling platform Deepwater Horizon. All whales looked healthy and had no oil cover at their skin, and moved far from crude oil lumps. Their nickel contents correlated with the distance to the site of the disaster. Because nickel resorption from the gastrointestinal tract is low, and pot whales and finbacks feed on quite different prey, and sorption of the skin seems marginal, the most probable path is the uptake of fine dust to the lungs from the oil combustion during the oil catastrophy (WISE ET AL. 2014).

Similar to meat, milk and dairy products are much lower in nickel than green plants (see below). Commercially available cheeses in Austria contained about 0,25 mg.kg<sup>-1</sup> in wet weight (SAGER 2012), which was less than Ni in Turkish fresh cheeses at 0,59±0,13 mg.kg<sup>-1</sup> wet weight sampled at about the same time. Packing into metal containers additionally increased the nickel level to 1,28±0,08 mg.kg<sup>-1</sup> wet weight (BAKIRCIOGLU ET AL. 2011).

#### UPTAKE IN HUMAN NUTRITION

Among human nutritional items richest in nickel, there are cocoa (5,3-12,6 mg.kg<sup>-1</sup>) and its products, soy beans (4,7–8,1 mg.kg<sup>-1</sup>), sun flower seeds (2,3–5,8 mg.kg<sup>-1</sup>) and nuts (3,6 mg.kg<sup>-1</sup>). Stainless steel vessels and pots as well as in-house water tubings can release much nickel also (SCHELLER ET AL., 1988). Investigations of commercial dairy products in Austria, however, revealed no different nickel contents to raw milk sampled at the cow, thus inputs from the dairy process remain negligible (SAGER, HOBEGGER 2013; SAGER 2015; SAGER 2016). Similar to many samples from Austria (table 4), nickel in meat, fish and eggs was below detection limits in Denmark also (LARSEN ET AL., 2002).

In cooking oils, nickel ranged within 20-70  $\mu$ g.kg<sup>-1</sup>, which makes inputs from this source marginal for the daily intake. Hardened fat, like margarine, contains some more nickel (1,70±0,32 mg.kg<sup>-1</sup>) because of catalysts abrasions (IEGGLI ET AL., 2011).

### METABOLIS M

Nickeliferous vapours, in particular from occupational exposition in smelters, cause lung and throat carcinomas, especially  $Ni_2S_3$  particles (COSTA ET AL., 2005). Lung tissues stores Ni, indipendent from the kind of exposition (DENKHAUS, SALNIKOW 2002).

The daily pulmonal uptake can be calculated from the concentration (ng.m<sup>-3</sup>) times absorption rate times air breath volume (15-20 m<sup>3</sup>.d<sup>-1</sup> for an adult). The absorption rate in lung tissue had been simulated by use of artificial serum. For the Saloniki region in 1997/98, the daily pulmonal intake in urban areas was thus determined as 56 ng, and in industrial areas as 65 ng (VOUTSA, SAMARA 2002)

The oral LD<sub>50</sub> amount for rats as 350 mg.kg<sup>-1</sup> body weight, and for mice as 420 mg.kg<sup>-1</sup> boddy weight, seems rather high. Nickel, however, is teratogenic and exerts a cancerogenic potential, lowering Mg, Mn, and Zn in various tissues (DENKHAUS, SALNIKOW 2002). In the gastro- intestinal tract, usually only 1-2 % get resorbed, the rest gets excreted in the faeces. After incorporation, nickel gets excreted half via urine and half via faeces, the halftime for renal excretion is rather short at 20-60h, but does not exclude deposition in the body (DENKHAUS, SALNIKOW 2002). Quite different reports about resorption and toxicity, however, indicate that the resorption is strongly influenced by simultaneously ingested food, and is maximum for potable water. Different resorption rates resulted in significantly higher blood levels after uptake of 2,5-5,0 mg from potable water or Coca Cola, than from cow milk, orange juice, coffee or tea. Addition of 5 mg Ni to a splendid breakfast did not increase blood nickel levels (SCHELLER ET AL., 1988). In spite of high nickel levels in tea leaves (median 1,70 mg.kg<sup>-1</sup>, range 1,2-2,6mg.kg<sup>-1</sup>), sampled in entire Asia, nickel remains low in the final beverage because of high adsorption at the leaves (TADAYON, LAHIJI 2011).

Nickel in blood plasma of healthy patients was 1,0  $\pm$  0,3 µg.l<sup>-1</sup>, there was no difference between patients from psychiatry and cardiology. But patients suffering from terminal renal insufficiency had 5,2  $\pm$  4,9 µg.l<sup>-1</sup> before and 5,8  $\pm$  2,9 µg.l<sup>-1</sup> after their dialysis, which indicates lowered renal excretion, which is not improved by the dialysis procedure (STRECK ET AL., 2003). In serum of newborns, average nickel was 0,38 µg.l<sup>-1</sup> (range 0,30 – 4,80) (ALIMONTI ET AL., 1997). Contrary to Zn, Cd and Cr, Ni contents in scalp hair did not differ between healthy females and female diabetics 30-70 years of age (TADAYON ET AL., 2014).

Nickel metal and nickel salts can also be solubilized by sweat. The diffusion through the epidermis gets favoured from sweat and detergents and is similar for normal and nickel-sensitive persons. Nickel contact dermatitis develop due to the attempt of the organism to remove nickel-protein complexes, which had been formed in the Langerhans cells in the basal layer of the epidermis (SCHAUMLÖFFEL 2012).

#### MOLECULAR BIOLOGY

Ni and Co are bound in constant proportions to naturally occurring porphinoid products in some living organisms, which may be due to corresponding functions. It can be shown by ESR-spectra that enzyme-bound nickel can be monovalent and trivalent also, and thus function as a redox substrate in biosystems. Methanogenic bacteria have a methyl-CoM- reductase with a prosthetic group of Ni-porphinoide, where Ni is coordinated with the N of tetrapyrrole (NIELSEN 1991).

Ni-deficiency in rats causes changed distribution and function of Ca, Fe, Zn, and vitamine B12 in goats and rats (NIELSEN 1991). In rats during methionine deficiency, nickel acts synergistic to vitamine B12 and effects the concentration of Cu, Fe, and Mo in the plasma, as well as C, Cu and Mo in the liver, and Cu, Mn and Ni in the kidneys (NIELSEN 1991).

Nickel has been identified as an essential nutrient for the activations of urease in green plants (SCHAUMLÖFFEL 2012), or in the bacterium *heliobacter pylori* (DENKHAUS, SALNIKOW 2002). Nickel at ultratrace levels is needed to fix CO<sub>2</sub> to propionyl-CoA, to form D-Methyl-malonyl-CoA. It is a Co-factor of an enzyme to degrade branched amino-acids and oddnumbered fatty acids via the propionate route. The methylmalonyl-CoA, which depends on vitamine B12, catalyses the last step of the propionate metabolism, which increases after increased uptake of odd-numbered fatty acids. The daily need of man is below 100 µg (NIELSEN 1991).

In human serum, the Ni gets preferably bound to albumin, but it also moves to L-histidin and alpha-2macro-globulin (SCHAUMLÖFFEL 2012). Substitution at the albumin also explains the known effects of enhanced excretion of Zn and Cu. Similarly, Ni-intoxication of layers reduces the zinc levels met in eggs (WILPLINGER, PFANNHAUSER 1998).

Nickel causes oxidative damage of the DNA and prevents its repair. It replaces Fe inside the cells and simulates oxygen deficiency. Carcinogenesis depends from the kind of tissue, nickel speciation, and genetic predisposition. Particulate Ni gets incorporated into living cells by phagocytes, and dissolves there slowly in cytoplasmatic vacuoles at pH 4,5. In human lung cells, after 24h main amounts of incorporated nickel were found in the cytoplasm, but after 72h in the cell nucleus. In the nucleus, substitution of Mg by Ni leads to selective damages at the genetically inactive hetero-chromatine, but Ni per se is not mutagenic. Induction of methylations at the DNA results in switching off of genes because of increased condensation of the heterochromatine. Further on, substitution of Fe by Ni inhibits the hydroxylases of proline and asparagine, resulting in Fe-losses and signalling oxygen depletion inside the cell. This lowers the aerobic metabolism of ATP gains and results in anaerobic glycolysis, as well as to lower levels of acetyl-CoA in the respective cells (COSTA ET AL., 2005).

Patients, who develop genetically based ekzema and heavily itching inflammations of the upper skin because of nickel allergy (table 5), show serious immunological reaction towards membrane blisters of staphylococcus aureus, which penetrate the epidermis. Staphylococcus aureus increases a special messenger substance. Increased water losses and pH increase proliferate staphylococcus aureus in the skin of respective dermatitis patients, counteracted by specific antibiotics and vitamine D (LIMONE, JACOB 2018).

The nickel sensitivity of the skin of 28 nickelsensitive patients could be lowered by fixation of nickelsoaked filterpaper disks during 3 months daily application of 50 µg Ni. a dose which does not develop ekzema. The area of harmed skin was lowered to ½ after an hour, and to 1/3 after 4 days of application. Continuous Ni-release provoked a steady substantial decrease of the reactions of the T-cells with the metal ion to ¼. The number of in vitro tested T-blood cells of the CD4+ and CD8+ type as well as the number of cell partitions got severely reduced. At the end of the treatment, the nickel-stimulated T-cells of patients released less interferon-gamma (BONAMONTE ET AL., 2011).

#### DAILY INTAKE AND ALLERGICAL REACTIONS

In Great Britain, the daily intake of nickel was estimated from the average concentrations of 20 food groups and the average consumption habits, to be 130  $\mu$ g. Because data below the detection limit were set as the detection limit, the 130  $\mu$ g are a maximum value (YSART ET AL., 1999). For Austria, a similar daily intake level of nickel was estimated as 79  $\mu$ g (range 50-127  $\mu$ g), but utilizing largely different concentration levels of the ingested nutritional items (WILPLINGER, PFANNHAUSER 1998). Therein, the high nickel levels in carrots and cocoa were confirmed.

The median concentrations of nickel in food found in this work, analytically obtained for wet weight, and combined with the average figures of consumption (Statistik Austria 2012), result in a daily intake of 152  $\mu$ g Ni. This figure has been calculated without considering consumptions of Ni-carriers like mushrooms, nuts, rice and leafy vegetables, but for wholemeal bread. If consumption of white flour is assumed, the daily Niintake would be just 106  $\mu$ g, which resembles about the daily needs (Table 6). Wilplinger and Pfannhauser had estimated similar levels for Austria already in 1998.

If consumption of milk is replaced by soy-,,milk", and the average consumption of meat replaced by nuts and vegetables of about equal nutritional value, and the proportion of carrots, cabbage and lettuce taken from the harvested amounts in Austria, this results in a daily intake of 496 µg Ni (Table 7). In this case, Ni-sensitive persons begin to react, and at the double amount of ingestion, about 10-30% will react (Table 7). Nickel allergic persons develop contact ekzema after oral ingestion of a few milligrams, an amount which can be easily reached by consumption of nuts, cocoa or soy drinks (JENSEN ET AL. 2006). 17 papers dealing with the probability of an onset of Ni-dermatitis could be assigned to 3 groups, depending on the kind of uptake – from water or solid food, on the visible symptoms and on the observation period (JENSEN ET AL. 2006).

APPENDIX

Table 5. Probability of nickel allergies for nickel-sensitive persons as a function of the daily intake in three groups ofexperiments, after Jensen (2006)

r i r						
% Reaction	´mg	´mg	´mg			
90	2,7	4,2	7,7			
80	2	3,2	5,5			
60	1,45	2,3	3,6			
50	1,27	2,0	3,1			
25	0,83	1,32	2,0			
10	0,55	0,87	1,33			
5	0,41	0,65	1,00			
2	0,29	0,45	0,70			
1	0,22	0,35	0,53			

 Table 6: Estimation of Ni-ingestion from the average food consumption (2011/12): without rice, mushrooms, nuts and leafy vegetables, but with wholemeal flour

1 a par yoor		´mg.kg <sup>-1</sup> wet	ma Ni nar yaar	
kg per year		weight	nig ini per year	
74,8	fruits (apples)	0,011	0,82	
109,1	vegetables(tomatoes)	0,018	1,96	
61,1	Potatoes	0,223	13,62	
99,7	meat (sausage)	0,054	5,38	
89,1	Milk	0,004	0,36	
19,4	Cheese	0,248	4,81	
90,2	cereals(wheat)*	0,255	23,00	
2,0	Chocolate	2,644	5,29	
1,1	Honey	0,064	0,07	
	Sum		55,3 mg	
			156 µg/d	

\* If the figure for German standard bread is taken instead (0,069 mg.kg<sup>-1</sup>; BRÜGGEMANN, KUMPULAINEN 1995) the daily intake is lowered to 106 µg; eggs contained nickel below detection limit, and need not to be considered

Table 7: Estimation of Ni-ingestion from the estimated average food consumption for vegans, substituting milk by soy-,, milk " and meat by vegetables and nuts (2011/12):

	2	0	,	
kg per year		´mg.kg <sup>-1</sup> wet weight	´mg per year	
74,8	fruits (apples)	0,011	0,823	
109,1	vegetables(tomatoes)	0,018	1,964	
61,1	Potatoes	0,223	13,625	
52	Carrots	0,45	23,40	
22	Cabbage	0,21	4,62	Estimated conc.
8	Lettuce	0,21	1,68	Estimated conc.
20	Nuts	2,5	50,00	Reference
89,1	Soy-,,milk"	0,635	56,52	

90,2	cereals(wheat)	0,255	23,00	
2,0	Chocolate	2,644	5,288	
1,1	Honey	0,064	0,070	
			181 mg	
			496 µg/d	

#### REFERENCES

- [1] ALIMONTI A., PETRUCCI F., FIORAVANTI S., LAURENTI F., CAROLI S. 1997. Assessment of the content of selected trace elements in serum of term and pre-term newborns by ICP-MS. Anal. Chim. Acta 342, 75-81
- [2] ANDER E.L., WATTS M.J., SMEDLEY P.L., HAMILTON E.M., CLOSE R., CRABBE H., FLETCHER T., RIMELL A., STUDDEN M., LEONARDI G. 2016. Variability in the chemistry of private drinking water supplies and the impact of domestic treatment systems on water quality. Environ. Geochem. Health 38; 1313-1332
- [3] Austrian Federal law about sustainable waste economy = Bundesgesetz über eine nachhaltige Abfallwirtschaft (Abfallwirtschaftsgesetz 2002 – AWG 2002) StF: BGBl. I Nr. 102/2002, Fassung vom 14.05.2018
- [4] AZIZ H.A., MOHD N.A., ARIFFIN K.S. 2008. Heavy metals (Cd, Pb, Zn, Ni, Cu and Cr(III)) removal from water in Malaysia: post treatment with high quality lime stone. Biores. Technol. 99, 1578-1583
- [5] BAIZE D., SABY N., DESLAIS W. 2007: Content of eight trace metals (Cd, Cr, Cu, Hg, Ni, Pb, Se, Zn) in French arable topsoils. Jan 26th 2007, INRAreport Angers 2007
- [6] BAKIRCIOGLU D., BAKIRCIOGLU K.Y., UCAR G. 2011. Determination of some trace metal levels in cheese samples packaged in plastic and tin containers by ICP-OES after dry, wet and microwave digestion. Food and Chemical Toxicology 49, 202-207
- [7] BAUER H., SMIDT S., STOPPER S., HERMAN F., PUXBAUM H. 2008. Schwermetalleinträge in den Nordtiroler Kalkalpen. Centralblatt für das gesamte Forstwesen 125(2), 103-120
- [8] BELLAGAMBA B., CARIDI A., CEREDA E., BRAGA MARCAZZAN G.M., VALKOVIC V. 1993. PIXE application to the study of trace element behaviour in coal combustion cycle. Nucl. Instr.Meth. Phys. Res. B75, 222-229
- [9] BERG T., RØYSET O., STEINNES E. 1994. Trace elements in atmospheric precpitation at Norwegian Background stations (1989-90) measured by ICP-MS. Atmosph. Environ. 28 (21), 3519-3536

- [10] BODIŠ D., RAPANT S. 1999. Geochemical Atlas of the Slovak Republic, Part IV: Stream Sediments. Bratislava
- BONAMONTE D., CRISTAUDO A., NASORRI F., CARBONE T., DE PITA O., ANGELINI G., CAVANI A.
   2011. Efficacy of oral hyposensitization in allergic contact dermatitis caused by nickel. Contact Dematitis 65, 293-301
- [12] BREWER E.P., LI YIN M., CHANEY R.L., BURKE S., ZDIMAL S., CHEN K., ANGLE K.-Y: GREEN J.C., NELKIN J.P. 2001. Effect of soil pH on nickel and cobalt uptake by two hyperaccumulator Alyssum species grown on metal contaminated soils. Proc. 6th Intern. Conf. Biogeochem. Trace Elem., Guelph, 127
- BROOKS R.R., CHAMBERS M.F., NICKS L.J., ROBINSON B.H. 1998. *Phytomining*. Perspectives 3(9), 359-362
- BROWN P.H., WELCH R.M., CARY E.E. 1987.
   Nickel: a micronutrient for higher plants. Plant Physiol. 85, 801-803
- [15] BRÜGGEMANN J., KUMPULAINEN J. 1995. The status of trace elements in staple foods. II Some effects of cereal and potato processing. Z. Lebensm. Unters. Forsch. 201, 7-11
- [16] BRÜGGEMANN J., 1999. Erwünschte und unerwünschte Spurenelemente in Getreide, Kartoffeln und Ölsaaten. Schriftenreihe des BM für Ernährung, Landwirtschaft und Forsten Reihe A, 483, 32-51
- [17] CASALEGNO C., SCHIFANELLA O., ZENNARO E., MARRONCELLI S., BRIANT R., 2015. Collate literature data on toxicity of Chromium (Cr) and Nickel (Ni) in experimental animals and humans. EFSA Supporting Publications:EN-478. [287 pp.].
- [18] ČEJKA P., HORÁK T., DVOŘÁK J., ČULÍK J., JURKOVÁ M., KELLNER V., HAŠKOVÁ D. 2011. Monitoring of the distribution of some heavy metals during brewing process. Ecol. Chem. Eng. S, 18 (1), 67-74
- [19] CLARKE L.B. 1993. The fate of trace elements during coal combustion and gasification: an overview. Fuel 72, 731-736
- [20] COOPER C., JIANG J.Q., OUKI S. 2002. Preliminary evaluation of polymeric Fe- and Al-modified clays as adsorbents for heavy metal removal in water

treatment. J. Chem. Technol. Biotechnol.77, 546-551

- [21] CORDERO P.R.F., BENNETT R.M., BAUTISTA G.S., AGUILAR J.P.P., DEDELES G.R. 2015. Degradation of nickel protoporphyrin disodium and vanadium oxide octaethylporphyrin by Philippine microbial consortia. Bioremediation Journal 19 (2), 93-103
- [22] COSTA M., DAVIDSON T.L., CHEN H.B, KE QD, ZHANG P., YAN Y., HUANG CH.SH, KLUZ T. 2005. Nickel carcinogenesis: epigenetics and hypoxia signaling. Mutation Research 592, 79-88
- [23] Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption. Official Journal of the European Communities L 330/34, 5.12. 1998
- [24] Council Directive 1999/31/EC on the landfill of waste, Official Journal of the European Communities L 182, 16. 7. 1999
- [25] DANNEBERG O.H. 1999. Hintergrundwerte von Spurenelementen in den landwirtschaftlich genutzten Böden Ostösterreichs. Mitt. Österr. Bodenkundl. Ges. 57, 7-24
- [26] DENKHAUS E., SALNIKOW K. 2002. Nickel essentiality, toxicity, and carcinogenicity. Crit. Reviews in Oncology/Hematology 42, 35-56
- [27] DESPREZ A., BOUYSSIERE B., ARNAUDGUILHEM C., KRIER G., VERNEX-LOSET L., GIUSTI P. 2014. Study of the size distribution of sulfur, vanadium, and nickel compounds in four crude oils and their distillation cuts by gel permeation chromatography inductively coupled plasma highresolution mass spectrometry. Energy Fuels 28(6), 3730-3737
- [28] DOBROWSKY P.H., CARSTENS M., DE VILLIERS J., CLOETE T.E., KHAN W. 2015. Efficiency of a closed-coupled solar pasteurization system in treating roof harvested rainwater. Sci. Tot. Environ. 536, 206-214
- [29] DRBAL K. 1991. Heavy metals in some parts of the ecosystem of surface waters of South Bohemia. Ekologia (ČSFR) 10(3), 327-338
- [30] FERNANDEZ ESPINOSA A.J., RODRIGUEZ M.T., BARRAGAIS DE LA ROSA F.J., JIMENEZ SANCHEZ J.C., 2002. A chemical speciaton of trace metals for fine urban particles. Atmosph. Environ. 36, 773-780
- [31] Gesetz zum Schutz von schädlichen Bodenveränderungen und zur Sanierung von Altlasten (Bundes-Bodenschutzgesetz) 1999 ((german) act for the protection of hazardous soil changes and remediation of waste)
- [32] GIORDANI C., CECCHI S., ZANCHI C., 2005. Phytoremediation of soil polluted by nickel using

agricultural crops. Environmental Management 36(5), 675-681

- [33] GRANIER L., CHEVREUIL M., CARRU A.M., CHESTERIKOFF A. 1992. Atmospheric fallout of organochlorines and heavy metals in the Paris area (France). Sci Tot. Environ.126, 165-172
- [34] Grenzwerteverordnung 2006: Verordnung des Bundesministers für Wirtschaft und Arbeit, mit der die Grenzwerteverordnung 2003 und die Bauarbeiterschutzverordnung geändert werden, BGBl 242/2006 (Austria)
- [35] GRAY B.R., HILL W.R. 1995. Nickel sorption by peryphyton exposed to different light intensities.
   J.N.Am. Benthol. Soc 14(2), 299-305
- [36] GUÉRIN T., CHEKRI R., VASTEL C., SIROT V., VOLATIER J.L. 2011. Determination of 20 trace elements in fish and other seafood from the French market. Food Chem. 127, 934-942
- [37] GUO Y., SCHULZ R., MARSCHNER H. 1995. Genotypic differences in uptake and distribution of cadmium and nickel in plants. Angew. Botanik 69, 42-48
- [38] HELAL M., BAIBAGYSHEW E., SABER S. 1998. Uptake of Cd and Ni by spinach, Spinacea oleracea (L.) from polluted soil under field conditions as affected by salt water irrigation. Agronomie 18, 443-448
- [39] HÉRY M., PHILIPPOT L., MÉRIAUX E., POLY F., LE ROUX X., NAVARRO E. 2005. Nickel mine spoils revegetation attempts: effect of pioneer plants on two functional bacterial communities involved in the N-cycle. Environ. Microbiol. 7(4), 486-498
- [40] HORIE K., MIZUNO N., NOSAKA SH. 2000. Characteristics of nickel accumulation in native plants growing in ultramafic rock areas in Hokkaido. Soil Sci. Plant Nutr. 46(4), 853-862
- [41] IEGGLI C.V.S., BOHRER D., DO NASCIMENTO P.C., DE CARVALHO L.M. 2011. Flame and graphite furnace AAS for trace element determination in vegetable oils, margarine and butter after sample emulsification. Food Add. Contam. A, 28(5), 640-648
- [42] JENSEN C.S., MENNE T., JOHANSEN J.D. 2006. Systemic contact dermatitis after oral exposure to nickel: a revies with modified meta-analysis. Contact dermatitis 54: 79-86
- [43] JORHEM L., SUNDSTRÖM B., ÅSTRAND C., HAEGLUND G. 1989. The levels of Zn, Cu, Mn, Se, Cr, Ni, Co, and Al in the meat, liver and kidney of Swedish pigs and cattle. Z. Lebensm. Unters. Forsch. 188, 39-44
- [44] KHOKHOTVA O., WAARA S. 2011. The effect of environmental conditions on the stability of heavy

metal filter material complex as assessed by the leaching of the adsorbed metal ions. Environ. Poll.159, 1461-1463

- [45] KUKIER U., CHANEY R.L., PETERS C.E., BREWER E.P., ANGLE J.S., LI Y.M., NELKIN J.P. 2001. Growth and Ni-uptake from Ni-contaminated soil by agricultural crops and hyperaccumulator species – the pH effect. Proc. 6th Intern. Conf. Biogeochem. Trace Elem, Guelph, 125
- [46] KUO C.Y., WANG J.Y., CHANG S.H., CHEN M.C. 2009. Study of metal concentrations in the environment near diesel transport routes. Atmosph. Environ. 43, 3070-3076
- [47] LARSEN E.H., ANDERSEN N.L., MØLLER A, PETERSEN A., MORTENSEN G.K., PETERSEN J. 2002. Monitoring the content and intake of trace elements from food in Denmark. Food Additives and Contaminants 19(1), 33-46
- [48] LIMONE B.A., JACOB S.E. 2018. Staphylococcal infections in atopic dermatitis and nickel allergy: Immunologic implications and elemental oppurtunities. Journal of Trace Elements in Medicine and Biology 45, 21-22
- [49] LÓPEZ SALVADOR L., MÓNACO L. 2017. Vanadium, nickel and sulfur in crude oils and source rocks and their relationship with biomarkers: implications for the origin of crude oils in Venezuelan basins. Org. Geochem. 104, 53-68
- [50] MAVROS P., ZOUBOULIS A.I., LAZARIDIS N.K. 1993. Removal of metal ions from wastewaters, the case of nickel. Environ. Technol 14, 83-91
- [51] NIELSEN F.H. 1991. Nutritional requirements for boron, silicon, vanadium, nickel, and arsenic: current knowledge and speculation. The FASEB Journal 5, 2661-2667
- [52] NIKKARINEN M., MERTANEN E. 2004. Impact of geological origin on trace element composition of edible mushrooms. Journal of Food Composition and Analysis 17(3-4), 301-310
- [53] PAULSEN P., SAGER M. 2017. Nickel and copper residues in meat from wild artiodactyls hunted with nickel-plated non-lead rifle bullets. Eur J Wildl Res 63(4), Art.63
- [54] PLAHL F., ROGALSKI W., GILNREINER G., ERHART E 2002. Vienna's biowaste compost – quality development and effects of input materials. Waste Management and Research 20, 127-133
- [55] PIRKL H., SCHEDL A., PFLEIDERER S. 2015. Geochemischer Atlas von Österreich – Bundesweite Bach- und Flusssedimentgeochemie 1978-2010, Archiv für Lagerstättenforschung 28, 288 pp.

- [56] PIRONE N., KEELER G.J., WARNER P.O. 1995. Trends of ambient concentrations and deposition fluxes of particulate trace metals in Detroit from 1982-1992. Sci. Tot. Environ. 162, 43-61
- [57] RICHTER P., GRINO P., AHUMADA I., GIORDANO A. 2007. Total element concentration and chemical fractionation in airborne particulate matter from Santiago, Chile. Atmosph. Environ. 41 (32), 6729-6738
- [58] ROSS S M, WOOD M D, COPPLESTONE D, WARRINE M, CROOK P. 2007. Environmental concentrations of heavy metals in UK soil and herbage. Environment Agency, Bristol UK, June 2007
- [59] SAGER M., PUCSKO R., BELOCKY R. 1989. Evaluation of the speciation of inorganic constituents in sediments of the Reservoir at Altenwörth of the River Danube. Arch. hydrobiol. Suppl. 84, 37-72
- [60] SAGER M. 1995. Migration of Cd, Cu, Ni and Pb in low-permeable clay-type solids in presence of acid complexants in contaminated soils. Third International Conference on the Biogeochemistry of Trace Elements(Prost R. ed.), Colloque n°85, INRA Editions, Paris
- [61] SAGER M., VOGEL W. 1993. Heavy metal load of sediments of the River Gurk (Carinthia/Austria) -Merits and limitations of sequential leaching. Acta hydrochim. hydrobiol.21, 21-34
- [62] SAGER M., MITTENDORFER J. 1997. Influence of Milling or Cutting Procedures on Trace Element Contents of Plant Samples. Int. Journal of Environ. Anal. Chem. 67, 59-71
- [63] SAGER M. 1999. Environmental Aspects of Trace Elements in Coal Combustion. Tox. Environ. Chem. 71, 159-183
- [64] SAGER M. 2001. Barrier Effects of Low-Permeable Clay Type Solids. Experiments with Model Leachates Containing Cd, Cu, Ni, and Pb and Organic Acids. Geosystem Eng. 4(1), 1-12
- [65] SAGER M. 2005. Aktuelle Elementgehalte in Fleisch und Innereien aus Österreich (Current elemental composition of meat, liver and kidneys from Austria). Ernährung/Nutrition 29(5), 199-206
- [66] SAGER M. 2006. Micro- and macro-element composition of animal feedstuffs sold in Austria. Ernährung/Nutrition 30 (11), 455 – 473
- [67] SAGER M. 2009. Fertilization loads of less common elements to arable soils in Austria In; Organic Farming: Methods, Economics and Structure. ISBN 978-1-60692-864-6. Editors: Michael Nelson and Ivan Artamova © 2009 Nova Science Publishers, Inc. Chapter 7, p.145-178

- [68] SAGER M. 2010. Über die Elementzusammensetzung von in Österreich erhältlichen Fertiggerichten und Wurstwaren. Ernährung/Nutrition. 34: 2, 57-64
- [69] SAGER M. 2011. Mengen- und Spurenelemente in österreichischen Hühnereiern.
   Ernährung/Nutrition 35(2), 53-58
- [70] SAGER M. 2012. Element Composition from Urban Biowaste compared with Organic Fertilizers of Agricultural Origin, in: Progress on Heavy Metals in the Environment; Selected Papers of the ICHMET-15 Conference; J. Nriagu, J. Pacyna, P. Szefer, B. Markert, S. Wünschmann, J. Namiesnik eds., Maralte books, chapter 13.0: 1-14; 2321 DK Leiden, Niederlande
- [71] SAGER M. 2012. Haupt- und Spurenelemente von Käse in Österreich. Ernährung/Nutrition 36, 149-159
- [72] SAGER M. 2012. Chocolate and Cocoa Products as A Source of Essential Elements in Nutrition. J Nutr Food Sci 2:123
- [73] SAGER M., HOBEGGER M. 2013. Elementgehalte in Rohmilch aus drei Regionen Niederösterreichs; (Contents of elements in raw milk from three regions in Lower Austria). Ernährung/Nutrition 37 (7/8), 277-290
- [74] SAGER M. 2014. Element- und Spurenelementgehalte von Äpfeln (Element and Trace Element Content of Apples). Journal für Ernährungsmedizin Oktober 2014, 8-12.
- [75] SAGER M. 2015. Elementgehalte und Spurenelementgehalte in Rohmilch aus Österreich
   Vergleich Almmilch – Stallmilch. VDLUFA -Schriftenreihe 70, 483-492
- [76] SAGER M., CHON H.T., MARTON L. 2015. Spatial variation of contaminant elements of roadside dust samples from Budapest (Hungary) and Seoul (Republic of Korea), including Pt, Pd and Ir. Environ Geochem Health 37, 181–193
- [77] SAGER M. 2016. Element- und Spurenelementgehalte in handelsüblichen Milchprodukten in Österreich (Element and trace element contents in Austrian commercial dairy products). Journal für Ernährungsmedizin (jem); 16(1), 12
- [78] SAGER M., ERHART E. (2016). Spurenelemente in Getreide im Zusammenhang mit mobilen Bodenfraktionen untern konventioneller bzw. biologischer Bewirtschaftung. VDLUFA Schriftenreihe 73, 143-149
- [79] SAGER M. 2016. A simplified extraction schema to for the analytical characterization of apple

orchard soils. Journal of Soils and Sediments 16(4), 1193-1202

- [80] SAGER M. 2017. Main and Trace Element Contents of Tomatoes Grown in Austria. Journal of Food Science and Engineering 7(5), 239-248.
- [81] SAGER M. 2017. The honey as a bioindicator of the environment. Ecol.Chem. Eng. S. 24(4), 583-594
- [82] SAGER M. 2018. Content of elements and trace elements in Austrian commercial dairy products. Journal of Elementology 23(1): 381-400
- [83] SAGER M., LUCKE A., GHAREEB KH., ALLYMEHR M., ZEBELI Q., BÖHM J. 2018. Dietary deoxynivalenol does not affect mineral element accumulation in breast and thigh muscles of broiler chicken. Mycotoxin Research, 34(2), 117-121
- [84] SAKATA M., TANI Y, TAKAGI T. 2008. Wet and dry deposition fluxes of trace elements in Tokyo Bay. Atmosph. Environ. 42, 5913-5922
- [85] ŠČANČAR J., MILAČIČR., STRAŽAR M., BURICA O., BUKOVEC P. 2001. Environmentally safe sewage sludge diposal: the impact of liming on the behaviour of Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn. J. Environ. Monit. 3, 226-231
- [86] SCHAUMLÖFFEL D. 2012. Nickelspezies: Analyse und toxische Effekte. J. Trace Elem. Med. Biol. 26, 1-6
- [87] SCHELLER R., STRAHLMANN B., SCHWEDT G. 1988. Lebensmittelchemische und –technologische Aspekte zur nickelarmen Ernährung bei endogen bedingten Kontaktekzemen. Hautarzt 39, 491-407
- [88] SUK S.M., SU K.D. 2004. Adsorption Features of Nickel Ion on Waste Coffee Grounds. Fall convention of the Korean Society for Geosystem Engineering, Hoam Convention Centre of Seoul National University, 2004. ISBN 89-950026-9-7-93550
- [89] SPIEGEL H., SAGER M. 2008. Elementzusammensetzung von Weizen und Kartoffeln in Österreich unter Berücksichtigung des Einflusses von Sorte und Standort. Ernährung/Nutrition 32, 7/8, 297-308
- [90] STASINOS S., ZABETAKIS I. 2013. The uptake of nickel and chromium from irrigation water by potatoes, carrots and onions. Ecotoxicology and Environmental Safety 91, 122-128
- [91] Statistik Austria (2012): Standard-Dokumentation

   Metainformationen (Definitionen, Erläuterungen, Methoden, Qualität) zu den Versorgungsbilanzen für den tierischen und pflanzlichen Sektor. Version edited on April 27<sup>th</sup>, 2012. http://www.statistik.at

- [92] STRECK S., ROSKOS M., DEUFEL T., WINNEFELD K 2003. Elementscreening mit ICP-MS, AAS und ISE bei ausgewählten Erkrankungen. CANAS 03, P2-10
- [93] TADAYON F., LAHIJI N. 2011. Availability of essential and nonessential elements in tea samples produced in Iran. International Journal of Academic Research 3, 1071-1075
- [94] TADAYON F., ABDOLLAHI A., RAJABI N.S., OSTOVAR R. 2014. Relationship between the level of zinc, lead, cadmium, nickel and chromium in hair of people with diabetes. E3S Web of Conferences. 1. 41012. 10.1051/e3sconf/20130141012
- [95] THEVANNAN A., MUNGROO R., NIU C.H. 2010. Biosorption of nickel with barley straw. Biores. Technol. 101, 1776-1780
- [96] Verordnung des Bundesministers für soziale Sicherheit und Generationen über die Qualität von Wasser für den menschlichen Gebrauch (Trinkwasserverordnung - TWV), StF: BGBl. II Nr. 304/2001 [CELEX-Nr.: 398L0083], in der Fassung BGBl. I Nr. 51/2017
- [97] VOLKENING J., HEUMANN K.G. 1990. Heavy metals in the near-surface aerosol over the Atlantic Ocean from 60° South to 54° North. J. Geophys. Res. 95, 20623-20632
- [98] VOUTSA D., SAMARA C. 2002. Labile and bioaccessible fractions of heavy metals in the airborne particulate matter from urban and industrial areas. Atmosph. Environ. 36, 3583-3596
- [99] WELCH J.E., LUND L.J. 1987. Soil properties, irrigation water quality, and soil moisture level influences on the movement of nickel in sewage sludge treated soils. J. Environ. Qual. 16(4), 403-410
- [100] WILPLINGER M., PFANNHAUSER W. 1998.
   Essentielle Spurenelemente Cr, Cu, Mo, Ni, Se und Zn. Bericht über das Forschungsprojekt GZ.353.064. Wien: Bundeskanzleramt, Sekt. VI
- [101] WISE JR. J.P., WISE J.T.F., WISE C.F., WISE S.S., GIANIOS JR. C., XIE H. THOMPSON W. D., PERKINS C., FALANK C., WISE SR. J.P. 2014. Concentrations of the genotoxic metals, chromium and nickel, in tar balls, oil slicks, and released oil from the Gulf of Mexico in the immediate aftermath of the Deepwater Horizon oil crisis: is genetoxic metal exposure part of the deepwater horizon legacy? Environmental Science and Technology 48, 2997-3006
- [102] SUH Y.J., JANG H.D., CHANG H.K., HWANG D.W., KIM H.CH. 2004. Kinetics of nickel chloride

reduction in preparing Ni nanoparticles in the gasphase. Fall convention of the Korean Society for Geosystem Engineering, Hoam Convention Centre of Seoul National University, 2004. ISBN 89-950026-9-7-93550

- [103] YOUNGS W.D., RUTZKE M., GUTENMANN W.H., LISK D.J. 1993. Nickel and vanadium in foliage in the vicinity of an oil-fired power plant. Chemosphere 27(7), 1269-1272
- [104] YSART G., MILLER P., CREWS H., ROBB P., BAXTER M., DE LARGY CH., LOFTHOUSE S., SARGENT CH., HARRISON N. 1999. Dietary exposure estimates of 30 elements from the UK total diet study. Food Add. Contam. 16(9): 391-403
- [105] ZATKA V.J., WARNER J.S., MASKERY D. 1992. Chemical speciation of nickel in airborne dusts: analytical method and results of an interlaboratory test program. Environ. Sci. Technol. 26(1), 138-144
- [106] ZIEGLER E.N. 2012. Encyclopedia of Environmental Science and Engineering, 6th Ed., CRC Press Boca Raton – London - New York