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IMPACT OF ENVIRONMENTAL CONDITIONS ON MICRO- AND MACROELEMENT CONTENT IN SELECTED FOOD FROM LATVIA

Summary of doctoral thesis

Submitted for the degree of Doctor of Chemistry, Environmental Science
Subfield of Environmental Chemistry and Ecotoxicology

Rīga, 2014

The research for doctoral thesis was carried out at the Department of Environmental Science, Faculty of Geography and Earth Sciences, University of Latvia, from 2009 to 2013, and it has been supported by the European Social Fund within the project "Support for Doctoral Studies at University of Latvia", No. 2009/0138/ 1DP/1.1.2.1.2./ 09/IPIA/ VIAA/004.

Eiropas Sociālā fonda projekts „Atbalsts doktora studijām Latvijas Universitātē " Nr.2009/0138/ 1DP/1.1.2.1.2./ 09/IPIA/ VIAA/004.

The thesis contains the introduction, 3 chapters, conclusions, reference list, 4 appendices.

Form of the thesis: dissertation in chemistry, field of environmental science, subfield of environmental chemistry and ecotoxicology.

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The thesis will be defended at the public session of the Doctoral Committee of Environmental Science, University of Latvia, at the Faculty of Geography and Earth Sciences of the University of Latvia (Alberta Street 10, Riga, Latvia) on April 24, 2014 at 10:00.

The thesis is available at the Library of the University of Latvia (Raiņa blvd. 19, Riga, Latvia).

The thesis was accepted for the commencement of the degree of Doctor of Chemistry, Environmental Science on January 16, 2014 by the Doctoral Committee of Environmental Science, University of Latvia.

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Contents

Annotation

Besides the transfer of essential micro- and macroelements from environment to food, contamination of food chain with toxic and potentially toxic elements, e.g., As, Cr, Cd, Hg, Pb may occur. The aim of the doctoral research “Impact of environmental conditions on micro- and macroelement content in selected food from Latvia” included quantitative investigation of food samples collected in Latvia to discover factors influencing the concentration and possible transfer routes of elements in food. In addition, element bioavailability in food chain was studied by experimental food crop growth in contaminated soil. Obtained results revealed influence of several factors, e.g., seasonality, botanical origin, site-specific factors, applied agricultural practice, food processing on the concentration of elements in food.

Key words: micro- and macroelements, quantitative analysis, element transfer, food composition, environment, Latvia.

General overview of the work

Introduction

Food and drinking water are the main sources of nutrient element supply for human body. Apart from basic substances of nutrition as proteins, carbohydrates and lipids, human body requires fibres, vitamins, amino acids, enzymes and range of essential chemical elements. Macroelements such as Ca, K, Mg, Na and microelements (e.g., Cr, Cu, Fe, Mn, Mo, Se, V, Zn) are essential compounds which affect vital functioning of human body – development, growth, reproduction. Although, the information of the chemical and nutritional content of majority of foodstuffs is established and aggregated in series of handbooks about nutrition and healthy diet, e.g., *Burgerstein's handbook of nutrition* (Zimmermann, 2001), *Handbook of nutrition and food* (Berdanier et al., 2007), *Uztura mācība* (*Nutrition studies*) written by Latvian dieticians (Zariņš un Neimane, 2009), and several databases constituted by agricultural and food research institutions (e.g., USDA, s.a.), micro- and macroelement content in food regionally is very variable (e.g., Aberoumand and Deokule, 2010; Ekholm et al., 2007; Ferre-Huguet et al., 2008; Hashmi et al., 2007). Specific or natural environmental conditions with interconnection of anthropogenic influences may affect element content in food. For example, element content in soil can influence composition of vegetation that is consumed by animals or is used as human food, thus resulting in the specific element transfer into food chain which may affect human health, longevity and life quality in general (Combs, 2005; Fraga, 2005; Nabrzyski, 2007). Food contamination with toxic and potentially toxic elements (e.g., As, Cr, Cd, Hg, Pb) may occur resulting in reduced quality of daily nutrition and adverse health effects. Therefore, the assessment of the content and concentration of micro- and macroelements in connection with estimation of environmental and anthropogenic impacts are the issues of a high importance. Information of tendencies in the content of elements in food also can be used as an indicator of regional environmental element background (Fernandez-Torres et al., 2005; Fodor and Molnar, 1993; Pisani et al., 2008). Quantitative data of micro- and macroelement concentration is an indispensable tool for risk assessment analysis that can be associated with occasional intakes of elements in too high levels and may lead to the toxic adverse effects in human body or, contrary, can be connected with possible insufficiency of element intake that may determine deficiency of certain elements in human body (Goldhaber, 2003). Thus, interdisciplinary studies of micro- and macroelement concentration in foodstuffs are of importance for many branches of science including environmental science, chemistry, food and nutrition science, and health sciences. And the aim of such studies is not only to investigate impacts of environmental pollution, but also to identify element inputs from environment to food due to the natural environmental conditions as well as to discover the element transfer routes and accumulation processes. The research of micro- and macroelement concentration in food within the interconnection of impact of environmental conditions is of great importance from the public healthcare perspective as support to regional or site-specific food production, especially considering growing role of biological farming and domestic farming as well as for further development of food quality control system.

Aim of the work

The aim of the work was to study concentration of micro- and macroelements in selected foodstuffs collected over the territory of Latvia to characterize the impact of environmental conditions influencing element content, concentration and transfer in food, and to study the provisional bioavailability of elements in food chain *soil-plant-human.*

Tasks of the work

- Application and development of methodology for foodstuff sampling, pretreatment and quantitative analysis of element concentration considering quality assurance requirements.
- Collection of food samples in Latvia and subsequent quantitative analysis of element concentration, data statistical analysis, assessment of the impact of environmental conditions influencing element content in foodstuffs in respect to, e.g., environmental pollution, impact of natural and anthropogenic conditions.
- Study of the routes of micro- and macroelement movement within the food chain *soil-plant-human* and assessment of provisional bioavailability of elements in food chain segments *soil-plant* and *plant-human*.
- Provisional risk and benefit assessment of element contribution in human nutrition as well as comparison of micro- and macroelement concentration in food in Latvia with corresponding data from other countries.

The main focus of the work was the implementation of screening analysis of selected food in Latvia to discover the tendencies of micro- and macroelement concentration within the framework of impact of environmental conditions.

Hypothesis

Quantitative analysis of micro- and macroelements in food samples in Latvia is one of the indicators of food quality, safety and nutritional value that can be affected by natural and anthropogenic environmental conditions.

Proposed theses

1. Quantitative analysis of micro- and macroelements in food samples using methods of analytical chemistry – a challenge for the improvement of food analysis methodology and development of screening methods.
2. Analysis of micro- and macroelements in food is a significant indicator of food safety and quality that can be assessed estimating specific conditions of food production process.
3. Seasonality, site specific, botanical factors, impact of agricultural practice, food processing specifics – conditions that affect micro- and macroelement composition and concentration in food.
4. Investigation of bioavailability of elements in food chain segments – important aspect of pollution transfer into nutrition with food.
5. Quantitative analysis of food is a perspective research direction within the context of environmental science, chemistry and health sciences that has to be developed in larger scale.

Scientific novelty

- Further improvements of analytical methodologies of food and environmental sample analysis, supporting advancement of prospective in food quality monitoring principles, with the prospective implementation of quality assurance procedures.
- Development of interdisciplinary approach for the investigation of natural and anthropogenic factor impacts on food composition.
- Comparative evaluation of the accumulation processes of elements in foodstuffs derived in different conditions, e.g., biological farming versus conventional farming etc.
- Development of micro- and macroelement analysis (fingerprint concept) as a tool for tracking food origin, identity and quality.

Practical importance

The first comprehensive quantitative analysis of micro- and macroelement concentration in representative foodstuffs in Latvia that reveals in general beneficial (in respect to human nutrition) composition of elements in food produced in Latvia, low impacts of environmental pollution and good perspectives to identify and label food produced in Latvia as compliable to highest quality criteria. Determined tendencies of element transfer in food chain and provisional bioavailability assessment may be developed further in a favour of sustainable agriculture and gardening. Estimation of food nutritional value regarding micro- and macroelements, local dietary specifics, food safety and provisional consumer risk assessment in Latvia can be used for further analysis of public health and for comparison of food composition on a worldwide scale.

Approbation

The results of the doctoral thesis are published in 12 scientific articles. The results of the research work have been presented in 15 reports at international conferences and in 10 reports at local conferences in Latvia.

Related to the research field the author of the thesis has supervised 4 bachelor research works and has advised the preparation of 3 master theses.

Scientific publications:

1. **Vincevica-Gaile, Z.**, Klavins, M. (2013) Concentration of elements in food: How can it reflect impact of environmental and other influencing factors? *Scientific Journal of Riga Technical University, Series: Environmental & Climate Technologies* 12: 15-19.
2. Stapkevica, M., **Vincevica-Gaile, Z.**, Klavins, M. (2013) Metal uptake from contaminated soils by some plant species – radish, lettuce, dill. *Research for Rural Development* 1: 43-49.
3. **Vincevica-Gaile, Z.**, Klavins, M., Rudovica, V., Viksna, A. (2013) Research review trends of food analysis in Latvia: Major and trace element content. *Environmental Geochemistry & Health* 35: 693-703.
4. **Vincevica-Gaile, Z.**, Rudovica, V., Burlakovs, J., Klavins, M., Priedite, E. (2013) Analysis of major and trace elements in food: Aspects of methodological applications. *SGEM 2013 GeoConference Proceedings on Ecology, Economics, Education and Legislation* 1: 49-56.
5. **Vincevica-Gaile, Z.**, Gaga, K., Klavins, M. (2013) Food and environment: Trace element content of hen eggs from different housing types. *APCBEE Procedia* 5: 221-226.
6. **Vincevica-Gaile, Z.**, Klavins, M. (2012) Transfer of metals in food chain: An example with copper and lettuce. *Scientific Journal of Riga Technical University, Series: Environmental & Climate Technologies* 10: 21-24.
7. **Vincevica-Gaile, Z.**, Klavins, M. (2012) Root vegetables from Latvia: Quantitative analysis of potentially toxic elements. *Research for Rural Development* 1: 131-136.
8. **Vincevica-Gaile, Z.**, Klavins, M., Rudovica, V., Viksna, A. (2012) Potentially toxic metals in honey from Latvia: Is there connection with botanical origin? In: Ramos, R.A.R., Straupe, I., Panagopoulos, T. (eds.) *Recent Researches in Environment, Energy Systems and Sustainability*. WSEAS Press: Faro, 297 p., 158-163.
9. **Vincevica-Gaile, Z.**, Klavins, M., Rudovica, V., Viksna, A. (2011) Trace and major elements in food articles in Latvia: Root vegetables. *Scientific Journal of Riga Technical University, Series: Environmental and Climate Technologies* 13(7): 119-124.

10. **Vincevica-Gaile, Z.**, Klavins, M., Rudovica, V., Viksna, A. (2011) Geographical dissemination of trace and major elements in honey. In: Brebbia, C.A. (ed.) *Sustainability Today*. WIT Press: Southampton, 488 p., 211-220.
11. **Vincevica-Gaile, Z.**, Klavins, M., Zilgalve, L. (2011) Trace and major element concentration in cottage cheese from Latvia. In: Mastorakis, N., Mladenov, V., Savkovic-Stevanovic, J. (eds.) *Recent Researches in Sociology, Financing, Environment and Health Sciences*. WSEAS Press: Meloneras, 356 p., 169-173.
12. **Vincēviča-Gaile, Z.** (2010) Makro- un mikroelementu saturs medū / Macro- and trace elements in honey. [In Latvian] *Proceedings of the Latvia University of Agriculture* 25(320): 54-66.

Reports presented at international conferences:

1. Riga Technical University 54th International Scientific Conference. Latvia, Riga, October 14-16, 2013. Report "Quantitative content of elements in food: How can it reflect impact of environmental and other influencing factors?" (**Vincevica-Gaile, Z**., Klavins, M.)
2. The 44th IUPAC (*International Union of Pure and Applied Chemistry*) Word Chemistry Congress. Turkey, Istanbul, August 8-16, 2013. Report "Metal uptake and bioavailability: From soil to food through crops" (**Vincevica-Gaile, Z.**, Stapkevica, M., Dudare, D., Klavins, M.)
3. The 13th International Multidisciplinary Scientific Geo Conference *SGEM 2013*. Bulgaria, Albena, June 16-22, 2013. Report "Analysis of major and trace elements in food: Aspects of methodological applications**"** (**Vincevica-Gaile, Z.**, Rudovica, V., Burlakovs, J., Klavins, M.)
4. The 19th Annual International Scientific Conference *Research for Rural Development 2013*. Latvia, Jelgava, May 15-17, 2013. Report "Metal uptake from contaminated soils by some plant species (radish, lettuce, dill)" (Stapkevica, M., **Vincevica-Gaile, Z.**, Klavins, M.)
5. International Conference *Environmental Health 2013, Science and Policy to Protect Future Generations*. USA, Massachusetts, Boston, March 3-6, 2013. Report "Presence of arsenic in baby food: Is it the issue of concern?" (**Vincevica-Gaile, Z.**, Lawgali, Y.F., Meharg, A.A., Klavins, M.)
6. The 14th International Conference on Environmental Science and Development. UAE, Dubai, January 19-20, 2013. Report "Food and environment: Trace element content of hen eggs from different housing types" (**Vincevica-Gaile, Z.**, Gaga, K., Klavins, M.)
7. Riga Technical University 53rd International Scientific Conference. Latvia, Riga, October 11-12, 2012. Report "Transfer of metals in food chain: An example with copper and lettuce" (**Vincevica-Gaile, Z**., Klavins, M.)
8. Sino-European Symposium on Environment and Health *SESEH 2012*. Ireland, Galway, August 20-25, 2012. Report "Research of food from Latvia: Analysis of essential elements and possible contaminants" (**Vincevica-Gaile, Z.**, Klavins, M., Rudovica, V., Viksna, A.)
9. The 18th Annual International Scientific Conference *Research for Rural Development 2012*. Latvia, Jelgava, May 16-18, 2012. Report "Root vegetables from Latvia: Background levels and risks of contamination with toxic elements" (**Vincevica-Gaile, Z.**, Klavins, M.)
10. The 8th IASME/WSEAS (*International Association of Mechanical Engineering* / *World Scientific and Engineering Academy and Society*) Conference on Energy, Environment, Ecosystems and Sustainable Development *EEESD 2012*. Portugal, Faro, May 2-4, 2012.

Report “Potentially toxic metals in honey from Latvia: Is there connection with botanical origin?” (**Vincevica-Gaile, Z.**, Klavins, M., Rudovica, V., Viksna, A.)

11. The 12th Eurasia Conference on Chemical Sciences *$EuAsC_2S$ 2012*. Greece, Corfu, Dassia, April 16-21, 2012. Report “Trace and major elements in root vegetables: A study in Latvia” (**Vincevica-Gaile, Z.**, Klavins, M., Rudovica, V., Viksna, A.)
12. The 3rd United World Congress of Latvian Scientists and the 4th Letonika (Latvian Studies) Congress, section *Quality of the environment of Latvia: Current situation, challenges, problem solutions*. Latvia, Riga, October 24-27, 2011. Report “Trace and major element analysis within the context of environmental science” [in Latvian] (**Vincevica-Gaile, Z.**, Klavins, M., Rudovica, V., Viksna, A.)
13. The 4th International Conference on Medical Geology *GEOMED 2011*. Italy, Bari, September 20-25, 2011. Report “Risk and benefit assessment of trace and major elements detected in honey of different origins” (**Vincevica-Gaile, Z.**, Klavins, M., Rudovica, V., Viksna, A.)
14. The 1st International Conference on Food and Environment *FENV 2011*. United Kingdom, New Forest, Lyndhurst, June 21-23, 2011. Report “Geographical dissemination of trace and major elements in honey” (**Vincevica-Gaile, Z.**, Klavins, M., Rudovica, V., Viksna, A.)
15. The 2nd WSEAS *(World Scientific and Engineering Academy and Society)* International Conference on Environment, Medicine and Health Sciences *EMEH 2011*. Spain, Gran Canaria, Playa Meloneras, March 24-26, 2011. Report “Trace and major element concentration in cottage cheese from Latvia” (**Vincevica-Gaile, Z.**, Zilgalve, L., Klavins, M.)

Reports presented in local conferences in Latvia:

1. The 72nd Scientific Conference of University of Latvia. Riga, January 27, 2014. Report “Impact of environmental conditions on the content of microelements in food: Analysis of cereal products” [in Latvian] (**Vincēviča-Gaile, Z.,** Gāga, K., Rudoviča, V., Kļaviņš, M.) Abstract published in: *Geography. Geology. Environmental Science: Book of abstracts*, 67-69.
2. The 71st Scientific Conference of University of Latvia. Riga, January 29, 2013. Report “Transfer of heavy metals in food chain soil-plant” [in Latvian] (Stapkēviča, M., **Vincēviča-Gaile, Z.,** Kļaviņš, M.) Abstract published in: *Geography. Geology. Environmental Science: Book of abstracts*, 215-216.
3. The 70th Scientific Conference of University of Latvia. Riga, January 31, 2012. Report “Content of micro- and macroelements in root vegetables in Latvia” [in Latvian] (**Vincēviča-Gaile, Z.,** Kļaviņš, M., Rudoviča, V., Vīksna, A.) Abstract published in: *Geography. Geology. Environmental Science: Book of abstracts*, 398-399.
4. The 70th Scientific Conference of University of Latvia. Riga, January 31, 2012. Report “Transfer of metals within the food chain soil-plant (example of Cu^{2+})” [in Latvian] (**Vincēviča-Gaile, Z.,** Kļaviņš, M.) Abstract published in: *Geography. Geology. Environmental Science: Book of abstracts*, 397-398.
5. The 70th Scientific Conference of University of Latvia. Riga, January 31, 2012. Report “Application of total reflection X-ray spectrometry for direct analysis of liquid samples” [in Latvian] (**Vincēviča-Gaile, Z.,** Purmalis, O., Kļaviņš, M.) Abstract published in: *Geography. Geology. Environmental Science: Book of abstracts*, 400-401.
6. The 70th Scientific Conference of University of Latvia. Riga, January 31, 2012. Report “Influence of seasonality on micro- and macroelement content of hen eggs” [in Latvian]

(Gāga, K., **Vincēviča-Gaile, Z.,** Kļaviņš, M.) Abstract published in: *Geography. Geology. Environmental Science: Book of abstracts*, 291-292.

7. The 70th Scientific Conference of University of Latvia. Riga, January 31, 2012. Report "Influence of botanical origin on the element content of honey in Latvia" [in Latvian] (Priedīte, E., **Vincēviča-Gaile, Z.,** Kļaviņš, M., Rudoviča, V., Vīksna, A.) Abstract published in: *Geography. Geology. Environmental Science: Book of abstracts*, 356-357.
8. The 69th Scientific Conference of University of Latvia. Riga, February, 2011. Report "Environmental conditions influencing fluctuation of micro- and macroelement content of cottage cheese" [in Latvian] (**Vincēviča-Gaile, Z.,** Zilgalve, L., Kļaviņš, M.) Abstract published in: *Geography. Geology. Environmental Science: Book of abstracts*, 501-504.
9. The 69th Scientific Conference of University of Latvia. Riga, February, 2011. Report "Significance of micro- and macroelement content of honey within the context of environmental science" [in Latvian] (**Vincēviča-Gaile, Z.,** Bula, R., Kļaviņš, M.) Abstract published in: *Geography. Geology. Environmental Science: Book of abstracts*, 499-501.
10. The 68th Scientific Conference of University of Latvia. Riga, February, 2010. Report "Biogeochemical relevance of selenium" [in Latvian] (**Vincēviča-Gaile, Z.**) Abstract published in: *Geography. Geology. Environmental Science: Book of abstracts*, 440-442.

1. Literature review

1.1. Characteristics and transfer of micro- and macroelements in food

Along with basic elements (C, H, N and O) that form up to 97 % of the matter of living systems, chemical elements are subdivided into groups of macroelements and microelements depending on their average concentration in organism, and taking into account required daily provision. Macroelements are Ca, Cl, K, Mg, Na, P, S and Si, each of them accounts about 0.03-1.4 % of human body weight. Microelement concentration in human body is variable – from less than 0.1 mg/kg to more than 100 mg/kg. Microelement group involves such elements as Ag, Al, As, Au, B, Ba, Br, Cd, Co, Cr, Cs, Cu, F, Fe, I, Mn, Mo, Ni, Pb, Rb, Sc, Se, Sn, Sr, V, Zn, but the list may vary due to the elemental traits of the lifestyle, diet and habitation environment of an individual. The requirement for microelements generally do not exceed 100 mg/day, while macroelements are required from 100 to >1000 mg/day (Abrahams, 2002; Aras and Ataman, 2006; Fraga, 2005). From all known chemical elements about 50 elements can be found in living organisms, including plants, animals and humans, but only for 23 elements the physiological relevance for humans has been revealed (Combs, 2005; Fraga, 2005). According to A. Kabata-Pendias and A.B. Mukherjee (2007), elements that are found in detectable levels in human body can be listed as follows: a) essential elements – As, B, Br, Cl, Co, Cr, Cu, F, Fe, I, Li, Mn, Mo, P, S, Se, Si, V and Zn; b) possibly essential elements – Al, Ba, Ge, Ni, Rb, Sn, Sr and Ti; c) non-essential elements – Ag, Au, Cs, Hf, In, Ir, Sb, Ta, Te, U, Y, Zr and rare earth elements; d) non-essential and highly toxic elements – Be, Bi, Cd, Hg, Pb and Tl. In the group of suspected essentials G.F. Combs (2005) involves such elements as Ni, Pb, As, B, V, Si. However, the classification of elements is conditional and may vary due to the subjective research results and up-to-date scientific findings.

Food is the most important source that supplies human body with nutrients including macro- and microelements. It is important to assess possible routes of element transfer from environment, soil, water and air, into the food chain, because not only essential elements can be transferred but also food contamination by toxic or potentially toxic elements may appear. Nowadays industrial food production has been developed rapidly and is steady restricted by laws and regulations that set down limitations for composition of food. However, food products derived from plant or animal origin and produced by small farms or individual households still are exposed to the influence of regional environmental impacts and these regional impacts are not widely explored.

Element circulation in ecosystems is a process without cease in-between the main constituents of biosphere soil, water and air, vegetation is the primary recipient of elements from environment. Element transfer into the food chain continues from plants to herbivorous animals and then to carnivorous animals, resulting in food of plant origin and food of animal origin (Figure 1.1.).

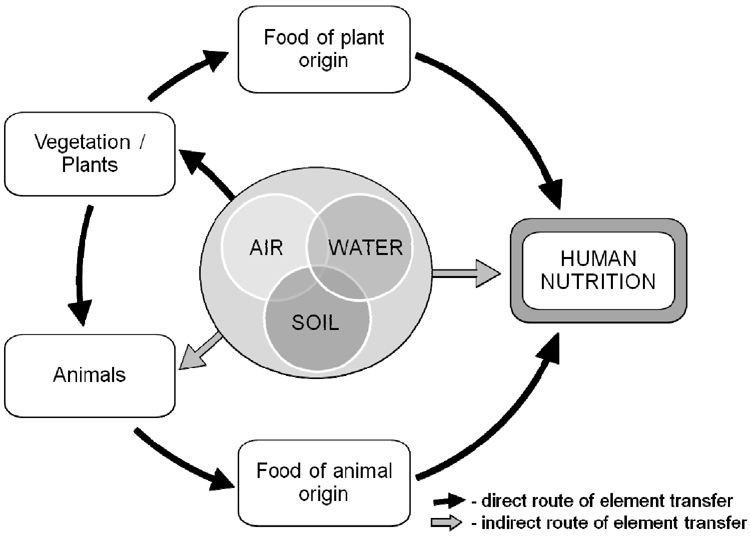

Figure 1.1. Schematic overview of element transfer from environment to human nutrition

If compared with animal origin, plants can be assessed as the major components of ecosystem involved in element transfer into food due to their capacity to take up, store, bioconcentrate and synthesize or resynthesize compounds containing certain elements available in soil and water. As soil is the main environmental provider of elements, the issue of element transfer into food and mineral nutrition can be assessed as well to geological issues (Bowman et al., 2003; Combs, 2005).

Element transfer from environment to food chain via atmospheric deposition generally occurs to a lesser extent and is dependent on the size of particulate matter, as well as chemical composition of particles is important. As smaller particles are, as easier they can be absorbed by plants and inhaled by animals and humans bringing subsequent effects on nutrition and human health (Allen et al., 2001).

Food contamination risk is important issue that is not widely studied in Latvia. Such natural factors as regional characteristics of elements in soil, geochemical anomalies can affect the element content and concentration in regionally derived food. But applied agricultural practice, environmental pollution can be associated with the influence of anthropogenic factors on element transfer from environment to food. The relevance of these factors is within the scope of the thesis.

1.2. Bioavailability of elements in food chain

Bioavailability is the amount of a nutrient that is potentially available for absorption from a matrix (e.g., from soil for crops or from food for humans) and when absorbed, utilizable for metabolic processes in the organism (Welch and Graham, 2005). The investigation of element bioavailability is complicated interdisciplinary issue dependent on chemical, environmental, nutritional, physiological and epidemiological impacts.

Element bioavailability in food chain segment *soil-plant* is tightly associated with the solubility of chemical compounds. Elements can be taken up by plants if they are present in the soil as soluble ions in the forms of organic or inorganic complexes. In addition, not only concentration of ions but also type and chemical character of complexes formed, as well as soil properties such as organic matter content and pH are important in case of plant ability to accumulate potentially toxic elements (Gardea-Torresdey et al., 2005; Inaba and Takenaka, 2005; Peralta-Videa et al., 2009).

Element bioavailability in upper segments of food chain *food-human* is especially important concerning essential elements, as well as potential pollutants and it is dependent not only on chemical properties of compound but also on composition of nutrition and individual health conditions. Total element content does not reveal element bioavailability but provisional assessment can be based on calculated bioavailability extent (usually expressed in %) based on widely done in vivo and in vitro studies (ATSDR, s.a.), that can be applicable for the estimation of food nutritional value and food safety, if total element quantitative content is available.

1.3. Recent studies of micro- and macroelement analysis in Latvia

The assessment of recent research studies of element concentration investigation in Latvia was based on the information available in the main international scientific databases *Scopus*, *Science Direct*, *Springer Link* and *ISI Web of Knowledge* for the time period 2000-2013.

Element content in environmental and biological samples has been studied by G. Čekstere with colleagues who analysed chemical composition of Riga street greenery, particularly, leaves of lime trees and environmental impacts on element content (Čekstere, 2011; Cekstere and Osvalde, 2013; Cekstere and Osvalde, 2010a; Cekstere and Osvalde, 2010b; Cekstere et al., 2008). Air pollution and element content interactions in mosses in Latvia have been studied under the guidance of professor O. Nikodemus and G. Tabors (Nikodemus et al., 2004; Tabors et al., 2004). Finnish scientist R. Salminen with colleagues (2011) also investigated element distribution in terrestrial mosses and organic soil layer in the Eastern Baltic Region. Soil element content has been investigated in details by A. Gilucis (2007) that is described in his doctoral thesis, but metal deposition in forest soils of Latvia and the influencing environmental factors has been studied by other scientists of Latvia (Brumelis et al., 2002; Kasparinskis and Nikodemus, 2012).

Another group of research widely studied involves the analysis of inland surface waters with the aim to detect element and nutrient content (Aldahan et al., 2006; Klavins et al., 2001; Klavins et al., 2000; Kokorite et al., 2010; Stalnacke et al., 2003) and element content of lake sediment investigation (Klavins et al., 2011; Klavins and Vircavs, 2001). But latest studies are tended to bog investigation (Klavins et al., 2009b; Klavins et al., 2003; Silamikele et al., 2011). Prof. M. Kļaviņš with colleagues (2009a) has investigated heavy metal content in fish from lakes in Latvia.

Analytical approach of the analysis of elements by X-ray fluorescence techniques has been investigated under the supervision of professor A. Vīksna (Viksna et al., 2004; Viksna et al., 2001), while P. Sudmalis (2013) in his doctoral thesis was dealing with problems connected with possibilities to detect persistent organic pollutants in environment and biological samples.

Trace metal analysis in water samples from Gulf of Riga and Daugava River estuary have been done (Pohl et al., 2006; Poikane et al., 2005; Yurkovskis, 2004; Yurkovskis and Poikane, 2008). The studies on metal pollution in environment also have been done in Latvia (Kulikova et al., 2003; Muller-Karulis et al., 2003).

Only few studies in Latvia are related to food composition investigations. The information can be found about the studies of nutrient composition of American cranberries in Latvia (Osvalde and Karlsons, 2010) and potatoes (Murniece et al., 2011). F. Dimiņš (2006) in his doctoral thesis investigated composition of honey, including analysis of some element concentration.

Some studies revealing food consumption specifics in Latvia have been done (Melece, 2009; Melece et al., 2008; Pomerleau et al., 2001a; Pomerleau et al., 2001b). However, in these studies only economical aspects were taken into account in the description of food consumption habits in Latvia. The studies of nutrition regarding health issues and interconnection with environmental impacts have been done (Luse et al., 2000; Muceniece et al., 2007; Richardson et al., 2013), but these are specific investigations in the field of environmental and occupational medicine where biosamples such as human blood and hair were analyzed.

Research in the field of agriculture in Latvia concerning food quality improvement are represented by some studies done by I. Alsina with colleagues who have investigated selenium impact on yield quality of lettuce (Alsina et al., 2012; Zegnere and Alsina, 2008).

However, survey of recent studies in Latvia of analysis of micro- and macroelements revealed that there is lack of information about the analysis of the content and concentration of elements in food consumed and produced in Latvia. Therefore, the importance of current research is highly valuable within the interdisciplinary fields of environmental science, chemistry, food science and health sciences.

2. Materials and methods

2.1. Food sampling, sample preparation and pretreatment

2.1.1. Collection of food samples

Locally available food samples were collected over the territory of Latvia in the time period 2009-2013. Food for sampling was selected as follows (methodology after Aras and Ataman, 2006; Ekholm et al., 2007): (I) vegetable products – unprocessed (apples, carrots, onions, potatoes) and processed (cereal meals and cereal mixtures for porridge preparation); (II) animal products – unprocessed (bee products such as honey, pollen and bee bread; hen eggs) and processed (cottage cheese); (III) beverages – unprocessed (apple juice, birch sap) and processed (apple wine). Selection of food samples collected for analyses was based on the length of element transfer from the environment to the food, as well as possible impact factors such as seasonality, agricultural praxis or processing were taking into account. In total more than 500 food samples were analysed within the research.

Collected food samples of plant origin:

- Root vegetables – onions *Allium cepa* (n_s[1]$=98$), carrots *Daucus carota* ($n_s=81$), potatoes *Solanum tuberosum* ($n_s=55$) and potato peel ($n_s=6$) (Figures 2.1., 2.2., 2.3.);
- Leafy vegetables – leafy lettuce *Lactuca sativa* (collected over the territory of Latvia ($n_s=7$) and grown in contaminated soil ($n_s=3$) (Figure 2.4.);
- Fruits – apples *Malus domestica* ($n_s=21$) and apple peel ($n_s=3$) (Figure 2.4.);
- Cereal meals (cereal meals and cereal mixtures for porridge preparation) – cereal mixtures such as 3-grain flakes for porridge preparation ($n_s=10$), rice products ($n_s=10$), wheat products ($n_s=12$) and buckwheat products ($n_s=11$).

At the sampling the origin of samples was identified. Sampling was carried out by selecting 3-5 pieces of fresh vegetables or fruits within every single sample subsequently making mixed samples. Except for porridge cereals which were initially collected in commercial packaging, vegetables of every sample were washed, peeled, crushed with ceramic knife (*Kiocera*) and dried in drying oven (*Labassco*) at temperature 80-105 °C, depending on moisture content in samples. After drying every sample was triturated until the consistence of powder. Until analyses samples were stored in closed disposable plastic bags in dry and dark place in room temperature (Aras and Ataman, 2006).

[1] Here and further n_s – number of samples

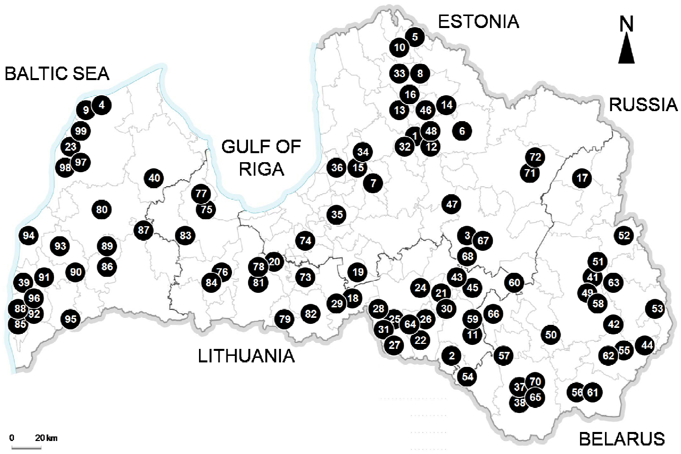

Figure 2.1. Origin of onion (*Allium cepa*) samples[1]

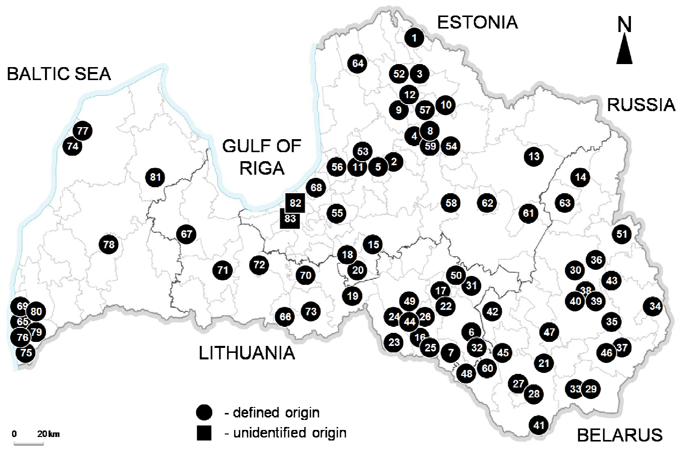

Figure 2.2. Origin of carrot (*Daucus carota*) samples

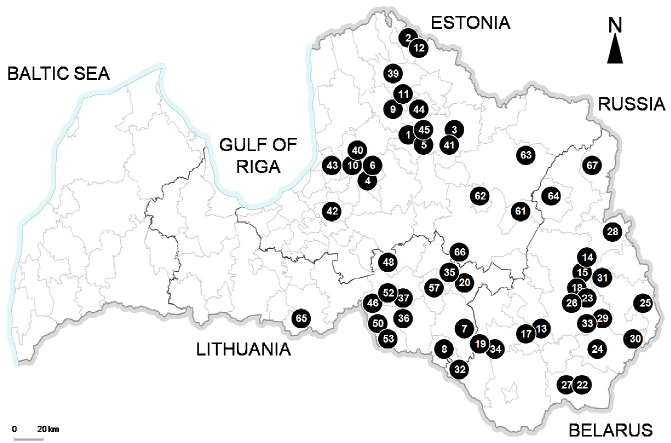

Figure 2.3. Origin of potato (*Solanum tuberosum*) samples

[1] Here and further on schematic maps numbers indicate the number of a sample

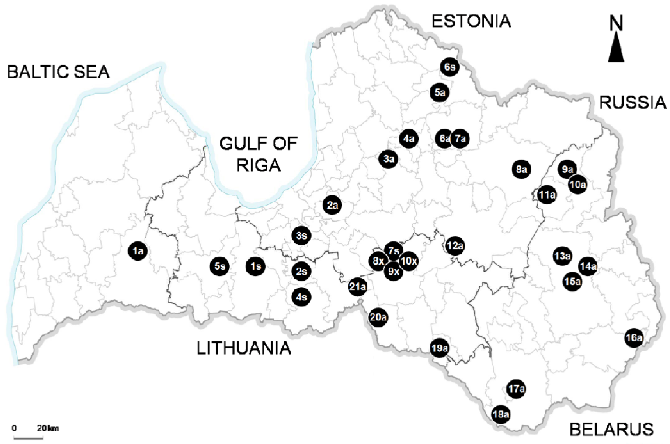

Figure 2.4. Origin of lettuce (*Lactuca sativa*) samples (s, collected samples and x, samples grown in contaminated soil); origin of apple (*Malus domestica*) samples (a)

Collected food samples of animal origin:

- Bee products (Figure 2.5.) – honey (n_s=*80*), pollen (n_s=*5*) and bee bread (n_s=*5*);
- Cottage cheese (n_s=*27*) of different origin (from individual dairy farms and large-scale dairy producers) collected over summer and winter seasons (Figure 2.6.);
- Hen eggs (n_s=*33*) of different origin (from organic farms, domestic farms and large-scale poultry farms), and samples (n_s=*24*) for seasonality impact assessment from an domestic farm with known poultry breeding conditions (at Aizkraukle, Latvia) (Figure 2.7.).

Samples of animal origin such as bee products were stored in closed polypropylene vessels in dark, dry and cool place. Cottage cheese samples were dried in drying oven (Labassco) at 60 °C and stored in hermetically closed disposable bags in freezing camera at -20 °C. Sampled eggs were washed, carefully separated by making yolk, albumen and mixed samples, and stored in hermetically closed disposable bags in freezing camera at -20 °C (Aras and Ataman, 2006).

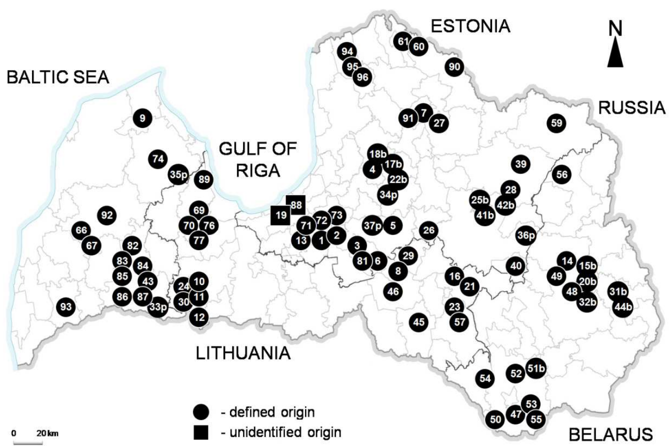

Figure 2.5. Origin of bee products: pollen and bee bread (p), and honey, including samples from organic farms (b)

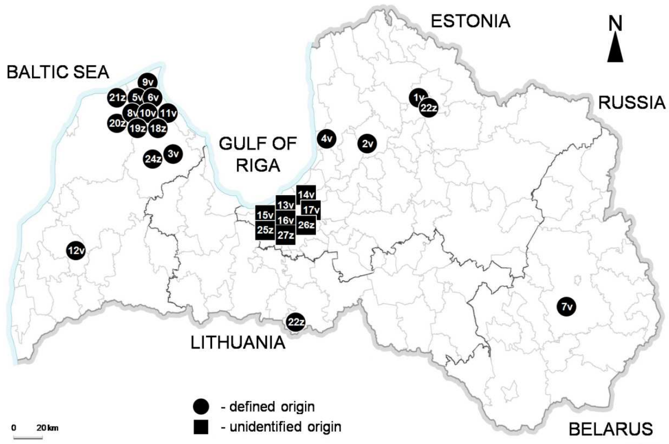

Figure 2.6. Origin of cottage cheese samples collected over summer season (v) and winter season (z)

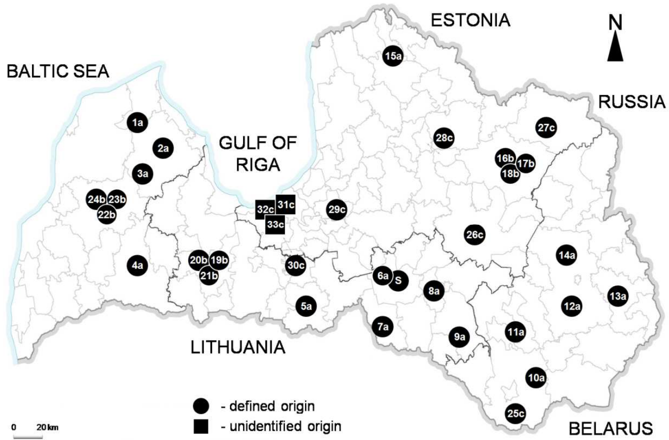

Figure 2.7. Origin of hen eggs from domestic farms (a), organic farms (b), large-scale poultry farms (c) and samples for seasonality detection (s)

Samples of beverages (Figure 2.8.) such as apple juice (n_s*=9*), birch sap (n_s*=10*) and apple wine (n_s*=5*) were kept in closed polypropylene tubes in refrigerator (+4 °C) and were analysed immediately after delivering to the laboratory.

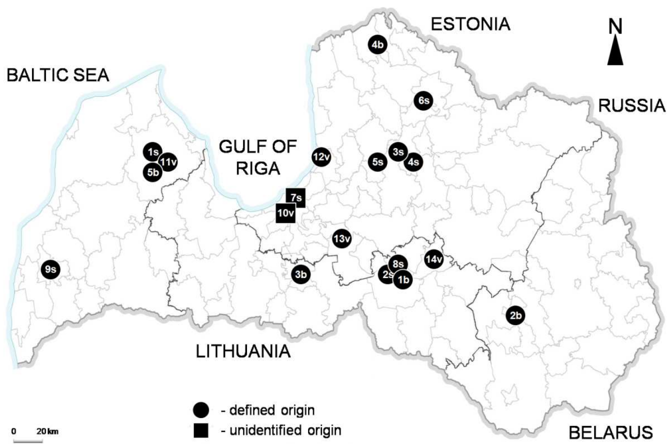

Figure 2.8. Origin of beverage samples: apple juice (s), birch sap (b) and apple wine (v)

2.1.2. Pretreatment of food samples prior quantitative analysis

Pretreatment of food samples prior quantitative analysis involved wet mineralization. In overall, the pretreatment procedure can be described as follows: precise weight of a sample was dissolved in concentrated analytically pure HNO_3 (65 % w/v, *Scharlau*, *Penta* or *Merck*) adding concentrated analytically pure H_2O_2 (30 % w/v, *Merck*). After hold overnight the process was accelerated by heating of solutions on a heating block (*Biosan*) or in a microwave digestion system (*Milestone*) until full sample mineralization. Sample solutions were poured into polypropylene tubes and diluted with deionised water (<0.1 µS/cm, 18 MΩ/cm, *Millipore*) up to a certain volume. Some samples, e.g., beverages, egg samples and honey samples were analysed also without pretreatment which is technically acceptable if total reflection X-ray fluorescence spectrometry is used for element quantification (Klockenkamper, 1997).

2.1.3. Methods of quantitative analysis

For detection of quantitative concentration of micro- and macroelements in food samples such quantitative methods were used: TXRF – total reflection X-ray fluorescence spectrometry (Rontec PicoTAX, *Rontec GmbH*), AAS – atomic absorption spectrometry (AANALYST 200, *Perkin Elmer*) and ICP-MS – inductively coupled plasma mass spectrometry (ELAN DRC-e, *Perkin Elmer*). The most appropriate method was chosen depending on specifics of a sample and spectra of detectable elements. Samples of certified reference materials such as *CS-CR-2 Carrot root powder*, *NCS ZC73017 Apple powder, IAEA-336 Lichen*, *BCR-063R Skim milk powder* and *PT Red wine Chilian* were used for verification of applied analytical methods. Pretreatment of reference samples was done in the same manner as it was described for food samples (mineralization with concentrated HNO_3).

Data describing accuracy and recovery of applied analytical techniques after analysis of *NCS ZC73017 Apple powder* are summarized in Table 2.1.

Table 2.1. Accuracy and recovery of applied analytical methods (TXRF, AAS and ICP-MS) detected by the analysis of certified reference sample *NCS ZC73017 Apple powder*

Element	Certified value of concentration ($\bar{x}$±s), mg/kg	Concentration[1] ($\bar{x}$±s; n_m=5) detected by corresponding analytical technique, mg/kg (Recovery, %)		
		TXRF	AAS	ICP-MS
Ca	490±10	316±9 (65)	480±44 (91)	-
Cd	0.0058±0.0012	-	<0.0100 (-)	0.0051±0.0002 (88)
Co	0.026±0.006	-	0.020±0.010 (94)	0.023±0.001 (89)
Cr	0.30±0.06	<0.76 (-)	0.11±0.02 (36)	0.35±0.03 (117)
Cu	2.50±0.20	2.41±0.15 (96)	2.35±0.24 (94)	2.46±0.10 (98)
Fe	16.0±2.0	14.0±0.5 (88)	9.1±0.6 (57)	-
K	7700±400	5806±173 (75)	7578±49 (98)	-
Mg	390±60	-	322±2 (83)	-
Mn	2.70±0.20	2.54±0.43 (94)	2.60±0.25 (96)	2.65±0.07 (98)
Na	1160±90	-	1173±44 (101)	-
Ni	0.14±0.05	<0.25 (-)	<0.40 (-)	0.11±0.02 (79)
P	660±40	518±57 (79)	-	-
Pb	0.084±0.032	-	0.054±0.011 (64)	0.081±0.037 (96)
Rb	5.00±0.60	4.84±0.18 (97)	-	4.96±0.10 (99)
Sr	6.90±0.50	7.26±0.37 (105)	-	7.04±0.05 (102)
Zn	2.10±0.40	2.04±0.12 (98)	2.08±0.05 (99)	1.97±0.08 (94)

[1] Here and further $\bar{x}$ – mean, s – standard deviation, n_m – number of measurements

2.2. Experimental setup of element transfer study

2.2.1. Preparation of soil samples

In spring of 2011 five soil samples were collected in Latvia, the southwest of Vidzeme Upland (Vecpiebalga region, Taurene rural municipality, vicinity of Lode manor), considering their representativeness for soils in Latvia (Kārkliņš u.c., 2009; Kasparinskis, 2011; Nikodemus, 2011). Soil samples were collected from upper layer (H or Ap horizon, depth 0-20 cm). The type of soil samples was identified as follows: S1 – fen peat soil; S2 – sod-podzolic soil / sandy loam; S3 – sod-podzolic soil / sand; S4 – sod-podzolic soil / loamy sand; S5 – sod-podzolic soil / sandy clay loam (FAO, 2006; Kārkliņš u.c., 2009; Nikodemus, 2011; Noteikumi 804, 2005). Soil texture and other characteristic properties such as pH_{H2O} un pH_{KCl}, soil organic matter expressed as content of humic substances, cation base saturation, total element content were defined in laboratory using standard methodology (FAO, 2006; Pansu and Gautheyrou, 2006).

To model the transfer of metals from soil to plants and for the bioavailability assessment soil contamination was applied treating soil subsamples with corresponding metal salt solutions:

a) Soil monocontamination using copper sulphate pentahydrate $CuSO_4 \times 5H_2O$ solution at five target Cu concentrations (40, 70, 100, 130 and 200 mg/kg);

b) Soil multielement contamination using such soluble salts of metals as cadmium acetate dihydrate $Cd(CH_3COO)_2 \times 2H_2O$, copper sulphate pentahydrate $CuSO_4 \times 5H_2O$, lead (II) nitrate $Pb(NO_3)_2$ and zinc sulphate heptahydrate $ZnSO_4 \times 7H_2O$ at certain target concentrations of elements (6 mg/kg Cd, 130 mg/kg Cu, 750 mg/kg Pb and 300 mg/kg Zn).

Soil contamination procedure was applied as described in literature, i.e., calculated amount of certain contaminant was diluted in water and sprayed over the soil piles followed by complete soil homogenization (mechanical mixing) (Alexander et al., 2006; Inaba and Takenaka, 2005). In addition, the half of each portion of contaminated soils and also control soil samples were saturated with the solution of humic substances (3 g/kg; ombrotrophic bog peat: C 54,35 %, H 2,36 %, N 1,26 %, Mw 4 500 – 12 000 dal). Two weeks after contamination repeated mechanical homogenization was done. Then contaminated and control soil samples were poured into pots and used for experimental cultivation of selected food crop species: radish *Raphanus sativus* L. 'Saxa 2', leafy lettuce *Lactuca sativa* L. 'Grand Rapids' and dill *Anethum graveolens* L. 'Mammut'. The study was done during the summer season of 2011 in the central part of Latvia, in a field area at Aizkraukle, Latvia.

2.2.2. Element speciation analysis

Speciation analysis of studied soil samples was performed to detect bioavailability of elements in food chain segment *soil-plant*. Speciation analysis was done by fractioning by extracting 5 fractions of compounds: 1) fraction of water soluble metal forms; 2) fraction of acid soluble forms of metals; 3) fraction of reduced forms of metals; 4) fraction of organic bound forms of metals; 5) fraction of insoluble forms of metals, mostly bound with sulphides (Arthur et al., 2007; Malandrino et al., 2011; Tessier et al., 1979). Consequent extraction step by step was performed as shown in Figure 2.9.

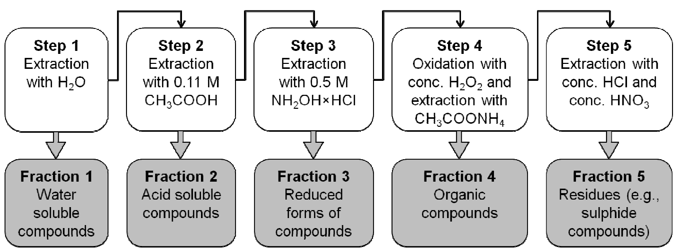

Figure 2.9. Schematic overview of fractioning analysis

To assess the element bioavailability in food chain segment soil-human fractioning was done by extracting 3 fractions of compounds: 1) fraction of water soluble metal forms; 2) fraction of acid soluble forms of metals; 3) fraction of reduced forms of metals (Arthur et al., 2007; Malandrino et al., 2011; Tessier et al., 1979).

Sample solutions of every fraction were analysed to quantify element concentration with atomic absorption spectrometry and inductively coupled plasma mass spectrometry.

3. Results and discussion

3.1. Impact of conditions influencing element concentration in analysed food samples

3.1.1. Impact of seasonality on element concentration in food

Impact of seasonality was assessed taking into account detected element concentration in cottage cheese samples and hen egg samples.

Cottage cheese. Samples of cottage cheese were collected over two seasons, spring/summer and autumn/winter. Concentration of macroelements, especially Ca and K, was detected higher in samples from winter season (Figure 3.1.) that can be associated with seasonal distinctions in dairy cattle breeding conditions and feeding.

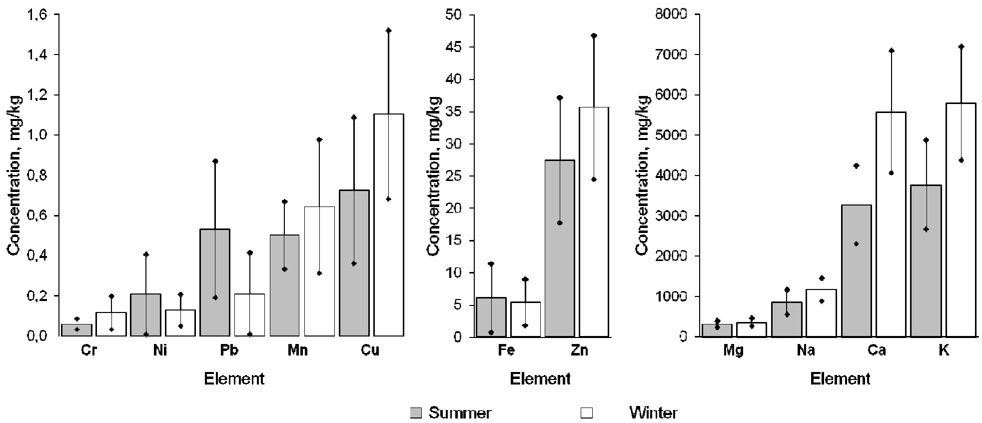

Figure 3.1. Average concentration of elements in cottage cheese depending on season

Higher concentration of microelements (e.g., Cr, Mn, Cu, Zn) can also be referred to samples collected in winter season. However, some elements such as Fe, Ni and Pb are detectable in higher concentration in samples from summer season. That can be associated with influence of environmental factors such as airborne particle deposition on grassland near roads or railway, e.g., particles containing Pb and Ni can become contaminants of food chain. Seasonality of dairy cattle breeding differs especially due to different feeding regime – feed used in winter is more enriched with vitamins, micro- and macroelements but in summer cattle can be fed on grassland and is likely exposed to possible environmental pollution impact.

Hen eggs. Hen egg samples for seasonality assessment were collected each month from April, 2011 to March, 2012 in a courtyard farm at Aizkraukle (Latvia) with known poultry breeding conditions: in spring and summer season birds were kept in free-range conditions outdoors with possibility to find feed and as additional feed grass, vegetables and grains were fed; in autumn and winter season birds were kept in a shelter and fed with ready-to-use combined poultry feed and grains. Whole egg, egg yolk and egg albumen samples were analysed. In overall, it was detected that higher concentration of microelements (e.g., Cu, Fe, Zn) is detectable in egg samples collected in summer or spring season (Figure 3.2.). The exception is Se which can be found in higher concentration in samples collected in winter. In addition, in egg yolk Se was quantified only in samples from winter season that can be associated with impact of seasonality as soils of Latvia contain very low Se content (Zegnere and Alsina, 2008). This can explain lowered Se concentration in egg samples from summer and spring season when birds are fed outdoors and consume soil, mesobiota and plants.

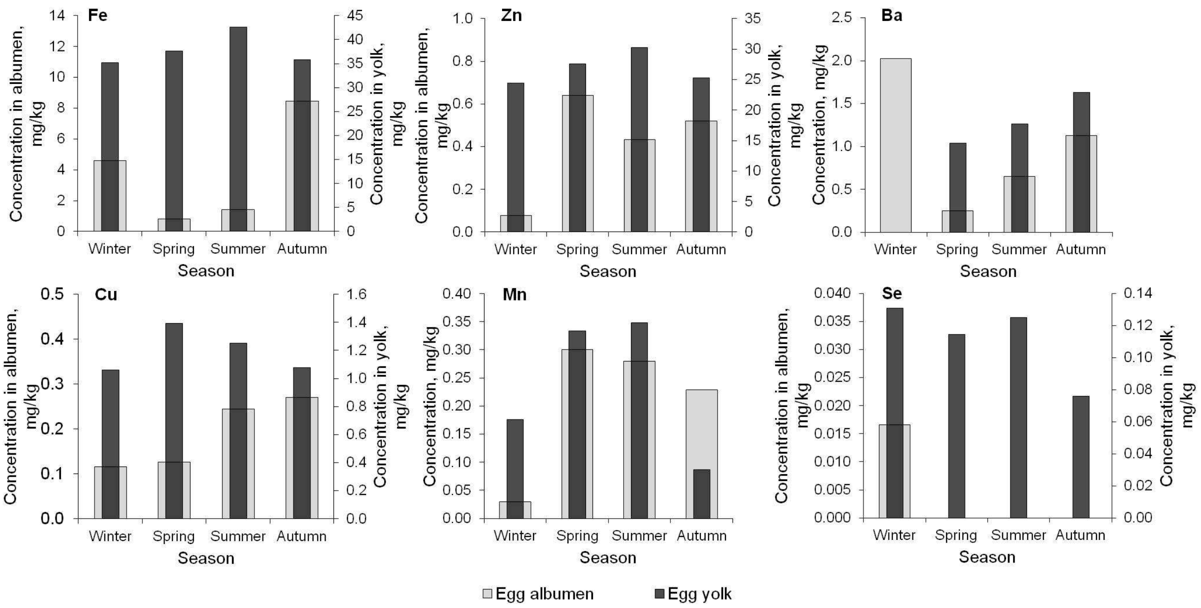

Figure 3.2. Seasonal differences in concentration of Fe, Zn, Cu, Ba, Mn and Se in hen egg samples

Similarly as found for cottage cheese sample also in egg samples higher concentration of macroelements can be attributed to the samples derived in winter season which is connected with poultry breeding and feeding seasonal distinctions.

3.1.2. Impact of botanical origin on element concentration in food

It was possible to assess the impact of botanical origin on element concentration in food after the analysis if honey samples. Honey samples were divided in 7 groups according to their botanical origin: 1) polyfloral not defined honey ($n_s=33$); 2) heather and forest blossom honey ($n_s=16$); 3) rape and spring blossom honey ($n_s=5$); 4) buckwheat and clover species honey ($n_s=9$); 5) linden honey ($n_s=6$); 6) meadows blossom honey ($n_s=8$) and 7) commercially manufactured honey mixtures with unknown botanical origin ($n_s=3$).

To detect also the impact of pollution attention was paid in detection of potentially toxic elements. The analysis of honey samples collected in Latvia revealed that in overall potentially toxic elements can be quantified in the following sequence: Zn >Al >Cu >Ni >Cr >Pb >Co >Cd >As (based on mean results, $n_s=80$). The overall list of metals detected leads to think of possible contamination at storage and processing as, e.g., Al, Cu, Ni and Zn are the ordinary constituents of metallic household and kitchen equipment (Joudisius ir Simoneliene, 2009).

Taking into account the botanical origin of honey collected in Latvia significant differences in concentration of potentially toxic metals were detected among the species. According to mean values of quantified potentially toxic metals possible honey contamination by honey type can be ranged as follows (from higher to lower element content): commercially manufactured honey mixtures with unknown botanical origin >heather / forest blossom honey >polyfloral honey >meadows blossom honey >linden honey >buckwheat / clover honey >rape

/ spring blossom honey. Detected concentration of some microelements is figured out in Figure 3.3.

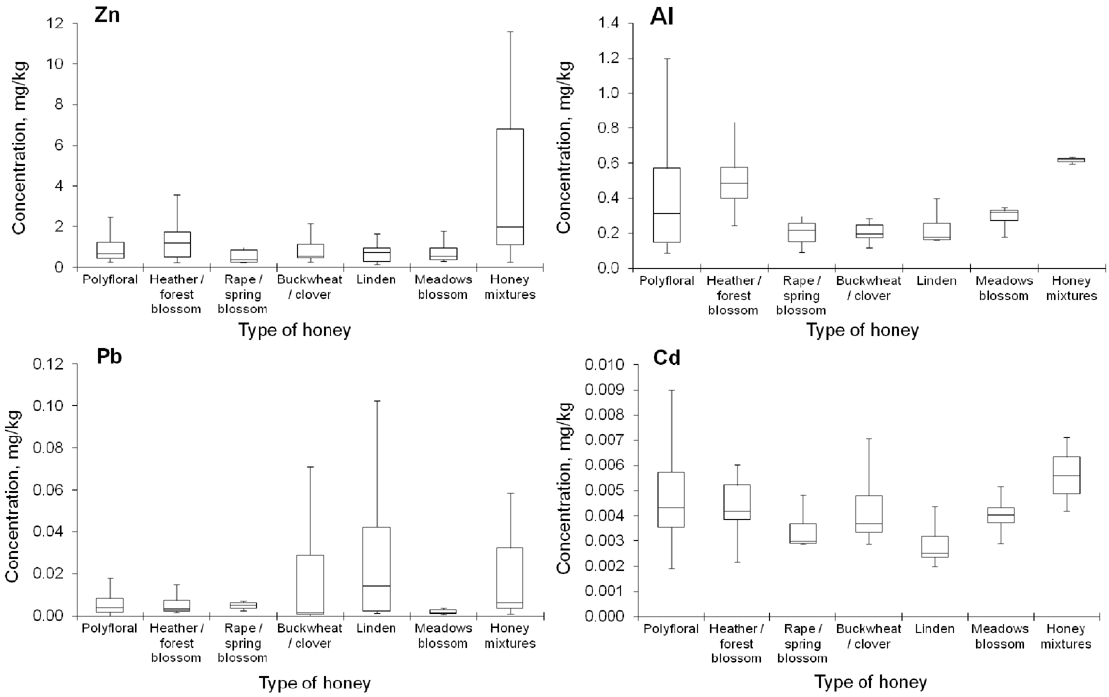

Figure 3.3. Concentration of Zn, Al, Pb and Cd in honey samples of different botanical origin

Impact of botanical origin on element concentration can be connected with environmental factors. For example, such elements as As and Pb are found in higher concentration in linden blossom honey that knowing that linden trees are common part of urban greenery and therefore can be exposed to contamination by dust and airborne particles from roads, railroad and exhaust fumes from transport and industry. But rape or buckwheat blossoms and, respectively, element content in honey, can be affected by applied agriculture practice, use of agrochemicals and fertilizers. However, higher detected concentration of microelements in honey mixtures of unknown origin can be associated with inappropriate use of equipment (e.g., containing metal alloys) for honey preparation.

3.1.3. Impact of agricultural practice on concentration of elements in food

The impact of agricultural practice on concentration of elements in food was assessed analysing data of root vegetables, cottage cheese and hen eggs.

Root vegetables. Knowing origin and applied agricultural practice in growth of root vegetable samples onions and carrots, it was possible to detect differences in element concentration for vegetables grown under the different agricultural conditions. Statistical analysis of the data by using Fisher's criteria and appropriate t-tests allowed comparison of vegetable samples grown in different agricultural conditions, i.e., divided by subgroups of samples grown in farmlands versus samples grown in allotment gardens. Regarding the analysis of onion bulbs, significant differences between the mentioned subgroups were detected for several microelements. Sr, Ni, Cd, Se and Co were the elements the amounts of which were significantly higher in onions grown in farmlands, while Rb was the only single element which was detected in higher amounts in onions grown in allotment gardens. But the analysis of subgroups of carrots revealed a significant difference only for the three microelements: carrot samples grown in allotment gardens were significantly richer in Zn, Mn and Rb. These coherences purport the fact that farmlands are more likely influenced by possible contamination sources, mainly such as agrochemical impact that can result in increased amounts of potentially toxic metals in vegetables, but the microelement analysis of vegetables grown in rural allotment gardens may reveal possible influence of geochemical background.

Farmlands can be affected by agricultural activities such as the use of fertilizers and pesticides much more intensively than allotment gardens, while private allotment gardens most frequently are small and located close to the roadsides and urban areas, as well as can be situated within cities and towns near industrial territories or on recultivated contaminated lands that can negatively influence air, soil and water conditions in gardens. Within the current research elevated concentration of potentially toxic elements was not detected for samples derived in allotment gardens; that is associated with sample collection in rural areas where risk of contamination is likely to be less.

Hen eggs. Data of hen egg analysis revealed differences among element concentration in samples derived from organic farms, domestic farms and large-scale poultry farms. For example, in egg samples from organic farms higher concentration of Cu, Fe, Mn, Pb and Zn (Figure 3.4). But Pb was not detected in any of samples derived from poultry farms.

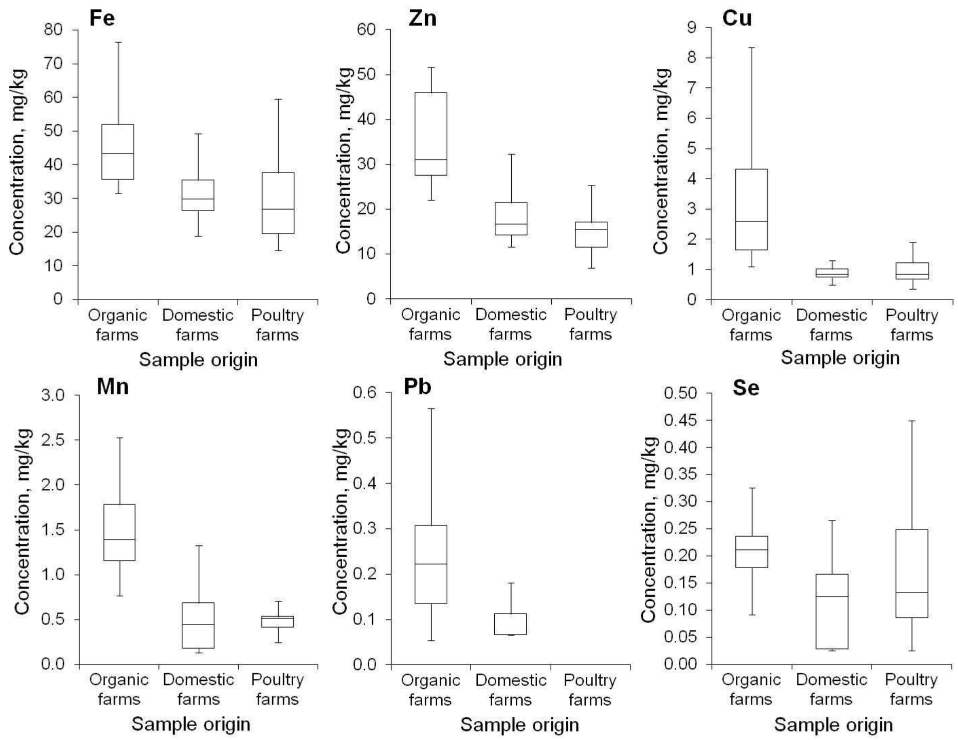

Figure 3.4. Concentration of Fe, Zn, Cu, Mn, Pb and Se detected in hen egg samples from different poultry housing types

In all cases the highest mean values of elements were determined for egg samples derived from organic farms, while element content of eggs from domestic farms and poultry farms was lower and relatively similar. As it is known that organic farming is strictly controlled and use of chemicals is restricted within this agricultural practice (EC Regulation 889, 2008), the results detected in the present study could not be associated with possible avian feed pollution of agricultural or veterinary chemicals, but might be connected with the impact of environmental factors on element content of egg samples, likely in relation to potential environmental contaminants (e.g., Cu, Pb, Zn).

3.2. Assessment of element bioavailability

3.2.1. Characteristics of soil samples

To assess element bioavailability the experiment with selected food crops was done using five different soil samples: S1 – fen peat soil; S2 – sod-podzolic soil / sandy loam; S3 – sod-podzolic soil / sand; S4 – sod-podzolic soil / loamy sand; S5 – sod-podzolic soil / sandy clay loam (FAO, 2006; Kārkliņš u.c., 2009; Nikodemus, 2011; Noteikumi 804, 2005).

Higher pH was detected for soil S1 (pH_{H2O} 5.31 / pH_{KCl} 5.06), but the lowest for S5 (pH_{H2O} 4.61 / pH_{KCl} 5.11). Content of organic matter varied from 2.9 % to 4.2 % in mineral soil samples (S2-S5), but the lowest was detected for fen peat soil (S1) – 29.3 %. Cation exchange capacity (CEC) or cation base saturation (CBS) in great extent is dependent on soil pH. CBS in mineralsoils (S2-S5) detected 3.13-8.17 cmol/kg but in fen peat soil (S1) – 142.29 cmol/kg. Ca^{2+} content was 70.9 % of CBS for sod-podzolic soil / sandy clay loam (S5), but for fen peat soil (S1) 87.5 % of CBS, that indicates that selected soil samples are of high fertility and are applicable for crop growing (Hodges, s.a.). Total element content before soil contamination is summarized in Table 3.1.

Table 3.1. Concentration of elements in studied soil samples prior contamination

Element	Soil sample				
	S1	S2	S3	S4	S5
	Element concentration ($\bar{x}$±*s*; n_m=3), g/kg				
Ca	24.88±0.24	0.98±0.03	0.60±0.03	1.18±0.09	1.03±0.07
Fe	20.60±0.22	10.94±0.62	3.50±0.24	5.25±0.17	14.21±0.54
K	0.89±0.02	1.87±0.09	0.52±0.06	0.84±0.02	2.12±0.15
Mg	1.93±0.08	1.83±0.08	0.61±0.02	0.97±0.03	2.36±0.11
	Element concentration ($\bar{x}$±*s*; n_m=3), mg/kg				
Cd	0.45±0.05	0.10±0.01	0.11±0.10	0.17±0.08	0.08±0.02
Co	3.49±0.75	4.45±0.15	1.58±0.03	2.60±0.20	6.74±0.65
Cr	15.79±0.89	15.32±0.11	5.10±0.14	6.46±0.23	19.45±1.07
Cu	13.96±2.27	6.77±0.25	2.32±0.21	10.30±0.56	8.24±0.32
Na	66.1±13.2	61.0±34.6	38.3±18.7	57.0±15.6	56.9±15.1
Ni	10.42±2.16	8.20±0.39	2.81±0.27	4.07±0.35	10.66±0.44
Mn	241.7±16.6	194.1±7.0	117.8±10.7	395.7±26.1	401.0±31.6
Pb	14.66±3.16	6.29±1.35	3.22±1.70	5.86±1.49	8.73±0.78
Zn	28.67±6.39	27.57±2.61	16.46±0.55	60.50±2.97	35.36±0.84

Sod-podzolic soil / sandy clay loam (S5) contained higher concentration of Cr, Ni and Pb compared with other soil samples that can be associated with element adsorption on clay particles as this sample is richer with clay. Significant correlation (*r>0.8*) was detected for such element pairs: Zn with Ca, Co, Cr, Fe, K, Ni, Mg; K with Cu, Pb; Ca with Co, Mn.

After soil contamination with $CuSO_4 \times 5H_2O$ solution in different target concentration (40, 70, 100, 130 un 200 mg/kg) or with Cd, Cu, Pb and Zn salt solution mixture the hyperaccumulation of some elements was observed, especially in fen peat soil (S1) (Table 3.2.).

Table 3.2. Element concentration in soil samples after contamination with Cd, Cu, Pb and Zm salt mixture

Element	Target concentration of element, mg/kg	Actual concentration of element in soil sample ($\bar{x}$±*s*; n_m=3), mg/kg				
		S1	S2	S3	S4	S5
Cd	6	17±2	5±1	5±1	6±1	6±1
Cu	130	425±35	147±1	148±8	150±4	165±6
Pb	750	2232±199	737±49	761±48	751±10	865±29
Zn	300	880±73	296±53	345±23	359±9	349±11

Obtained data indicates tight association between soil contamination level and organic matter content, as well the importance of soil texture.

3.2.2. Accumulation of elements in experimentally grown vegetables

In contaminated soil samples such food crops as leafy lettuce *Lactuca sativa*, dill *Anethum graveolens* and radish *Raphanus sativus* were grown. To detect the element transfer and accumulation intensity from soil to plants the transfer factor (TF) was calculated. Higher TH values (>10) were gained for Zn transfer in mineral soils (S1-S4) to lettuce, while lower TF is attributed to soil with higher content of organic matter, e.g., fen peat soil (S1). Addition of humic substances diminishes element transfer from soil to plants as well (Table 3.3).

Table 3.3. Transfer factors (TF) for lettuce and radish samples grown in soils contaminated with salt mixture containing Cd, Cu, Pb and Zn

Element	Food crop	TF in corresponding soil sample without (S) or with (S_H) addition of humic substances									
		S1	S2	S3	S4	S5	$S1_H$	$S2_H$	$S3_H$	$S4_H$	$S5_H$
Cd	Lettuce	0.11	1.84	1.52	1.06	0.63	0.09	0.41	0.53	0.35	0.50
	Radish	-	-	-	-	-	0.06	0.43	0.31	0.18	0.35
Cu	Lettuce	0.02	0.49	1.55	0.82	0.04	0.02	0.11	0.07	0.07	0.08
	Radish	-	-	-	-	-	0.02	0.18	0.33	0.16	0.06
Pb	Lettuce	0.005	0.28	0.64	0.59	0.03	0.003	0.09	0.07	0.02	0.04
	Radish	-	-	-	-	-	0.005	0.09	0.16	0.04	0.09
Zn	Lettuce	0.48	10.47	11.95	11.43	1.51	0.38	1.29	1.90	1.67	1.21
	Radish	-	-	-	-	-	0.28	3.48	3.31	2.21	2.12

Among elements the lowest TF were calculated for lead. In overall higher TF values can be attributed to element transfer from soil to plant roots than to foliage. Data revealed that multielement contamination in soil increases the intensity of element accumulation in plants, e.g., interaction among Cu, Cd, Pb and Zn can intensify copper accumulation in lettuce for 31.4 %, if compared with monocontamination. Addition of humic substances can diminish element accumulation for 90 % in leafy vegetables (e.g., lettuce) and for about 25 % in root vegetables (e.g., radish).

3.2.3. Element bioavailability in food chain segment "soil-plant"

Element bioavailability assessment was done after the sample fractioning analysis. In overall it was detected that differences in element concentration among the fractions can be comparable for fen peat soil (S1) and mineral soil samples (S2-S5). Higher amount of elements is bound in the fraction of reduced forms of compounds in soils S1 and S4, 41 % and 35 %, respectively, soil samples richer in organic matter (Figure 3.5.).

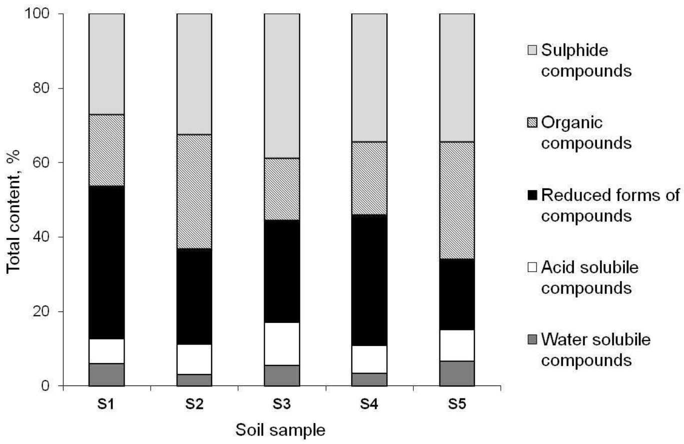

Figure 3.5. Distribution of total element content by fractions in analysed soil samples (S1 – fen peat soil; S2 – sod-podzolic soil / sandy loam; S3 – sod-podzolic soil / sand; S4 – sod-podzolic soil / loamy sand; S5 – sod-podzolic soil / sandy clay loam)

Greater part of elements incorporated in sulphide compounds refers to soil S3 (39 %). Element incorporation in the fraction of water soluble compounds forms the smallest part (7-12 %). It indicates that only small amount of elements from total element content in soil is bioavailable for plants, but greater part of elements is incorporated in fractions of compounds with low bioavailability. By quantifying 13 elements (As, Cd, Ce, Co, Cs, Cu, La, Ni, Pb, Rb, Sr, V and Zn) in each of fractions the comparison of element bioavailability depending on soil type was done.

3.2.4. Element bioavailability in food chain segment "plant-human" after the case study with lettuce

Element bioavailability assessment in food chain segment plant-human is complicated issue affected by various factors – environmental, chemical, biochemical and individual for organism. Therefore only provisional assessment based on revealed data and extrapolations is discussed here. Taking into account the importance of element solubility on the bioavailability, the fractioning analysis of lettuce samples in three fractions were done: 1) fraction of water soluble compounds; 2) fraction of acid soluble compounds; 3) fraction of reduced forms of compounds. In each fraction 14 elements were quantified (As, Ba, Cd, Ce, Co, Cu, La, Mn, Ni, Pb, Rb, Se, Sr and Zn). In overall it was detected that elements in great extent are bound in fraction of water soluble compounds (47 %) and in fraction of reduced forms of compounds (37 %), while in acid soluble compounds element incorporation was the lowest (15 %). These findings are quite different from those detected at soil fractioning. Distribution of individual elements reveals that lower bioavailability can be attributed to As, Cd and Sr as their incorporation fraction of water soluble compounds is the lowest (Figure 3.6.).

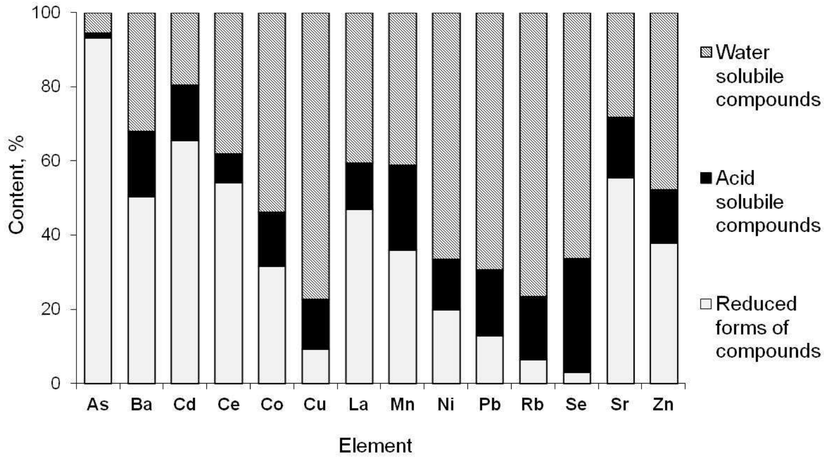

Figure 3.6. Element distribution by fractions in lettuce samples

In fraction of water soluble compounds more are bound (>50 %) such elements as Co, Cu, Ni, Pb, Rb and Se, that is in favour for essential elements but may also better bioavailability of potentially toxic elements which can result in consumer contamination risk.

Taking into account these findings in provisional element transfer intensity it can be estimated that for largest part of elements transfer from soil into food plants is fairly low. However, by increase of element concentration soil also element concentration in grown crops can increase inducing possible risk for consumer. Current findings allow rapid theoretical estimation of food chain contamination risk by elements of concern based on matrix (i.e., soil) properties.

Conclusions

- Obtained results revealed recognizable influence of several factors (impact of seasonal, site-specific, botanical factors, applied agricultural practice, processing) on the concentration of elements in analysed food samples but pattern of element transfer is not uniformed and depends on composition of foodstuff or foodstuff group in association with environmental conditions within the formation or production process of foodstuff.
- Assessment of natural environmental conditions such as seasonality revealed differences in element concentration for analysed food samples of animal origin indicating tight linkage with the agricultural practice applied in production of food. Indirectly this impact can be associated also with influence of environmental pollution.
- Assessment of anthropogenic impact factors such as applied agricultural practice revealed distinctions in the element (e.g., Cd, Co, Na, Ni, Se) composition among the species of vegetables grown under different agricultural conditions that is linked to various tendencies and intensity in use of agrochemicals and fertilizers; however, it is strongly dependent on the crop species.
- It is important to emphasize detected differences between organically and conventionally derived foodstuffs that indicate the impact of element composition from environment as well as of natural origin such as geochemical background and of anthropogenic origin as environmental pollution. Conditions of organic food production should be explored for the recognition of possible impact of environmental conditions that can affect food composition.
- Comparison of element content in edible and non-edible parts of vegetables revealed that several microelements, including potentially toxic elements (e.g., As, Co, Cr, Pb) are tended to remain in peel while other elements (e.g., Cd, Se, Zn) are taken up by crop tissues and therefore may become food chain contaminants more easily.
- Geographical impact on concentration of elements in food cannot be assessed unambiguously as detected distribution of elements, e.g., in honey samples, revealed some geographical differences, but strong correlation with characteristic environmental conditions was not identified. The impact of site-specific factors taking into account the environmental specifics of Latvia could be assessed as more relevant, however, further more specific studies should be implemented.
- Experiment of element transfer and bioavailability assessment in food chain segment *soil-plant* ascertained that the uptake and accumulation of metals and metalloids by food crops is significantly affected by soil organic matter content among the other soil properties. Soil texture can be assessed as another important factor that can affect element transfer from soil to plants as well as the selective ability of plant species to accumulate some chemical elements can be accented. The properties of organic substances to bind heavy metals in stable complexes can be developed as a prospective trend for practical use of application of humic substances on metal contaminated soils, e.g., in agricultural lands.
- Assessment of element bioavailability data in food chain revealed that only a small part of elements can be available up the food chain from soil to upper segments *soil-plant-human*. However, cumulative accumulation can occur if element concentration is the environment is high. It can lead to subsequent risk for humans as consumers on the highest segment of food chain. Detected tendencies of element bioavailability dependent on soil composition can be useful tool for risk analysis.
- Influence of both natural and anthropogenic environmental conditions may cause food contamination with potentially toxic elements that is the issue of high importance

regarding consumers' safety. Therefore, regional monitoring of food composition is preferable, especially regarding domestic production. In overall, quantitative analysis of food samples revealed the significance of food research within the context of environmental science, chemistry and health sciences, and this investigation has to be developed in the future in larger scale.

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