UNIVERSITY OF LATVIA
FACULTY OF GEOGRAPHY AND EARTH SCIENCES
DEPARTMENT OF ENVIRONMENTAL SCIENCE

Zane Vincēviča-Gaile

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

VIDES APSTĀKĻU IETEKME UZ MIKRO- UN MAKROELEMENTU SATURU PĀRTIKAS PRODUKTOS LATVIJĀ

Doctoral Thesis

Rīga, 2014

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Scientific supervisor:
Professor, *Dr. habil. chem.* Māris Kļaviņš

Submitted for the degree of Doctor of Chemistry in Environmental Science
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Supervisor: professor, *Dr. habil. chem.* **Māris Kļaviņš**

Reviewers:
professor, *Dr. habil. chem.* **Andris Zicmanis**, University of Latvia, Latvia;
professor, *Dr.* **Stanley Lutts**, Catholic University of Leuven, Belgium;
Dr. chem. **Vadims Bartkevičs**, Institute of Food Safety, Animal Health and Environment BIOR, Latvia.

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Chairman of the Doctoral Committee:
prof., *Dr. biol.* **Viesturs Melecis**

Secretary of the Doctoral Committee:
assoc. prof., *Dr. biol.* **Gunta Spriņģe**

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ABBREVIATIONS AND GLOSSARY

AAS	atomic absorption spectrometry
CEC	cation exchange capacity
DW; WW	dry weight; wet weight
EAR	estimated average requirement: *a nutrient intake value that is estimated to meet the requirement of half of the healthy individuals in a life stage and gender group* (Duffus et al., 2007)
FAAS	flame atomic absorption spectrometry
GFAAS	graphite furnace atomic absorption spectrometry
ICP-AES; ICP-OES	inductively coupled plasma atomic emission spectrometry; inductively coupled plasma optical emission spectrometry
ICP-MS	inductively coupled plasma mass spectrometry
LD	lethal dose
LOD	limit of detection
MRL	minimal risk level
PTFE/TFM®	polytetrafluoroethylene/TFM® (teflon)
RDA	recommended dietary allowance: *the dietary intake level that is sufficient to meet the nutrient requirements of nearly all healthy individuals in a life stage and gender group* (Duffus et al., 2007)
RNI	reference nutrient intake
SUL	safe upper level
TXRF	total reflection X-ray fluorescence spectrometry
UL	tolerable upper intake level: *the highest level of nutrient intake that is likely to pose no risk of adverse health effects for almost all individuals in the general population* (Duffus et al., 2007)

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, Cd, Hg, Pb may occur. The aim of the doctoral thesis "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.

ANOTĀCIJA

Bez vitāli svarīgo mikro- un makroelementu ieneses pārtikā no vides (augsnes, ūdens un gaisa) ir iespējams arī barības ķēdes, t. sk., pārtikas piesārņojums ar toksiskiem vai potenciāli toksiskiem elementiem, piemēram, As, Cd, Hg, Pb. Promocijas darba mērķa ietvaros tika veikta Latvijā iegūtu pārtikas produktu paraugu mikro- un makroelementu sastāva kvantitatīvā analīze, lai noskaidrotu vides apstākļu ietekmi uz elementu koncentrāciju un ieneses ceļiem pārtikā. Papildus, lai vērtētu elementu biopieejamību barības ķēdē, tika veikta eksperimentāla pārtikas kultūraugu audzēšana mākslīgi piesārņotā augsnē. Iegūtie dati liecina par vairāku dabiskas un antropogēnas izcelsmes vides apstākļu, piemēram, sezonalitātes, botāniskās izcelsmes, vietas specifisku apstākļu, lauksaimniecības prakses, pārtikas pārstrādes, ietekmi uz elementu koncentrāciju pārtikā.

Atslēgvārdi: mikro- un makroelementi, kvantitatīvā analīze, elementu pārnese, pārtikas sastāvs, vide, Latvija.

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, Cd, Cr, 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 a great importance from the public healthcare perspective as support to regional or site-specific food production, especially considering growing role of biological and domestic farming as well as for further development of food quality control system.

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

1. 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.
2. Development of interdisciplinary approach for the investigation of natural and anthropogenic factor impacts on food composition.
3. Comparative evaluation of the accumulation processes of elements in foodstuffs derived in different conditions, e.g., biological farming versus conventional farming etc.
4. 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*[1] 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*[2] 1: 43-49.

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[1] *Peer reviewed journal, indexed by the databases SCOPUS, EBSCO, CSA-ProQuest, VINITI; ISSN:1691-5208 (print version).*

[2] *Peer reviewed proceedings, indexed by the databases AGRIS, CAB ABSTRACTS, CABI full text; EBSCO Academic Search Complete, Thomson Reuters ISI Web of Science, SCOPUS; ISSN:1691-4031.*

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*[1] 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 & Legislation*[2] 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*[3] 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*[4] 10: 21-24.
7. **Vincevica-Gaile, Z.**, Klavins, M. (2012) Root vegetables from Latvia: Quantitative analysis of potentially toxic elements. *Research for Rural Development*[5] 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*[6]. 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*[7] 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*[8]. 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*[9]. WSEAS Press: Meloneras, 356 p., 169-173.

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[1] *Peer reviewed journal, imprint of SPRINGER (IF=2.076 (2012)), indexed by the databases SpringerLink, SCOPUS; ISSN:0269-4042 (print version), ISSN:1573-2983 (electronic version).*

[2] *Peer reviewed proceedings, indexed by the databases SCOPUS, EBSCO, Thomson Reuters ISI Web of Knowledge, CrossRef Database, CrossRef Cited By Linking, ProQuest, Scirus, GeoRef; ISBN:978-619-7105-04-9, ISSN:1314-2704.*

[3] *Peer reviewed journal, imprint of ELSEVIER, indexed by the database Science Direct, SCOPUS; ISSN:2212-6708.*

[4] *Peer reviewed journal, indexed by the databases SCOPUS, EBSCO, CSA-ProQuest, VINITI; ISSN:1691-5208 (print version).*

[5] *Peer reviewed proceedings, indexed by the databases AGRIS, CAB ABSTRACTS, CABI full text; EBSCO Academic Search Complete, Thomson Reuters Web of Science, SCOPUS; ISSN:1691-4031.*

[6] *Peer reviewed proceedings, indexed by the databases Thomson Reuters ISI Web of Knowledge, SCOPUS, British Library, EBSCO etc.; ISSN:2227-4359, ISBN:978-1-61804-088-6.*

[7] *Peer reviewed journal, indexed by the databases SCOPUS, EBSCO, CSA-ProQuest, VINITI; ISSN:1691-5208 (print version).*

[8] *Edited book; ISBN:978-1-84564-652-3, eISBN: 978-1-84564-653-0.*

[9] *Peer reviewed proceedings, indexed by the databases Thomson Reuters ISI Web of Knowledge, SCOPUS, British Library, EBSCO etc.; ISBN:978-960-474-287-5.*

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*[1] 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,

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[1] *Peer reviewed journal, indexed by the databases CAB Abstracts, AGRIS; ISSN:1407-4427 (print version), ISSN:2255-8535 (electronic version).*

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$_2$S 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 at 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 of elements in human health and diet – interconnection with environment

Basic elements (C, H, N and O) form up to 97 % of the matter of living systems. Content of these elements in the tissues and organs of human body is estimated as follows: O (61 %) >C (23 %) >H (10 %) >N (2.6 %), respectively, in average of human body weight. Other elements can be subdivided in macro- and microelements. 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 traits of the lifestyle, diet and habitation environment of an individual (Aras and Ataman, 2006; Baltes, 1998; Fraga, 2005; Garrett, 2005; Goldhaber, 2003).

Nutrition, including food, beverages and drinking water, is the main source of elements for human body. Therefore, the composition of chemical elements in diet can be assessed as important transition matter for the uptake of nutritionally important as well as potentially toxic elements. In this chapter essentiality and toxicity of elements in respect to human health and element transition routes in food from the environment is discussed.

1.1.1. Essentiality of elements

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). Elements are essential if they are vitally important and irreplaceable for normal physiology of the organism (Aras and Ataman, 2006; Goldhaber, 2003). Essentiality to the element is attributed if the consumption of element at levels above the safe adequate intake induces alterations in physiological functions of organs and tissues (Aras and Ataman, 2006). The group of essential compounds involve not only chemical elements, but also amino acids, fatty acids, vitamins – compounds that cannot be synthesized by organism itself but are unambiguously needed for the biological functions (Combs, 2005). However, the term *essentiality* is a relative designation due to the specific needs of biological systems for various elements in different amounts, i.e., some elements considered as essential for certain species can be non-essential or even toxic for another species and some elements can be essential in certain amount while in higher concentration they become toxic. For example, V and Co are essential elements for blue-green algae, one within the function of photosynthesis and another is involved in the process of nitrogen fixation. At the same time function of cobalt in higher plants is unknown and, if attributed to humans, biological function of V is not clearly understood (Kabata-Pendias, 2011).

C.A. Bowman with colleagues (2003) listed elements that are essential for all living organisms (C, Co, Cu, Fe, H, K, Li, Mg, Mn, Mo, N, P, S and Zn) and those essential for most of the living organisms (Al, As, B, Br, Ca, Cd, Cl, Cr, F, I, Na, Ni, O, Se, Si and V). The role of some elements (e.g., Al, As, B, Sn, V) in human health is still under the scientific investigation and, therefore, the term *possibly essential elements* can be attributed. Elements can be toxic, potentially toxic or non-toxic elements, nevertheless, it depends on the element concentration (ATSDR, s.a.; Szefer and Grembecka, 2007; WHO, 1996). 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, including 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) involved such elements as As, B, Ni, Pb, Si, V. However, the classification of elements is conditional and may vary due to the subjective research results and up-to-date scientific findings.

General contribution of elements in human physiology is following: a) Ca, F, Mg and P are involved in structures of bones and membranes; b) Cl, K and Na supports the balance of water and electrolytes; c) Cu, Mg, Mo, Se and Zn participate in metabolic catalysis; d) Fe is involved in binding of oxygen; e) I and Cr are associated with hormone formation and activity (Aras and Ataman, 2006; Combs, 2005). In details the main functions of essential and possibly essential elements and the main food sources are summarized in Appendix I.

Nutritionally important elements can be subdivided in macroelements or macronutrients (e.g., Ca, K, Mg, Na) and microelements or micronutrients (e.g., Co, Cr, Cu, Mo, Ni, Se), depending on the required daily consumption amounts. Daily requirement of microelements usually is less than 100 mg/day, while macronutrients for human body are necessary in larger quantities (Abrahams, 2002; Fraga, 2005). Requirements usually are calculated taking into account the studies of regional dietary surveys. Several terms are used to set and describe required element concentration for humans, e.g., *recommended daily allowance* (RDA), *estimated average requirement* (EAR), *upper intake level* (UL), *reference nutrient intake* (RNI) etc. (Duffus et al., 2007; FSA, 2006; IOM, s.a.; Schrauzer, 2002; White and Broadley, 2005). Requirements of essential elements for humans derived after the USA and the UK guidance documents are summarized in Table 1.1.

1.1.2. Toxicity of elements

According to the definition stated by the International Union of Pure and Applied Chemistry (IUPAC), a substance can be estimated as toxic if it has '*capacity to cause injury to a living organism defined with reference to the quantity of substance administered or absorbed, the way in which the substance is administered and distributed in time (single or repeated doses), the type and severity of injury, the time needed to produce the injury, the nature of the organism(s) affected and other relevant conditions*' (Duffus et al., 2007). Toxic substances can cause cumulative and non cumulative effects. Cumulative effects are adverse effects that occur after repeated exposure by a toxic substance, while non cumulative effects may be caused by rapidly absorbable and rapidly eliminated toxic substances (Duffus et al., 2007). Cumulative effects usually are associated with accumulation of a substance in tissues or organs of living organisms or in elements of ecosystems.

Table 1.1

The requirements of intake of essential elements for adult human organism

(after FNIC, s.a.; FSA, 2006; IOM, s.a.; Schrauzer, 2002; White and Broadley, 2005)

Element	After the USA guidance		After the UK guidance	
	Recommended daily allowance (RDA)	Tolerable upper intake level (UL)	Daily reference nutrient intake (RNI)	Safe upper levels (SUL)
	Macroelements, mg/day			
Ca	1000-1200	2500	700	1500*
Cl	750-3400	n.	2500	n.
K	1600-3500	n.	3500	3700*
Mg	310-420	350*	300	400*
Na	500-2400	<2400	1600	n.
P	700	4000	550	250*
S	n.	n.	n.	n.
	Microelements, mg/day			
B	n.	20.0	n.	9.6
Cu	0.9	10.0	1.2	10.0
F	3.0-4.0	10.0	n.	n.
Fe	8.0-18.0	45.0	11.4	17.0*
Mn	1.8-2.3	11.0	>1.4	4.0*
Si	n.	n.	n.	1500
Zn	8.0-11.0	40.0	9.5	25.0*
	Microelements, μg/day			
Co	2.4**	-	-	-
Cr	25-35	n.	>25	n.
I	150	1100	140	500*
Li	1000 *(suggested)*	-	-	-
Mo	45	2000	50-400	n.
Ni	n.	1000	n.	260
Se	55	400	75	450
V	n.	1800	n.	n.

n. - not specified.
** - including non-food sources.*
*** - for vitamin* B_{12} *which contains 0.1 μg of Co*

Adverse effects can be initiated by excess or deficiency of elements in human body, including essential elements, but the exposure of toxic elements to human organism can be caused by very small concentration and may result in serious adverse health problems (Abrahams, 2002). The ability of elements to affect the organ systems of humans in general is summarized in Table 1.2.

Table 1.2

Essentiality of elements and affected organ systems of human body

(after ATSDR, s.a.; WHO, 1996)

Element	Proved essentiality for humans	Organ system of human body													
		Ocular	Dermal	Respiratory	Cardiovascular	Musculoskeletal	Neurological	Gastrointestinal	Renal	Hepatic	Haematological	Immunological	Endocrine	Reproductive	Developmental
Ag									+					+	
Al				+		+	+								
Am						+	+								
As	+/-		+	+			+	+		+					
B	+/-				+										+
Ba					+			+						+	
Be				+				+				+			
Cd				+	+		+	+	+					+	+
Cl	+	+		+											
Co	+			+	+						+				+
Cr	+ (Cr^{3+})			+					+			+			
Cs															+
Cu	+							+		+	+				
F	+		+	+		+									
Hg		+					+	+	+						+
I	+												+		
Mn	+			+	+		+			+					
Ni	+		+	+	+							+			
P	+	+	+	+										+	
Pb		+			+	+	+	+	+		+			+	+
Pu				+		+				+					
Ra						+				+					
Rn				+											
Sb				+	+										
Se	+		+											+	+
Sn				+			+				+	+			
Sr						+									
Th				+						+	+				
Ti*				+											
Tl							+	+	+	+					
U									+						
V	+/-			+	+			+	+					+	
W				+											
Zn	+			+				+			+				

* Ti tetrachloride

Special attention should be focused on elements and substances with revealed or suspected carcinogenity as the adverse effects caused by them are cumulative, more destructive and irreversible (Table 1.3).

Table 1.3

Known information of carcinogenity of compounds containing certain elements
(after ACS, 2011; ATSDR, s.a.; ECHA, 2013; IRIS, s.a.; NTP, 2011)

Element	Radio-nuclide	Evidence of human carcinogen	Substances of carcinogenic concern
Al		+/-	
Am	+ (^{241}Am)		
As		+	As acid; Ca arsenate; diarsenic pentaoxide; diarsenic trioxide; triethyl arsenate
Be		+/-	
Cd		+/-	
Co	+ (^{60}Co)	+/-	Co dichloride; Co (II) carbonate; Co (II) diacetate, Co (II) dinitrate; Co (II) sulphate; Co-W carbide
Cr		+/-	Cr (VI) and its compounds; acids generated from chromium trioxide and their oligomers; ammonium dichromate; Cr trioxide; dichromium tris(chromate); pentazinc chromate octahydroxide; K chromate, K dichromate; K hydroxyoctaoxodizincate dichromate; Na chromate; Na dichromate
Cs	+ (^{137}Cs)		
Hg		+/-	Hg chloride
I	+ (^{129}I, ^{131}I)	+/-	
Ni		+	Ni carbonyl; Ni refinery dust; Ni subsulphide; metallic nickel
P		+/-	
Pb		+	Pb and its compounds; Pb chromate; Pb chromate molybdate sulphate red; Pb hydrogen arsenate; Pb sulphochromate yellow; trilead diarsenate
Pu	+	+	
Ra	+	+	
Rn	+	+	
Se		+/-	Se sulphide
Sr	+ (^{90}Sr)	+/-	Sr chromate
Th	+	+	Th dioxide
U	+		

Adverse effects induced by the deficiency of elements or excessive intake of elements are summarized in Appendix II.

Toxicity is dependent on the characteristics of an action of a substance, intensity and time of exposure. Toxicity of substances can be subdivided: a) acute toxicity – expressed as LD_{50} or lethal dose that induces death of 50 % of representatives of an exposed individual – $LD_{50} < 1$ mg/kg: extremely toxic substances, $1 < LD_{50} < 50$ mg/kg: very toxic substances, $50 < LD_{50} < 500$ mg/kg: medium toxic substances, $500 < LD_{50} < 5000$ mg/kg: slightly toxic substances; b) chronic toxicity – continuous and reiterative exposure of non lethal doses of a substance that causes cumulative damage for organism (EXTOXNET, s.a.; Liguts, 2001). However, in the assessment of food contamination it is more correct to deal with minimal risk levels (MRL) derived by the Agency for Toxic Substances and Disease Registry in the USA. *'An MRL is an estimate of the daily human exposure to a hazardous substance that is likely to be without appreciable risk of adverse or non-cancer health effects over a specified duration of exposure'.* Minimal risk levels are derived from acute-duration (1-14 days), intermediate-duration (>14-364 days) and chronic-duration (≥365 days) oral exposure studies (ATSDR, s.a.). Oral MRLs as well as estimated oral intake levels for several elements are summarized in Appendix III. The abbreviation *MRL* discussed here should not be confused with *maximum residue levels* set by European institutions for contaminants such as pesticides.

As it was mentioned previously, highly toxic elements for humans are Be, Bi, Cd, Hg, Pb and Tl. Predominant exposure as well as acute and chronic adverse effects caused by highly toxic elements for humans are summarized in Table 1.4.

1.1.3. Transfer routes of elements in human nutrition

Food and drinking water are the main sources that supply human body with nutrients including micro- and macroelements; slight amounts of elements can be inhaled from air. 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 or site-specific environmental conditions. Although 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, mainly taking up micro- and macroelements by roots and foliage (Kabata-Pendias, 2011; Kabata-Pendias and Mukherjee, 2007; Voutsa et al., 1996). Element transfer into the food chain continues from plants to animals, finally reaching food of plant origin and food of animal origin and human nutrition (Figure 1.1).

If compared with animals, plants can be assessed as the major components of ecosystem involved in element transfer from environment to food due to their capacity to take up, store chemical elements, synthesize or resynthesize chemical compounds containing certain elements available in soil and water. As soil is the main environmental provider of elements, the research of element transfer into food and mineral nutrition can be assessed as well to geological issues (Bowman et al., 2003; Combs, 2005). Plants can take up and accumulate from the environment where they grow not only essential elements needed for plant nutrition but also toxic elements, thus successive element transfer into the food chain can appear and may cause potential risks for both, plant and human or animal health (Voutsa et al., 1996).

Different plant species in distinctive growth conditions may be affected variously, but after the toxicological experiments it has been revealed that most toxic elements

Table 1.4

Exposure assessment and observed adverse effects after oral exposure caused by highly toxic elements for humans

(after ATSDR, s.a.; Baltes, 1998; Kabata-Pendias and Mukherjee, 2007; Liguts, 2001; WHO, 1996; WHO, s.a.)

Element	Exposure of general population	Observed adverse effects after oral exposure	
		Acute	Chronic
Be	▪ Inhalation: predominant ▪ Ingestion: possible ▪ Dermal: rare	Berylliosis	Chronic beryllium disease, anorexia, blueness of hands and feet, DNA damage
Bi	▪ Inhalation: predominant ▪ Ingestion: possible ▪ Dermal: rare	Nausea, loss of appetite and weight, malaise, albuminuria, diarrhoea, skin reactions, stomatitis, headache, fever, sleeplessness, vague feeling, bodily discomfort, depression, rheumatic pain, black line on gums (deposition of Bi sulphide), skin irritation, eye irritation	Kidney damage, liver disfunction, anaemia, ulcerative stomatitis, exodermitis
Cd	▪ Inhalation: significant from smoking ▪ Ingestion: predominant ▪ Dermal: rare	Diarrhoea, stomach pains, vomiting, bone fracture, cardiomyopathy, psychological disorders	Accumulation in kidneys with subsequent kidney damage, damage of liver, reproductive failure, potentially teratogenic, DNA damage, cancer
Hg	▪ Inhalation: possible, especially from smoking ▪ Ingestion: predominant ▪ Dermal: rare	Disruption of nervous system, brain function damage with subsequent personality changes, tremors, vision changes, deafness, muscle discoordination, memory loss), allergic reactions (skin rushes, tiredness, headaches), DNA and chromosomal damage (causes mongolism), negative reproductive effects (sperm damage, birth effects, miscarriages)	
Pb	▪ Inhalation: significant (15 %) ▪ Ingestion: predominant (dietary intake 65 %; water intake 20 %) ▪ Dermal: possible (organic Pb compounds)	Haematologic effects, anaemia, neurological effects, kidney damage, brain damage, emphysema and lung cancer, reproductive disorders (declined fertility, miscarriages, subtle abortions), can cross placenta barrier, behavioural disruptions for children	
Tl	▪ Inhalation: rare ▪ Ingestion: predominant (mainly caused by ingestion of rat poison containing Tl sulphate) ▪ Dermal: rare	Stomach aches, damage of nervous system	Disturbance of nervous system, tremor, tiredness, headaches, depression, lack of appetite, hair loss, vision changes, nerve pains, joint pains

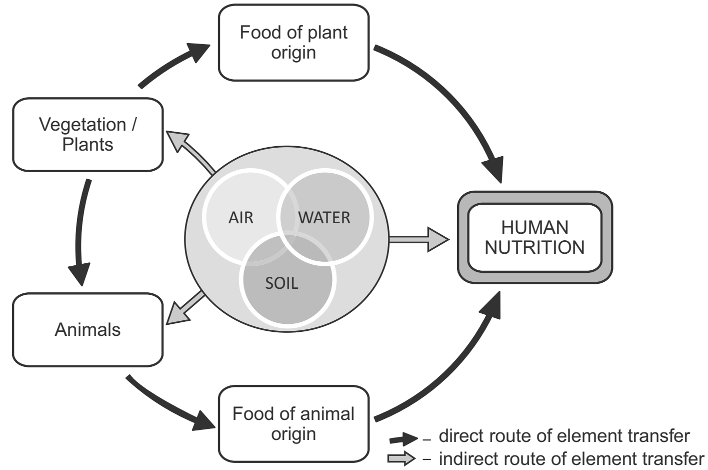

Figure 1.1. **Schematic overview of element transfer from environment to human nutrition** (author's work out)

for higher plants and also for several microorganisms are such elements as Ag, Be, Cd, Co, Cu, Hg, Ni, Pb and Sn. There are plant species that are tolerable to toxic elements in excessive concentration, while other species are more sensitive to certain elements (Kabata-Pendias, 2011; Kabata-Pendias and Mukherjee, 2007). Element transfer from soil to plants is a natural process of element circulation in the environment. It is a cluster of complicated biochemical reactions that can be affected by natural as well as anthropogenic influence. Therefore, estimation of plant uptake of elements should be assessed not only based on the soil properties, where plants were grown, but within the complex of biotic and abiotic factors (Kabata-Pendias, 2011). Element transfer into the food chain can be realized through different pathways as shown in Figure 1.2.

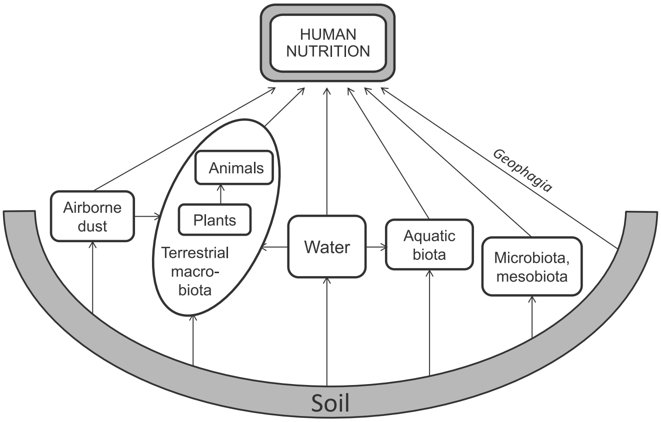

Figure 1.2. **Routes of element transfer from soil to human nutrition by the food chain** (author's work out; after Kabata-Pendias and Mukherjee, 2007)

Element transfer from environment to food chain via atmospheric deposition is dependent on the size of particulate matter; also chemical composition of particles is important. Particulate matter containing toxic substances may deposit on the surface of soil, water and plants. 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).

Some authors mention also direct route of element transfer to human nutrition from soil. Small soil particles may be digested with consumption of unwashed vegetables and fruits thus increasing the possibility also of airborne particle deposition and admission into food chain. Rarely observed direct route of element transfer from soil to nutrition is called *geophagia* or *soil eating* that can be intentional or in most cases unwitting, and might be joint with specific cultural traditions or folk-medicine where soil components (such as kaolin) are ingested (Abrahams, 2002; Combs, 2005; Kabata-Pendias and Mukherjee, 2007).

1.2. Contamination sources and natural occurrence of elements in food

Consumer safety is the main reason why food contamination is a question of high importance. Soil contamination and possible subsequent site-specific and vegetation pollution with potentially toxic elements may occur due to the natural environmental processes and anthropogenic activities. Respectively, volcanic releases, atmospheric depositions, mining and use of chemicals in agricultural practices can be mentioned as well recognized examples. Geochemical anomalies, variable site-specific content of elements in soil, agrochemical applications, and pollution influence element content and concentration in plants consumed by humans as foodstuffs resulting in dietary intake of micro- and macroelements (Hao et al., 2009; Kabata-Pendias, 2004; Kabata-Pendias and Mukherjee, 2007). Background element content of soil is not constant but influenced by natural processes in soil and affected also by human impact or anthropogenic factors which mainly bring moderate diffuse inputs of chemicals into the soil, therefore, concentration of elements can vary in time (Diez et al., 2009; Kabata-Pendias and Mukherjee, 2007).

Contamination with microelements may be caused by influence of natural environmental impact, environmental pollution, applied agricultural practice in food plant cultivation and animal breeding, food manufacturing, processing, packaging and storage that is discussed in this chapter.

1.2.1. Impact of natural environmental background on the concentration of elements in food

Micro- and macroelements naturally occur in the all phases of environmental systems: lithosphere, hydrosphere and atmosphere, but the ambient element concentration and forms of speciations are very variable and may influence biology and physiology of plants, animals and humans (Bowman et al., 2003). It is not possible to estimate unitary environmental backgrounds of elements in any of environmental systems all over the Earth, but, by estimating regional or site-specific environmental background of micro- and macroelements it is possible to indicate potential risks for populations in selected areas (Garrett, 2005).

Scientific discipline that investigates impact of environmental conditions on plant, animal and human health is medical geology (Bowman et al., 2003). C.A. Bowman with colleagues (2003) stated that in this field of research there can be selected two main investigation trends that are based on the variability of element sources in the environment: a) natural occurrence of elements in the environment – mostly connected with investigation of regional or site-specific geological background that can influence local populations via food chain; b) occurrence of elements by impact of environmental hazards, e.g., influence of volcanic eruptions, flooding, landslides.

Naturally occurring micro- and macroelements in the soil-plant transfer generally are originated from mineral material of soil that become available for plants after weathering of soil or other processes in the soil system. Element behaviour can differ: some elements circulate from deeper layers of soil, while other elements are concentrated in the soil surface (Steinnes, 2009).

The majority of elements are naturally occurring in the environment. Soil erosion and volcanic eruptions can be mentioned as the main release sources of elements globally. However, soil can be assessed as the basic matrix of elements from where it can reach food via food chain and water. Although almost all elements are detectable in soils of different regions of the world, several elements can be brought forward. The main attention should be paid to the absence or excessive presence of essential elements (e.g., I, Se) in soil and, consequently, in plants and food of the certain area. Another very important group involves the presence of toxic and potentially toxic elements (e.g., As) in soil. Among the elements that have been recognized worldwide as potential food chain affectors As, F, Fe, I and Se can be listed (Abrahams, 2002).

Occurrence of several essential elements is tightly connected with the geological background. For example, Mn is predominant element of silicate rocks, Zn and Se is found in silicates and sulphides; Cu and Mo are constituents of sulphides or can be found as basic elements together with Fe, while Fe can be found as well as in sulphides and silicates, as native metal, and it is one of the most abundant elements in the Earth's crust (Combs, 2005).

Elements in soils can be located in various ways: a) lithogenic – natural occurrence from parent material of lithosphere; b) pedogenic – depending from lithogenic sources but influenced by soil forming processes; c) anthropogenic – element settling in soils or on their surface after the anthropogenic activities (Gilucis, 2007; Kabata-Pendias and Mukherjee, 2007).

A. Kabata-Pendias and A.B. Mukherjee (2007) stated that mutual interactions exist within micro- and macroelements in soil, and elements can be characterized by antagonistic and synergistic nature. The main element relationships in soils can be assessed in-between elements as follows:

- Ca and B, Ba, Cd, Co, Cr, Cs, Li, Mn, Ni, Pb, Sr, Zn;
- P and As, Cr, Hg, Mo, Mn, Ni, Pb, Rb, Se, Zn;
- Mg and Cr, Mn, Zn, Ni, Co, Cu;
- Fe and Co, Ni, Mn, Mo, Cr, Zn;
- Mn and As, Cr, Cu, Mo, Ni, V, Zn;
- Cu and Mo;
- Cd and Zn.

These interactions of elements are closely connected with sorption processes by soil particles and are giving important impact for system of plant root nutrition. However, influence of soil constituents should be assessed within the interconnections in whole environment: soil-atmosphere, soil-hydrosphere, soil-biosphere (Abrahams, 2002).

Element occurrence in soil is dependent on character of element mobility, e.g., some elements in soils are more mobile while others are immobile. It differs by the composition of soil layers vertically, i.e., element concentration in deeper soil layers is not equal with the top soil layers and several elements are tended to be transferred from deeper soil layers to the top. Plant growth with its function to uptake elements from deeper soil layers to the top layers works as natural *plant pump* of elements. That can result in the rise of certain element concentration in the surface layers of soil, if compared with deeper layers. This is particularly evident for plant nutrients such as K, Ca, Mn, and Zn, but may also explain surface enrichment of other elements readily absorbed by some plants such as Ba, Cd, Cs and Rb (Steinnes, 2009).

It is important to assess the natural environment as the unitary system *soil-water-air*. Within the almost all processes of living systems water takes the role of a fundamental solvent and the most important bearer of micro- and macroelements. However, chemical composition of water cannot be estimated just by itself due to the tight environmental system *soil-water-air*. Hydrosphere consist of surface waters of the Earth, including oceans and seas, rivers and streams, lakes and ponds, where oceans and seas compose about 98 % of all the water mass. In case of waters, instead of the term *micro- and macroelements,* the expression *micro- and macroconstituents* should be used. Natural waters contain dissolved ions of such elements as Na^+, K^+, Mg^+, Ca^+, Cl^-, SO_4^{2-}, HCO_3^- which can be adsorbed by organic or inorganic colloidal particles (Kabata-Pendias and Mukherjee, 2007).

All established sources of dispersion of micro- and macroelements in the air or, on a larger scale, in the atmosphere, can be split in two to globally important sets: natural sources of elements and anthropogenic sources of elements. Such environmental processes as terrestrial, volcanic, meteoric outflows as well as soil erosion dusts spread by surface winds, forest fires or marine water aerosols are assessed as natural sources of elements, while anthropogenic sources of elements in atmosphere involve exhaustion of fumes from fuel and coal combustion, outflows from industry and agriculture. Although, anthropogenic influence on air composition is undoubted, also natural element input is estimated as noteworthy, e.g., more than 50 % of Cr, Mn and V and more than 20 % of Cu, Mo, Ni, Pb, Sb, Zn in air comes from natural sources. Volcanic outflows may contribute up to 20 % from As, Cd, Cr, Cu, Hg, Ni, Pb and Sb in air, but wave influence in the world ocean may release about 10 % from total emissions of metallic elements in atmosphere (Allen et al., 2001; Kabata-Pendias and Mukherjee, 2007).

Typical element condition in the atmosphere is their connection with particulate matter, except for Hg which mostly appears in gaseous form. In the air micro- and macroelements are absorbed by particles of solid matter suspended in a gas or liquid with average size of 0.01-100 μm. Particle size largely is liable for the element distribution on a global scale in the atmosphere – as particles are smaller as they may stay in the atmosphere for longer time, and they can be spread further from the point of source (Kabata-Pendias and Mukherjee, 2007). Chemical composition of particulate matter and size of individual particles plays significant role in potential impacts on human health as well as on overall conditions in the environment and vegetation where they are deposited (Allen et al., 2001). Atmospheric aerosols, that are suspensions of liquid or solid particles in gas, also can have variable chemical composition due to their generation mode: direct inflows of particles in the atmosphere originate primary aerosols but transformation of inorganic or organic gaseous substances in the atmosphere originate secondary aerosols; both types of them can be transported into troposphere and stratosphere for a long distances. Investigation of the content of atmospheric aerosols discovers the highest concentration of elements close to ground level that verifies the assumption that the main sources of air pollution comes from the earth surface. Concentration of almost all elements diminishes rapidly at altitude of 1 km, thereby indicating borders for vertical distribution of elements in the atmosphere (Braziewitzs et al., 2004).

However, elements dispersed in the air are exposed to the global circulation with the tendency to return to the Earth surface ecosystems by depositing on the soil and vegetation. Deposition of the atmosphere is the main pathway of metal circulation in the environment, even in areas with slight or none industrial activities (Allen et al., 2001).

As geological structure, particularly, soil is the main source of minerals, it can be assessed that geographically local element availability for humans and animals is dependent on the element concentration available in soil for plants and released in water which is used for drinking and cooking that can influence geographical distribution of element excess or absence in nutrition. Insufficient presence of elements in soils can occur due to naturally low mineral contents in soil (e.g., for I, Se), inefficient element uptake by crops (e.g., in case of Zn deficiency in areas with calcareous soils), excessive element uptake by plants (e.g., for Mo promoted by neutral-alkaline conditions in poorly drained soils) or excessive leaching of elements (e.g., for I, Zn). Anyway, there are still recognized certain regions with element deficiency in nutrition for such elements as B, Cu, Co F, Fe, I, Mo, Mn, Se, Zn (Abrahams, 2002; Combs, 2005). For several elements the risk areas worldwide are well recognized, e.g., Mo enriched regions in are in Armenia, but Mo deficiency is detected in South Africa that has influenced element concentration in locally cultivated crops such as maize, beans, pumpkins. But deficiency of Zn due to its limited uptake can be expected in areas with calcareous soils and leached arenaceous soils with naturally low Zn concentration (Abrahams, 2002). North Europe, including the territory of Latvia, is known as Se deficient area while in several regions in China naturally excessive Se concentration in soils and crops is discovered (Navarro-Alarcon and Cabrera-Vique, 2008; Zegnere and Alsina, 2008). Nowadays, along with the globalisation processes, in many societies food has not been derived (cultivated, bred, produced) at the habitation area, thus decreasing the regional or site-specific impact of element content on human nutrition.

The quality of human health, welfare and life in a great extent is dependent on the quality of food consumed daily as well as influenced by conditions of the surrounding environment. Soil, water and air are the essential units of the unitary global ecosystem and are the basic matters of the life on the Earth. Chemical content of soil, water and air is not constant and varies widely due to the different global and regional factors, e.g., climate zone and seasonal conditions, geochemical background, hydrological cycles, pollution rate.

1.2.2. Agricultural impact on the concentration of elements in food

Agroecosystem is the environment changed by human activities through the agricultural practice. Widely applied soil fertilizers and ameliorants usually contain impurity of microelements and may affect concentration of elements in soil in a great extent. Continuous use of these substances may lead to significant changes of soil chemical, physical and biological character that can be irreversible or reversible in long time period only. It is common that agriculture intensifies the weathering of soil that can result in the changes of the quantitative concentration of elements involved in mobile chemical forms that can intensify biogeochemical processes. This is assessed positively due to the increase of bioavailability of essential elements for crops; however, accumulation of potentially toxic elements also may occur (Карпова, 2005).

Soil always has been estimated as a valuable resource for humans with one of its main function – food and feed producing and supply for living organisms. Therefore, it can be assessed that soil is also the main source of micro- and macroelements for plants, animals and humans and at the same time soil can be a transmitter of hazardous pollutants, i.e., toxic or possibly toxic elements (Kabata-Pendias and Mukherjee, 2007). Nowadays, with the fast increase of the world's population the serious future problems may arise in connection with over-exploitation of soil in agriculture that can result in exhaustion of soil resources. As soil is the main source of nutrient elements for plants subsequently used as human food or animal feed, the impact of agricultural practice on element content and concentration in food is of high concern.

Elements that are basic microelements in agricultural and crop sciences are B, Cu, Co, I, Mn, Mo, and Zn (Карпова, 2005). In agricultural areas as well as in areas used for agriculture in the past, natural soil composition can be transformed by frequent applications of fertilizers and other agrochemicals. Use of mineral fertilizers may lead to higher concentration of Sr and F in soils, but application of organic fertilizers conveys significant amounts of As, Cu, Ni and Zn into the soils. Phosphorous fertilizers are the ones that substantially may affect soil element concentration by input of such elements as As, Cd, Cr, F, Ni, Pb, Sr and Zn (Карпова, 2005).

Apart from the food chain contamination that may occur as a consequences of excessive transfer of metallic elements or metalloids from soils to edible plants, environmental effects such as extinction of vegetation cover induced by plant intoxication can also occur (Kabata-Pendias, 2004; Кабата-Пендиас, 2005).

Transfer of metallic elements and metalloids from use of agrochemicals, fertilizers and sewage sludge in agriculture can be detected. For example, fungicides containing Cu applied in grape plantations may lead to wine contamination, use of some antifungal seed dressings may result in food contamination by organic Hg, but lead arsenate used as insecticide in orchards can contaminate fruits and their products with As in high levels. Sewage sludge can be applied as soil fertilizer, but in many cases they contain high concentration of Cd, Cu, Fe, Pb, Zn that can be transferred from soil to plants and food (Reilly, 2007). Application of fertilizers on agricultural soils is one of the main sources of nutrient element input in soils with subsequent transfer into biota. Long-term use of fertilizers should be deliberated due to prospective soil contamination with such element as As, Cd and Pb from phosphorous fertilizers (Jiao et al., 2012).

Among mineral based fertilizers phosphorous fertilizers are the richest in microelements. Potassium and nitrogen fertilizers contain low amounts of impurities – the highest amount is attributed to Mn, but low concentration of Ni and Pb can be detected, while As, Cd and Co are in negligible concentration. Phosphorous fertilizers contain significant amount of F and Sr as well as may contain such elements as As, Cd, Cr, Ni, Pb, and Zn. Microelement concentration in organic fertilizers varies widely, but it can influence input of As, Cd, Cu, Mn, Ni, Pb (Карпова, 2005).

Development of agriculture can increase the microelement concentration in grown food crops that is mainly attributed to cereal grains and edible seeds cultivated by different approaches (Welch and Graham, 2005). The main of them are summarized in Table 1.5.

Table 1.5

Influence of agricultural approach on food composition

(after Welch and Graham, 2005)

Approach	Objective	Effect on food composition
Crop field selection	Identification of soil type, element content and concentration in soil, and element bioavailability assessment	▪ Increased uptake of essential elements (e.g., Se, Zn) by food crops
Agricultural practice	Application of macronutrient fertilizers	▪ Impact on levels of macroelements (e.g., Ca, K, Mg, Na, N, P, S) ▪ Input of potentially toxic elements (e.g., Cd, Hg, Pb)
	Application method of micronutrient fertilizers	▪ Impact on levels of microelements ▪ Effective for Cl, I, Li, Mo, Ni, Se, Zn ▪ Limited effectiveness for B, Cu, Cr, Fe, Mn, V
	Diversity of cropping system	▪ Selection of micronutrient-dense varieties
	Utilization of micronutrient-rich food crops	▪ Microelement recycling
	Genetic crop modification	▪ Improvement of micronutrient concentration and bioavailability in food crops by breeding for increased levels of promoter substances ▪ Improvement of micronutrient concentration and bioavailability in food crops by breeding for decreased levels of inhibitor substances

Element variability differs in both, vertical and horizontal scaling and, as it was already mentioned before, is influenced not only by natural soil geochemical circulation but also is seriously affected by other factors. Soil fertilization, that is a common agricultural practice, may cause enrichment of soils with elements in excessive concentration that can reach exaggerated amounts of certain elements, e.g., from 700 to >10 000 mg/kg of Al, 100-320 000 mg/kg of Ca, <0.1-2.5 mg/kg of Ge and <0.1-4.3 mg/kg of Se (Reilly, 2007). However, some authors do not equitable the terms *soil pollution* and *soil contamination* and propose definition that soil contaminated with microelements may not be deemed as polluted soil unless a threshold concentration can be estimated that negatively affects biochemical and biological processes (Kabata-Pendias and Mukherjee, 2007).

Significant inputs of elements in soils can be achieved with applications of alternative soil fertilizing compounds such as sewage sludge or fly ash. The use of fly ash in agriculture fields due its alkaline nature can decrease plant uptake of metallic elements such as Cd, Cu, Cr, Fe, Mn and Zn. High concentration of such elements as Ca, Fe, K, Mg Na, Zn in fly ash composition may increase the yield of agricultural crops. However, tendency of unweathered fly ash to accumulate several elements (e.g., Al, B, Mo, Se) may lead to plant toxicity; subsequent food contamination is recognized to occur and this is the reason of the limited use of fly ash in agriculture (Basu et al., 2009).

Nowadays the problem of possible health hazards caused by consumption of contaminated food plants has been recognized not only for agricultural production but also concerning allotment or community gardens. Increasing urbanization constrains the formation of family gardens or domestic farms at sites that have been polluted by industry in the past or that are under the influence of daily urban contamination such as construction dust or traffic exhaust (Alexander et al., 2006; Wunderlich et al., 2011). Vegetables and fruits grown in such conditions mostly are consumed long term by small groups of people and therefore potential health impacts still are not considered important within the communities.

1.2.3. Environmental pollution as a source of potentially toxic elements in food

The main environmental pollution sources of trace inorganic pollutants are industry, mining and smelting, brick, pipe, cement, ceramic, glass manufacture, chemical plants, power generation, combustion of fossil fuels and municipal wastes, nuclear reactions, agricultural activities, transport and urban pollution. It has been estimated that the most hazardous elements for the biosphere are Ag, Au, Cd, Cr, Cu, Hg, Pb, Sb, Tl and Zn, while among the least hazardous elements Ga, La, Nb, Sr, Ta and Zr are ranked (Kabata-Pendias and Mukherjee, 2007).

However, pollution induced by industry, traffic or other anthropogenic activities recently is significant source of elements that revert to ecosystems. Elements with natural origination as well as elements from anthropogenic sources are circulating in the biosphere and are involved in biogeochemical cycles apart from the site of their origin (Voutsa et al., 1996).

It is verified by experiments that dust outflows from industrial or urban areas influence the concentration of chemical elements on foliage surface significantly. Dust may contain high amounts of Al, Ba, Fe, Mn and Pb, revealing that accumulation of elements is dependent on the intensity of traffic and the air quality in urban areas (Simon et al., 2011). On the contrary, investigating roots of plants grown in an industrial area it was detected that most element concentration detected in vegetables was not above the admissible levels. Just some elements, such as Cr, Mn, Pb and Zn appeared in high levels in vegetable leaves that was also verified by analysis of particulate matter. There are wide distinctions between the composition of vegetables, soil and air. The concentration of elements in vegetable roots and vegetable leaves was found to be related solely to a soil or an atmospheric input of each element, except for Cu and Mn in roots that appeared to receive additive contributions from both sources. The best relationships were found between Cd in vegetable roots and soil Cd as well as between Cd in vegetable leaves and atmospheric Cd. Highest accumulation due to atmospheric deposition was found for Pb in lettuce, and for Cr and Cd in the leafy vegetables. Root vegetables were found to accumulate soil Cd much more efficiently than other microelements (Voutsa et al., 1996).

Such elements as As, Be, Co, Cr, Cu, Hg, Mo, Mn, Ni, Sb, Se, V and Zn principally enter the atmosphere from fossil fuel combustion processes but largest worldwide emitter of As, Cd, Cu, Ni and Zn is metallurgical industry. Gasoline and diesel that are the most popular fuels used by motor vehicles make regular emissions of Cd, Cu, Fe, Ni, Pb and Zn into air in various amounts (Allen et al., 2001).

Quantitative analysis of particulate matter can be used not only for the assessment of air pollution but also for estimation of the risks that may arise from possible element contamination for humans, animals and plants. There are several microelements, e.g., Cd, Hg, Pb, that are toxic for living organisms even in very low concentration therefore particulate matter containing traces of these elements can be hazardous within environmental systems. It has been discovered that ultra small particles (<100 nm) has significantly higher value of toxicity than particles of larger size, and toxicological effects extends if particles are smaller (Meresova et al., 2008).

Dispersion of elements in the air has a seasonal fluctuation, for example, for such elements as Al, Ca, Ti, Mn, Ba and U, considered as originated from soil, seasonality can be observed if analyzing atmospheric particulate matter. It was detected that higher concentration of these elements appears in spring and summer season that can be influenced by the vertical mixing of the troposphere when warmer layers of air are rising from the surface of earth inducing resuspension processes. On the contrary, elements disposed by coal combustion, such as As, Se, V, Cd, appear in the atmosphere in higher concentration during winter season (Meresova et al., 2008).

Food contamination is important issue within the assessment of food safety. Several pollutants entering food chain via environmental pollution are found in food, for example, pesticides, organochlorine compounds such as polychlorinated biphenyls (PCBs), potentially toxic metals (e.g., As, Cd, Hg, Pb) are among the most concerning compounds (Khan et al., 2008; Koplik et al., 2004; Sharma et al., 2008; Villalobos et al., 2009).

Environmental pollution impact on the concentration of elements in food has been studied in industrial and urban areas where locally grown or breed food has obvious contact with potential contaminants. Release of metallic elements and metalloids from outflows of manufactures and mining areas as well as transport exhausts, are well known sources of environmental pollutants.

In relation to environmental research, food analysis can be a useful tool for the potential environmental impact assessment. For example, there have been extensive studies conducted on industrial pollution that can be spread widely around the pollution source via air, water or soil. The impact of anthropogenic activities can result in an increased risk of allotment garden contamination, mainly by potentially toxic metals, such as Pb, Cd, Cu, and by organic chemicals. The pollutants can easily enter the food chain, and animals or humans can be exposed to potential impacts of contamination, e.g., by consumption of vegetables and fruits that are home-grown in allotment gardens close to roadsides or in urban areas (Eggen et al., 2011; Samsoe-Petersen et al., 2002; Wunderlich et al., 2011).

F.-S. Zhang with colleagues (2001) has investigated the impact of applications of different waste ashes on rare element concentration in agricultural soils. The study revealed that sewage sludge ashes and incinerator bottom ashes may lead to Eu, Sc and Sm accumulation in soils with subsequent plant phytotoxicity.

Industrial pollution is well known contamination source with potentially toxic metals. The soils and waters in areas near industrial sites or ores are under the highest risk. Several cases has shown food crop contamination with such elements as Cd, Pb, Zn from leaching wastewaters as well from use of wastewater in irrigation of agricultural fields. High levels of Cd has been found in rice in Japan and in vegetables in UK, Hg in tissues of domestic animals in Brazil, As in vegetables in Urals, in Russia that have been grown near industrially active areas (Reilly, 2007).

Nowadays the problem of possible human health hazards by consumption of contaminated food crops has been recognized not only for agricultural production but also concerning allotment or community gardens. Increase of urbanization constrains the set up of family gardens at sites that have been polluted by industry in the past or those under the influence of daily urban contamination such as construction dust or traffic exhausts (Alexander et al., 2006; Wunderlich et al., 2011).

1.2.4. Impact of food processing on element concentration in food

Impact of food processing on food quality and composition has been established concerning several nutritional constituents as vitamins, antioxidants, proteins or in favour of organoleptic values such as taste, colour or smell (e.g., Awuah et al., 2007; Dewettinck et al., 2008; Odriozola-Serrano et al., 2013; Pingret et al., 2013). However, impact of processing on the element content and concentration in food has been studied quite fragmentary mainly due to the fact that assessment of processing is complicated issue affected by many factors. Food is not homogeneous and therefore has to be brought under different processing conditions that are specific for various product groups, starting from cutting and milling of vegetables and cereals up to cooking and fermentation of meat and milk products.

Harvesting of food crops and processing of food of animal or plant origin can induce food contamination through contact with equipment or substances used. For example, fish and meat products can become exposed to painted or varnished surfaces. Processing of food can be done in various ways, e.g., fermentation, sterilisation, drying, chemical preservation depending on the hygiene and processing requirements. The most common material of food contact surfaces is stainless steel; however, other contacting surface materials can come into contact with food, such as acryl-based coatings on the walls, polyester or epoxy-based powder coating products on metal substrates, epoxy or polyurethane coatings on the floors, polytetrafluoroethylene (PTFE) coated standard conveyor systems (Forrest, 2009). Transfer of metallic elements and metalloids from processing equipment during food and beverages canning (Pb), from using cooking utensils (Cu, Pb) and ceramic ware (mainly Pb) as well from plastics and other wrapping materials (Cd, Co, Cr, Hg, Pb) has been detected. Even use of certain detergents in cleaning of food processing equipment may lead to leaching of As, Cd, Hg and Pb from utensils made from stainless steel (Reilly, 2007).

Mineral content is inherent in natural foodstuffs. Apart being an substantial part of many enzymes, micro- and macroelement presence play important role in food processing, for example, in fermentation producing alcoholic beverages, fermented dairy products and meat aging. Processing as well may decrease element concentration in food and therefore food fortification with certain elements (e.g., Ca, Fe, Mg, Se) is practised frequently. Compounds used as dietary supplements or food additives with antimicrobial, sequestrant, antioxidant, flavour enhancing and leavening, texturizing, and buffering properties contain metallic cations that can change natural element balance in food (Karley and White, 2009; Nabrzyski, 2007).

K. Dewettinck and colleagues (2008) has investigated the impact of processing on food nutrient content. It was found that production of bread during the grain transformation processes involving milling, mixing, fermentation and temperature influence leads to loss of vitamins. However, use of different techniques of processing may result in decrease or increase of the levels of bioactive compounds as well as their bioavailability can be modified.

Another study done by F. Cheli with colleagues (2010) affirmed the influence of industrial milling of cereals such as wheat on Cd and Pb distribution in derived milling fractions. Distinctions were detected, for example, the fraction of cereals remaining for use in animal feed (shorts (middlings) and wheat-flour short) contained higher concentration of Cd and Pb, while fractions supposed for food production contained lower levels of these metals. It was also detected that debranning milling lead to significantly higher levels of contaminants than application of conventional milling, especially, in derived wheat by-products.

Also domestic food processing can influence element concentration in food. For example, milling of grains can reduce concentration of Ca, Fe, P and Zn, but fermentation of grain product increases bioavailability of Ca, Fe, P and Zn; cooking and storage over 6 months of fortified blended food reduces microelement concentration (Callanan, 2000).

Although historical facts confirm possibility of extremely high food pollution by Pb in the past from ceramic kitchen ware with lead enamel, dishes from zinc containing high impurity of lead, also nowadays there still certain risks remain of possible food contamination with potentially toxic elements (Baltes, 1998).

1.2.5. Food contamination from storage and packaging materials

The metals predominantly used in food packaging are aluminium and steel. Al is used to make cans, foil, for lamination of paper and plastics. Mg or Mn are often added to aluminium to improve its properties. Al is highly resistant to most forms of corrosion, its natural coating of Al oxide provides highly effective barrier to the effects of air, odours, temperature, light, moisture, microorganisms and chemical attack. Another metal widely used in food packaging materials is tinplate is produced from low-carbon steel coated with thin layers of Sn from both sides. Depending on manufacturing process, there are hot-dipped tinplate and electrolytic tinplate. Tin provides steel with some corrosion resistance, but for more protection tinplate containers are often lacquered to provide inert barrier between metal and the food. Commonly used lacquers are materials in the epoxy phenolic and oleoresinous groups and vinyl resins. Also tin-free steel known as electrolytic chromium or chrome oxide coated steel is used in food packaging materials (Forrest, 2009; Rial-Otero et al., 2009).

Food storage and packaging materials can influence not only food organoleptic and nutritional values but also may lead to food contamination if inappropriate materials are used and may lead to long term adverse health effects. For example, Al and Sn are widely used in cans for food storage as metals of low impact on human health. However, recent research studies suggest correlations between ingested Al and Alzheimer's disease development. It is detected that despite high Al resistance it can leach from the material of cans, cookware or other kitchen utensils to food (Joshi et al., 2003).

Tin-lined cans used to package food constitute the most important contribution to tin transfer into human nutrition. Organotin compounds exposure may occur by the ingestion of seafood and contact with consumer products that contain organotin compounds. Household commodities made from polyurethane, plastic polymers, and silicon contains butyltin concentration in ppm range. Mono- and dimethyltin and mono- and dibutyltin compounds have been detected in drinking water where PVC polyvinyl chloride pipes are used in the distribution of drinking water (ATSDR, s.a.).

Apart from the use of metals, other traditionally used materials for food packaging are glass, wide variety of plastics and paper with different coatings. Paper and paperboard are sheet materials made from an interlaced network of cellulose fibres derived from wood by using sulphate and sulphite with possible application of chemical bleaching. Commonly used in corrugated boxes, milk cartons, folding cartons, bags and sacks and wrapping paper. Packaging materials and systems for food storage contain many substances which can migrate to food during processing and storage. However, the major concern regarding safety of food-contact materials is that the effects of prolonged exposure in humans are still poorly known (Rial-Otero et al., 2009).

Information of food packaging materials and possible leaching of elements is summarized in Table 1.6.

1.3. Bioavailability of elements

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). Total content of elements is value that can characterise certain matrix, e.g., soil, plant or processed food, in general. Detailed information about the bioavailability of elements can be achieved if it is known in what chemical compounds they are involved. The investigation of element bioavailability is complicated interdisciplinary issue dependent on chemical, environmental, nutritional, physiological and epidemiological impacts that in many cases is still in the level of suggestions and assumptions even it has been investigated for decades. This chapter discusses the most relevant viewpoints of element bioavailability in food chain *soil-plant-human*.

Table 1.6

Food packaging materials and possible element leaching into food
(after Conti, 2007; Conti, 1997; Forrest, 2009; Rial-Otero et al., 2009)

Material	Properties leading to food contamination	Elements of concern	Use in contact with food
Glass	▪ Low risk of contamination only if raw material contain metals ▪ Rare impact by food chemical character (e.g., pH)	Pb, B	Bottles, jars mainly used for liquid food, kitchen utensils, dishes
Metals	▪ Corrosion ▪ Migration from coatings	Al, Cr, Cu, Fe, Ni, Sn, Zn	Cans, laminates, metalizes films used for liquid food and powdered food, kitchen utensils
Plastics	▪ Migration of components to food, especially due poor thermal stability	Cd, Pb	Epoxy/phenolic resins, polypropylene, polystyrole, polyethilene, polyvinilchloride etc. used for miscellaneous food, kitchen utensils, disposable dishes
Paper	▪ Very hygroscopic ▪ Poor barrier properties lead to food contamination from environment ▪ Not usable for liquid contact	Cd, Cr, Pb	Paper and paperboard boxes, wrappings used predominantly for dry food and for short term storage

1.3.1. Element bioavailability in soil-plant *system*

Microelements 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 are important in case of plant ability to accumulate potentially toxic elements (Inaba and Takenaka, 2005). Depending on plant capacity to transfer and accumulate elements in a higher or lower extent, a relative classification can be applied as follows: a) hyperaccumulators: plants that can accumulate high concentration of elements in their vegetative parts; b) accumulators: plants that tend to accumulate elements in their vegetative parts; c) indicators: plants that are able to take up elements and to reflect the ambient environmental content of these elements; d) excluders: plants that do not tend to take up and accumulate elements from contaminated environments (Gardea-Torresdey et al., 2005; Peralta-Videa et al., 2009). However, such properties of plants are widely studied for phytoremediation purposes at contaminated sites with polluted soil but less has been attributed to the investigation of capacity of metals' accumulation in food crops.

Bioavailability of elements for plants in a great extent is dependent not only on chemical properties of elements but also on soil composition and properties, among them pH, organic matter content can be mentioned.

1.3.2. Bioavailability of elements from food to human organism

Micro- and macroelements reaching human body can be absorbed by three pathways: a) gastrointestinal tract – element absorption from food, water, food supplements, drugs, soil, particular matter, atmospheric aerosols; b) respiratory system – element absorption from particular matter, atmospheric aerosols, gases; c) skin – element absorption from soil, water, atmospheric aerosols, gases, chemical substances (Kabata-Pendias and Mukherjee, 2007).

Depending on the mechanism of intake, ingestion, inhalation or dermal absorption, elements must pass through a series of organs before entering the blood stream. Ingested particles pass through the gastrointestinal tract, inhaled particles pass through the respiratory system and dermally absorbed elements enter directly into the blood stream. The intake of an element also dictates how much the body will absorb, for example only 6 % of ingested Cd is absorbed in contrast to 50 % of inhaled Cd. It accumulates in adrenal pericarp possibly binding with proteins. Elimination half-life period for cadmium is very long – 10 to 30 years, therefore contamination by high doses of cadmium can result in chronic intoxication (Baltes, 1998; Bowman et al., 2003). Absorption of ingested metallic mercury is very minimal (about 0.01 %), while organic mercury is absorbed from gastrointestinal tract up to 90 % of uptaken dose. Absorption of inorganic mercury is medium, 7-15 % (Liguts, 2001). Human body can absorb 5-10 % of uptaken amount of lead which is tended to accumulate in bone tissues and viscera. Accumulation of lead for humans is very dangerous due to the possible release of element in human body (Baltes, 1998).

Low element concentration in environment (soil and water) is not the only one reason for element deficiency in human nutrition. Important issue is the chemical form of element. For example, nowadays the Zn deficiency has been recognized in developing countries where local food contains Zn of low bioavailability. Other element, such as Fe, bioavailability can be affected by presence of phytate that is a plant substance and also by antagonist elements such as Co, Cu, Zn and Mn. Bioavailability of Zn also can be reduced by antagonism with phytates, Ca, Cu, Fe, Ni and P (Abrahams, 2002).

Bioavailability of elements is dependent on element chemical form, the composition of diet and health situation of the individuals. The data of concentration of micro- and macroelements in food can give important information about dietary habits of special group, health situation of individuals and origin of elements. Therefore, it is important to determine the daily dietary intake of microelements, their concentration and sources. Functions of microelements – as structural material, e.g., Fe is part of haemoglobin, Ca, P and other elements constitute a significant part of mass of teeth and bones, Na, K, phosphate, sulphate, chloride – constituents of fluids inside and outside body cells. Other function – regulation of biological activities – Ca for normal blood clotting, Mg stimulates activity of many enzymes etc. (Aras and Ataman, 2006).

Determination of total content of elements in a matrix is a tool to assess the overall understanding about the element amounts but deeper investigation is needed for the assessment of bioavailability of elements. The investigation of bioavailability is a complex set of mutual factors; schematic overview of a model of the complexity of element bioavailability from food of plant origin is shown in Figure 1.3.

The research of element bioavailability has been performed on staple food crops such as rice, wheat, maize, beans and cassava (Welch and Graham, 2005). It is too complicated

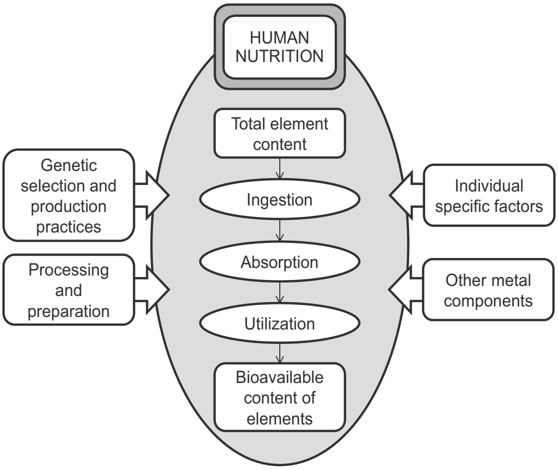

Figure 1.3. **Model of the impacts on element bioavailability from food of plant origin** (author's work out, after Welch and Graham, 2005)

to do complex investigation of the bioavailability of various elements at the same time; therefore, the basic target is to understand the overall principles and to create example models. More deep studies of element bioavailability from food crops have been studied concerning Ca and Fe on an in vitro Caco-2 cell model (Viadel et al., 2006). This model has been adopted also for determination of Zn bioavailability from food crops using such protein as metallothionein (Welch and Graham, 2005).

Zn absorption is lower for vegetarians than for those eating non-vegetarian diet. Therefore, it has been suggested that the zinc requirement for vegetarians is approximately 2-fold greater than for those consuming a non-vegetarian diet (IOM, s.a.).

Poor bioavailability is one of the reasons of dietary deficiency in humans. It can be attributed to such element as Zn and can be connected with phytate presence in food of plant origin such as unrefined cereals and legumes. It is also connected with Mg and K salts. Phytate tends to make strong chelated with metal ions, especially Zn, but also Fe and Ca and as a result insoluble complex compounds are derived that cannot be absorbed through gastro-intestinal tract of humans due to absence of intestinal phytate enzymes. High concentration of Ca may lead to even more insoluble complex formation such as Ca-Zn-phytate complex. Where Zn deficiency has been observed, also Fe deficiency is common, because these metals have similar distribution in nutritional sources and their bioavailability can be affected similarly (Abebe et al., 2007).

Several metallic elements (e.g., Ca, Cu, Fe, K, Mg, Mn, Na, Zn) function in cationic forms that allow them to be involved in chelation processes in contact with proteins or small organic molecules. Besides insoluble chelates (with phytic acid or oxalic acid) that cannot be assimilated in human organism, there are several chelates that are of high importance in metabolism. Here can be mentioned haemoglobin and myoglobin where Fe is chelated. Other chelates, such as amino acids, EDTA promote transportation, absorption and storage of mineral ions (Combs, 2005).

For such metallic element cations as Cu^{2+} and Zn^{2+} enteric absorption is very important. For mineral elements that tend to be highly absorbed (e.g., Se, B), homeostasis is achieved by control at the level of excretion, i.e., through the urine, bile, sweat, and breath. In the case of iron, access to active forms is regulated by altering the storage of the element in an inactive form, e.g., ferritin (Combs, 2005).

For several nutrients only a portion of the ingested amount is absorbed and utilized metabolically. Therefore, it is necessary to consider this when evaluating the nutritional adequacy of foods and diets. This concept, bioavailability, is particularly important in mineral nutrition, because some foods are less useful sources of essential minerals than might be expected from their absolute mineral content (Combs, 2005).

Micro- and macroelement bioavailability depends on both physiological and exogenous factors. Physiological determinants of element bioavailability include: a) age-related declines in the efficiency of enteric absorption of Cu and Zn; b) early postnatal lack of regulation of absorption of Cr, Fe, Zn; c) adaptive increases in the absorptive efficiencies of Cu, Cr, Fe Mn and Zn by receptor upregulation during periods of deficiency; d) dependence on other nutrients for the physiological functions of Se and I in thyroid hormone metabolism, and Cu and Fe in catecholamine metabolism; e) anabolic effects on tissue sequestration of Zn and Se; f) catabolic effects on Cr, Se and Zn losses (ATSDR, s.a.; Combs, 2005).

The ability of human body to absorb and utilize certain micro- and macroelement from food depends on several factors: I) the form of the element in food, e.g., Fe from meat (haem iron) can be more easily absorbed than Fe contained in plant foods (non-haem iron); II) other components of the nutrition, which either enhance or inhibit element absorption, e.g., the absorption of Fe from plant foods is enhanced by eating food with high concentration of vitamin C like oranges or tomatoes, but inhibited by compounds such as tannin (present in tea) and phytate (present in cereals); III) human health or specific diseases, i.e., several diseases adversely affect the ability of organism to absorb nutrients; e.g., persistent diarrhoea prohibits absorption of both micro- and macronutrients, including chemical elements; IV) food preparation or processing methods that can enhance the availability of micronutrients (Callanan, 2000).

Element bioavailability from oral intake and related factors for humans are summarized in Appendix IV.

1.4. Recent studies in Latvia – micro- and macroelement analysis

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) also 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 economic 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

There are two main targets of the current research: quantitative analysis of selected food available for consumers in Latvia and investigation of element bioavailability. With the aim to investigate the bioavailability of elements in food chain *soil-plant-human* five different soils were collected and subsequently contaminated with metallic elements. Contaminated and control soil samples were used for experimental growth of selected food crop species. Another main target of the research included collection of food samples of different kind over all the territory of Latvia with the aim to perform the quantitative analysis of micro- and macroelements. In this chapter the details of sampling, analytical methodology and data analysis are described.

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: (I) unprocessed vegetable products (apples, carrots, onions, potatoes) and processed vegetable products (cereal meals and cereal mixtures for porridge preparation); (II) unprocessed animal products (bee products such as honey, pollen and bee bread; hen eggs) and processed animal products (cottage cheese); (III) unprocessed beverages (apple juice, birch sap) and processed beverages (apple wine). Selection of food samples collected for analysis was based on the length of element transfer from the environment to foodstuff as well as possible impact of environmental conditions such as seasonality, agricultural praxis or processing were taken into account (Aras and Ataman, 2006). Suggestions from similar studies (e.g., Ekholm et al., 2007) and also the significance of the selected foodstuffs into common diet of inhabitants of Nordic countries and Latvia (Melece, 2009; Melece et al., 2008) were taken into consideration as well. Primary the food samples of local origin (grown, bred or produced in Latvia) were collected; only within the group of cereal meals available samples were of different origin that was identified after the information on packaging indicated by the producer. Special attention was attributed to the food labelled as organic (biological). In total more than 500 food samples were analysed within the research.

Sampling of food of plant origin. Fresh samples of root vegetables, carrot roots, onion bulbs, potatoes and apple fruits were collected over the territory of Latvia in harvesting season of 2010. Samples were obtained at markets or directly from farms and individual households. Samples were confirmed as locally grown products at the purchase as well as it was clarified whereas the vegetables were grown in farmlands or allotment gardens. Additionally to lettuce samples (n_s=7)[1] collected by purchasing them at the market or directly from the farms also lettuce samples (n_s=3) experimentally grown in contaminated soil were analysed. Sampling was carried out by selecting 3-5 pieces of vegetables or fruits within every single sample subsequently making mixed samples. Edible parts of

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[1] Here and further n_s – number of samples

vegetables (fruit flesh) were prepared for analysis as well as some peel samples were prepared. Carrot roots, onion bulbs, potatoes and apple fruits were cleaned, washed, peeled and crushed. Crushed samples were dried in drying oven at temperature 80-105 °C for 20 hours and at temperature 105 °C for extra 5-6 hours, if needed, depending on the moisture of sample type. Amount of moisture content was calculated. After drying every sample was triturated until the consistence of powder. Until analysis samples were stored in closed disposable plastic bags in dry and dark place. At the development of analytical procedures and pretreatment thoroughly suggestions from similar studies has been considered (Aras and Ataman, 2006; Ekholm et al., 2007; Luykx and van Ruth, 2008 Mohamed et al., 2003; Samsoe-Petersen et al., 2002).

Samples of cereal meals, i.e., cereal mixtures for porridge preparation were collected in spring of 2013 (n_s=*43*) purchasing them at supermarkets in commercially available packaging. Samples were of different origin that was identified after the information on packaging indicated by the producer Cereal meals as selected products represent part of infant nutrition common in Latvia (Melece et al., 2008; Zariņš un Neimane, 2009). Cereal meals were collected in 4 groups: mixed cereals, rice, wheat and buckwheat products, selecting at least 10 samples per group. Until analysis samples were stored in dry and dark place in disposable hermetically closed polyethylene bags.

Sampling of food of animal origin. The strategy for honey sampling was elaborated considering suggestions in other studies (Dimiņš, 2006; Joudisius ir Simoneliene, 2009; Lachman et al., 2007). Within a period of two seasons (2009 and 2010) honey samples (n_s=*80*) were collected over the territory of Latvia. Collected honey samples were grouped in sets based on the botanical origin. Botanical and also geographical origin of honey samples was identified taking into account the available information at the purchase. Honey samples were derived directly from bee-keepers or at food shops and markets with identifiable sources. All the equipment used for honey sample collection and storage excluded any metal tools. Honey samples mostly were poured into plastic containers with tight plastic covers. If honey was obtained in glass vessels, the samples were taken from the middle of the vessel to avoid contamination. Until analysis all collected honey samples were stored in a cool and dark place. For the comparison of element content within the bee products also pollen (n_s=*5*) and bee bread (n_s=*5*) samples were obtained in addition to honey samples from the same places of origination. Pollen and bee bread samples were stored in closed disposable plastic bags in dry and dark place.

The strategy for hen egg sampling was elaborated considering suggestions in other studies (Waegeneers et al., 2009a; Waegeneers et al., 2009b, Waheed et al., 1985). In total 33 hen egg samples were collected from different housing types of poultry farms in 2011-2012 over the territory of Latvia: from organic farms (n_s=*9*) (organic farming was confirmed by certificate), domestic farms (n_s=*15*) and large-scale poultry farms (n_s=*9*). Hen egg samples were purchased at the markets or obtained directly at the farms. Conditions of the hens' breeding type were identified and recorded at the moment of sample purchasing. In addition, 24 hen egg samples (2 samples every month) were collected from April of 2011 to March of 2012 in a domestic courtyard farm at Aizkraukle, Latvia, with known poultry breeding conditions. Within one sample 3-5 eggs were selected. Egg samples were kept in refrigerator (+4 °C) until delivery to the laboratory where sample preparation was done. Eggs were cleaned and egg yolk carefully was separated from albumen.

Also whole egg samples (egg yolk and albumen mixtures) were prepared. To avoid possible sample contamination no metal tools were used; egg sample preparation was done by using chemically stable plastic, polypropylene or glass equipment. All the samples were homogenized and were filled in disposable polyethylene bags, subsequently storing them frozen at -20 °C until sample pretreatment was applied directly prior analytical procedure.

The strategy for cottage cheese (in Latvian *biezpiens*) sampling was elaborated considering suggestions in other studies (Cashman, 2006; Mendil, 2006). Cottage cheese samples ($n_s=27$) were purchased from randomly selected individual dairy farms and supermarkets in Latvia over two seasons (summer of 2009 and winter of 2010). All samples chosen were labelled as cottage cheese derived from whole milk, i.e., cottage cheese with content of fat not lower than 9 %. For the reason to evaluate the impact of environmental conditions on cottage cheese manufacturing, only products of local origin were obtained. All samples were packed into disposable plastic bags and stored frozen at temperature -20 °C. Prior sample pretreatment cottage cheese samples were dried in drying oven at temperature 60 °C and subsequently triturated until the consistence of powder.

Sampling of beverages. The strategy for beverage sampling was elaborated considering suggestions in other studies (Farid and Enani, 2010; Magdas et al., 2012). Beverage samples of local origin derived in Latvia such as apple juice ($n_s=9$), birch sap ($n_s=10$) and apple wine ($n_s=5$). Beverage samples were kept in closed polypropylene tubes in refrigerator (+4 °C) and were analysed immediately after delivering to the laboratory.

2.1.2. Pretreatment of food samples prior quantitative analysis

Mineralization process is important step for sample pretreatment before analytical determination can be performed. It should be applied not only for cleavage of organic matrix of biological samples but also helps to prevent analytical techniques from unwanted residues that can settle on the burner head and in spray chamber, and can affect spectral interferences that can result in inaccuracy of measurements (Soceanu et al., 2007). Sample pretreatment can be done by several methods such as dry ashing, wet ashing, wet digestion that may be forced by heat, microwave or ultrasound influence (Alvarez et al., 2003). Carbohydrates, proteins and fats are the main matrix components of food samples that can influence quantitative micro- and macroelement detection. Wet digestion of organic matter, is widely applied for samples of biological origin, including food (e.g., Ekholm et al., 2007; Soceanu et al., 2007).

Pretreatment of samples of plant origin. Fruit and vegetables samples were wet digested as follows: a) 0.5000±0.0020 g of dry sample were weighed on analytical balance in 100 mL glass beaker; b) 10 mL of concentrated HNO_3 and 5 mL of concentrated H_2O_2 (analytically pure reagents) were added; c) after holding overnight sample solutions were digested by heating at 160 °C on heating block; d) after complete digestion and cooling sample solutions were filled up to 50 mL with ultra pure deionised water in polypropylene tubes.

Cereal products were wet digested in microwave digestion system as follows (Lawgali, 2010): a) 0.4000±0.0020 g of dry sample were weighed on analytical balance in PTFE/TFM tube; b) 4 mL of concentrated HNO_3 and 4 mL of concentrated H_2O_2 (analytically pure reagents) were added; c) after holding overnight sample solutions were digested in microwave digestion system (10 min at $T_1=55$ °C, 10 min at $T_2=75$ °C, 30 min at

T_3=95 °C, E=1500 W); d) after cooling sample solutions were filled up to 40 mL with ultra pure deionised water in polypropylene tubes.

Samples of lettuce, radish and dill were mineralized by wet digestion as follows: a) 0.1000±0.0020 g of dry sample were weighed on analytical balance in 50 mL glass beaker; b) 5 mL of concentrated HNO_3 and 2 mL of concentrated H_2O_2 (analytically pure reagents) were added; c) after holding overnight, sample solutions were digested by heating at 160 °C on a heating block; d) after complete digestion and cooling sample solutions were filled up to 10 mL with ultra pure deionised water in polypropylene tubes.

Pretreatment of samples of animal origin. For the assessment of differences between the pretreatment procedures one honey sample was treated in four different modes:

1) Wet digestion (after Tuzen et al., 2007): 1.0000±0.0020 g of sample were weighed on analytical balance in 50 mL glass beaker; then 8 mL of concentrated HNO_3 and 4 mL of concentrated H_2O_2 were added. After holding overnight sample solution was digested by heating at 160°C on heating block until the evaporation of nitrous gases. After cooling, sample solution was quantitatively poured into the polypropylene tube and filled up to 20 mL with ultra pure deionised water.
2) Dry ashing (after Tuzen et al., 2007): 1.0000±0.0020 g of sample were weighed precisely on analytical balances into the porcelain melting pot. Dry ashing was performed in the muffle furnace at the temperature 450 °C for 8 hours. Ashes were dissolved in 5 mL 25 % HNO_3 by heating slightly on heating block. After cooling, solution was quantitatively poured into the polypropylene tube and filled up to 20 mL with ultra pure deionised water.
3) Dissolution in deionised water under the influence of ultrasound (after Kropf et al., 2010): 1.0000±0.0020 g of sample were weighed on analytical balance in polypropylene tube, 2 mL of gallium solution (10 mg/L) were added as an internal standard and warm deionised water was added up to 20 mL. Sample solution was homogenised in the ultrasonic bath for 1 hour.
4) Dissolution in deionised acidified water (after Staniskiene ir kt., 2006): 0.5000±0.0020 g of sample were weighed on analytical balance in polypropylene tube and 50 mL of warmed-up deionised water was added. Solution was homogenized on vibro-homogeniser and acidified by 0.2 mL of concentrated HNO_3.

Pretreatment of pollen and bee bread samples was done as described above for honey wet digestion.

Prior analysis frozen samples of cottage cheese were desiccated at 60 °C in drying for 12 hours in an oven and triturated subsequently. Sample decomposition was done by wet digestion as follows: a) 0.1000±0.0020 g of sample were weighed on analytical balance in glass 50 mL beaker; b) 25 mL of concentrated HNO_3 and 5 mL of concentrated H_2O_2 (analytically pure reagents) were added; c) after holding overnight, sample solutions were digested by heating at 160 °C on heating block; d) after complete digestion and cooling sample solutions were filled up to 10 mL with deionised water in polypropylene tubes.

Egg sample pretreatment procedure was performed taking into account the requirements of the exploited analytical techniques (Hoefler et al., 2006; Kubala-Kukus et al., 2004; Szoboszlai et al., 2009). While total reflection X-ray (TXRF) spectrometry allows direct sample analysis, detection of elements in biological or environmental samples by atomic absorption spectrometry (AAS) requires more complicated sample pretreatment. Therefore egg samples were wet digested similarly as described in literature (e.g., Kilic et al., 2002): a) 3.0000±0.0020 g of frozen egg sample were weighed on analytical balance in 50 mL glass beaker and left to attain the ambient temperature; b) 20 mL of concentrated HNO_3 and 10 mL of concentrated H_2O_2 (analytically pure reagents) were added; c) after holding overnight, sample solutions were digested by heating at 160 °C on heating block; d) after complete digestion and cooling sample solutions were filled up to 50 mL with deionised water in polypropylene tubes. In case of sample solution analysis by TXRF spectrometry gallium solution (0.01 g/L) was added as internal standard immediately prior analysis.

Pretreatment of beverage samples. Samples of beverages were analysed without pretreatment procedure as well as after wet digestion that was applied as follows: a) 10 mL of sample was poured into 50 mL glass beaker; b) 8 mL of concentrated HNO_3 and 4 mL of concentrated H_2O_2 (analytically pure reagents) were added; c) after holding overnight, sample solutions were digested by heating at 160 °C on heating block; d) after complete digestion and cooling sample solutions were filled up to 20 mL with deionised water in polypropylene tubes. In case of sample solution analysis by TXRF spectrometry gallium solution (0.01 g/L) was added as internal standard immediately prior analysis.

2.2. Experimental setup of element transfer study

2.2.1. Soil sampling and the crop growth experiment

In spring of 2011 five soil samples (each 7-10 kg) 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). At the beginning soil type and texture were identified in the field conditions as follows: 1 sample of fen peat soil and 4 samples of sod-podzolic soil (with higher or lower content of organic matter and clay content) (Kārkliņš u.c., 2009; Nikodemus, 2011), but precise soil type was identified at the laboratory: 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; Regulation 804, 2005). Other characteristic properties of soil samples were defined precisely in laboratory using standard methodology (FAO, 2006; Pansu and Gautheyrou, 2006).

Bioavailability of metallic elements and metalloids in food chain *soil-plant-human* is complicated process influenced by different factors including soil chemical and physical characteristics. Therefore, it is necessary to determine such soil characteristic parameters as pH, content of organic matter or humic substances, cation exchange capacity (CEC) or cation base saturation and granulometric composition or soil texture (Salazar et al., 2012; Wang et al., 2004; Xu et al., 2013). Prior the analysis soil samples were dried in drying oven at 40°C, subsequently crashed with rubber pestle, sieved using 2 mm sieve for mineral soils and 4 mm sieve for peat soil with subsequent homogenization.

Qualitative analysis of soils was done based on standard methods applied widely in soil science (FAO, 2006; Pansu and Gautheyrou, 2006):

- Soil pH was detected in 1 M KCl / H_2O extract by using pH meter;
- Soil organic matter expressed as content of humic substances in soil samples was detected by Tiurin’s method;

- Cation base saturation was detected in 0.1 M $BaCl_2$ extract by atomic absorption spectrometry;
- Soil type and texture was identified by wet-sieving method and using pipetting technique.

Soil samples were divided into the equal subsamples (each 1-2 kg) by weighing on technical balance. To model metal transfer from soil to plants, except for control samples, soil contamination was applied, treating soil subsamples with corresponding metal salt solutions:

a) Soil monocontamination with copper was achieved by using copper sulphate pentahydrate $CuSO_4 \times 5H_2O$ solution at certain target Cu concentration (40, 70, 100, 130 and 200 mg/kg);

b) Soil multielement contamination with the mixture of metallic elements was achieved by 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 concentration of elements (6 mg/kg Cd, 130 mg/kg Cu, 750 mg/kg Pb and 300 mg/kg Zn). The target concentration of elements was selected taking into account the Regulation N° 804 of 25 October 2005 issued by the Cabinet of Ministers of Latvia *Requirements for quality normative of top and bottom soils*. These requirements provide the allowable metallic element concentration in soils depending on soil texture and category of pollutant, e.g., range of allowable concentration of elements in soils are 13-500 mg/kg for Pb, 16-700 mg/kg for Zn, 4-150 mg/kg for Cu and 0.08-10.00 mg/kg for Cd (Regulation 804, 2005). Soil contamination target values were selected also considering metal concentration values found in contaminated soils in Latvia and elsewhere (Gilucis, 2007). 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). For this treatment peat humic substances, isolated from ombrotrophic bog peat with certain characteristics (C 54.35 %, H 2.36 %, N 1.26 %, Mw 4 500 – 12 000 dal) were used. After the treatment with metal salt solutions the soil samples were incubated for 2 weeks to reach metal binding common for polluted soils as well as repeated homogenization was done before the filling of soils into the pots.

Contaminated and control soil samples were used for experimental cultivation of selected food crop species. Seeds of radish *Raphanus sativus* L. 'Saxa 2', leafy lettuce *Lactuca sativa* L. 'Grand Rapids' and dill *Anethum graveolens* L. 'Mammut' were directly sown into the pots filled with soil. For every contamination of every soil and vegetable type there were four pots filled and in every pot 5 seeds of the crop were put. Food crops used in this research were chosen due to the relatively rapid growth and moderate requirements for growth conditions as well as common their use in similar studies (Alexander et al., 2006; Wang et al., 2004; Xu et al., 2013). Crops were grown under the open-air conditions; however, when it was necessary the pots were covered with a plastic shed to protect them from the wind, heavy rainfall or excessive sunlight. 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. Pretreatment of soil samples

Soil samples used in the crop growth experiment were mineralized for quantitative detection of metallic elements and metalloids. Prior mineralization soil samples were sieved through 2 or 4 mm sieve and dried in drying oven for 120 min at 105 °C. To detect total element content in soil complete sample mineralization is required usually done by using *aqua regis* (HNO_3/HCl solution) (FAO, 2006; Gilucis, 2007; Pansu and Gautheyrou, 2006). *Aqua regis* containing strong acids is very corrosive and may negatively affect the analytical equipment. Therefore, sample mineralization was done by using concentrated HNO_3 as the results of measurements of element concentration by both methodologies are comparable (Rudoviča, 2012). Thus soil sample pretreatment was done as follows: control soil samples and contaminated soil samples were weighed in glass 50 mL beakers on analytical balance (1.0000±0.0020 g or 0.5000±0.0020 g), and 25 or 15 mL of concentrated HNO_3 and 5 or 3 mL of concentrated H_2O_2 (analytically pure reagents) were added, respectively. After holding overnight, samples were heated on heating block at 160 °C until 10 or 5 mL of solution were left. Additionally 15 or 10 mL of concentrated HNO_3 were added and heating was continued until the complete mineralization of samples. Sample solutions were filtrated into polypropylene tubes and filled up to 50 or 25 mL with deionised ultra pure water, respectively.

2.2.3. Sampling of experimentally grown vegetables

After the experimental cultivation of selected vegetables, samples of radish, leafy lettuce and dills grown in different soil were obtained. Since the growth of plants were affected by several factors, for instance, climate conditions, high concentration of metals in soil and unexpected presence of insects, it was not possible to collect all crop samples from all the pots; however, the failure to get grown plants was less than 10 %. Crop samples which were evolved enough and not damaged were harvested 35-45 days after the sowing, taking into account the maturity of grown plant species. Vegetables were carefully cleaned, rinsed thoroughly with deionised water and then edible parts of vegetables were separated for further analysis. Samples were air dried (lettuce leaves, dills) or dried in drying oven at 40 °C (radish) and well crashed by using ceramic knife as described in literature (Wang et al., 2006) to avoid contamination with metals. Until analysis samples were stored in closed disposable plastic bags in a dry and dark place.

2.2.4. Element speciation analysis

Transfer and bioavailability of elements in food chain *soil-plant-human* is strongly dependent on element speciation. Metallic elements and metalloids in environment can be found in form of hydrated ions, insoluble compounds such as carbonates, as well as can be bound with Fe and Mn oxides, organic complexes or other chemical compounds. Speciation analysis developed by A. Tessier in 1979 and modified by many other scientists (e.g., Favas, 2013; Malandrino et al., 2011; Okoro et al., 2012) is used as the basis for the detection of element speciation in soils and sediments. Within the current research, speciation analysis of studied soil samples was performed. Prior analysis air-dried soil samples were homogenized in porcelain mortar, sieved through 1 mm sieve and dried at 105 °C until the constant weight. Subsequently, consequent extraction step by step was performed as shown in Figure 2.1 and described in details further in the text.

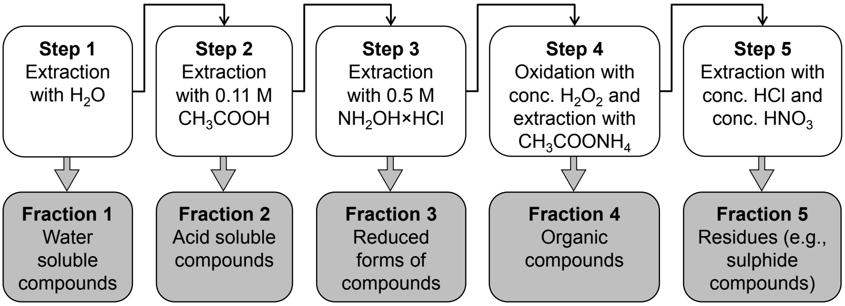

Figure 2.1. **Schematic overview of speciation analysis**

1) Fraction of water soluble compounds. 5.0000±0.0020 g of soil with low organic matter content or 3.0000±0.0020 g of soil with high organic matter content was weighed in 100 mL glass beaker; 50 mL of heated-up deionised water were added. Extraction was done on mechanical shaker for 2 hours. Extract was filtered through filter paper and 0.45 μm membrane filter into polypropylene tube, and acidified with 0.2 mL of HNO_3/H_2O (1:1) solution.

2) Fraction of acid soluble compounds. The rest of sediments from the 1st step of fractionation were carefully collected, poured into 100 mL glass beaker and 40 mL of 0.11 M CH_3COOH were added. Extraction was done on mechanical shaker for 16 hours. Extract was filtered through filter paper and 0.45 μm membrane filter into polypropylene tube, and acidified with 0.1 mL of HNO_3/H_2O (1:1) solution.

3) Fraction of reduced forms of compounds. The rest of sediments from the 2nd step of fractionation were carefully collected, poured into 100 mL glass beaker and 40 ml of 0.5 M $NH_2OH \times HCl$ were added. Extraction was done on mechanical shaker for 16 hours. Extract was filtered through filter paper and 0.45 μm membrane filter into polypropylene tube, and acidified with 0.2 mL of HNO_3/H_2O (1:1) solution.

4) Fraction of organic compounds. The rest of sediments from the 3rd step of fractionation were carefully collected, poured into 100 mL glass beaker and 10 mL of concentrated H_2O_2 were added. After holding for 1 hour, extraction was done by heating at 85 °C for until about 3 mL of solution were left. Then H_2O_2 addition and heating process was repeated. After cooling 50 ml of 1 M CH_3COONH_4 were added and hold for at least 1 hour until solution became transparent. Extract was filtered through filter paper and 0.45 μm membrane filter into polypropylene tube.

5) Fraction of residues (e.g., sulphide compounds). The rest of sediments from the 4th step of fractionation were carefully collected, poured into 100 mL glass beaker, and 7 mL of concentrated HCl and 3 mL of concentrated HNO_3 were added. After holding for

16 hours at room temperature, heating was started gradually and continued for 2 hours. Cooled extract was filtered through filter paper into polypropylene tube. Filter was rinsed with 0.5 M HNO_3 and filled up to 50 mL.

Similar speciation analysis approach was applied for detection of element bioavailability from food crops (extraction was done for lettuce samples):

1) Fraction of water soluble forms of metals. 0.5000±0.0020 g of lettuce sample were weighed in polypropylene tube; 20 mL of heated-up deionised water were added. Extraction was done on mechanical shaker for 2 hours. Extract was filtered through filter paper and 0.45 µm membrane filter into polypropylene tube, and acidified with 0.2 mL of HNO_3/H_2O (1:1) solution.

2) Fraction of acid soluble forms of metals. The rest of sediments from the 1st step of fractionation were carefully collected, poured into 100 mL glass beaker and 20 mL of 0.11 M CH_3COOH were added. Extraction was done on mechanical shaker for 16 hours. Extract was filtered through filter paper and 0.45 µm membrane filter into polypropylene tube, and acidified with 0.1 mL of HNO_3/H_2O (1:1) solution.

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2.3. Quantitative analysis of elements

2.3.1. Analytical methods

Several approaches of contemporary analytical techniques can be used for element quantification of miscellaneous biological and environmental samples, including food samples. The main demands for choice of analytical techniques are sensitivity and selectivity which can be achieved by such methods as atomic absorption spectrometry (AAS), inductively coupled plasma mass spectrometry (ICP-MS), atomic emission or optical spectrometry (ICP-AES, ICP-OES), total reflection X-ray fluorescence spectrometry (TXRF) or neutron activation analysis. AAS based methods are widely applied for analysis of samples with different matrix properties, e.g., flame atomic absorption spectrometry (FAAS) can be used for comparatively simple and fast quantitative detection of micro- and macroelements or atomic absorption spectrometry on graphite furnace (GFAAS) that is considered as highly sensitive and selective method (Hashmi et al., 2007; Kazi et al., 2009; Kilic et al., 2002; Lante et al., 2006; Samsoe-Petersen et al., 2002; Soceanu et al., 2007). ICP-MS or inductively coupled plasma atomic emission spectrometry (ICP-AES) are among the highly sensitive techniques and can be used for detection of quantitative concentration of microelements in trace amounts. ICP-MS has many advantages, including high selectivity, wide linear range and relatively low limit of quantification. In order to use ICP or AAS methodologies, it is necessary to do sample mineralization. However, this method is expensive and it can be applied for analysis of sample solution with certain properties such as acidity. By ICP-MS techniques it is preferable to detect elements in acidic media (Ekholm et al., 2007; Gonzalvez et al., 2008; Nisianakis et al., 2009; Samsoe-Petersen et al., 2002).

Total reflection X-ray fluorescence spectrometry (TXRF) is a relatively simple and cheap method for element quantification due to the possibility to analyse samples directly without complicated digestion procedure but only with addition of internal standard (Alvarez et al., 2003; Hoefler et al., 2006; Klockenkamper, 1997). TXRF spectrometry is a well-suited analytical technique for the studies of several micro- and macroelement concentration. The organic material has to be mixed with an internal standard, and method allows fast and accurate analysis of all microelements heavier than aluminium (Kubala-Kukus et al., 2004). TXRF spectrometry has several advantages: it is a rapid and non-destructive method and shows good sensitivity when analyzing organic samples. The sample can be measured directly, just diluted with deionised water, and therefore possible sample contamination at sample pretreatment can be avoided (Golob et al., 2005). The X-ray fluorescence spectrometry is a widely used multi-element analytical technique due to its simple application and it plays an important role in environmental monitoring (Szoboszlai et al., 2009).

In the current study AAS was applied for macroelement (Ca, Fe, K, Mg, Na) and some microelement (Cu, Mn, Zn) quantification. Depending on element to be detected, sample solutions were analysed by flame atomic absorption spectrometry (FAAS), electro-thermal atomic absorption spectrometry (ETAAS) or flame atomic emission spectrometry (FAES) depending on element. Content of K and Na was detected by FAES; content of Ca, Mg, Fe, Mn, Cu and Zn – by FAAS, but content of Co and Cr was detected by ETAAS. Measurements were done by atomic absorption spectrometer *AANALYST 200* (Perkin Elmer).

ICP-MS was applied for analysis of sample solutions as more sensitive method for quantitative detection of microelements (Ag, As, Ba, Cd, Co, Cr, Ni, Pb, Rb, Se, Sr, V) in trace amounts. Inductively coupled plasma mass spectrometer *ELAN DRC-e* (Perkin Elmer) was exploited.

AAS and ICP-MS were applied for the quantitative analysis of mineralized food and soil samples, as well as for acidified honey solutions.

TXRF was applied for analysis of beverages and egg samples. The range of elements (Ba, Ca, Cu, Fe, K, Mn, Ni, P, Pb, Rb, S, Se, Sr, V and Zn) were quantitatively detected by using total reflection X-ray fluorescence spectrometer *Röntec PicoTAX* (Röntec GmbH) equipped with X-ray tube (50 kV; Mo anode), Ni/C reflector (17.5 keV; level of reflection 80 %), Be detector (area 10 mm^2; thickness 7.5 μm), and applied exposition time 1000 seconds. The main limitations for use of wide range of analytical techniques are mostly connected with relatively high expenses.

2.3.2. Quality assurance of analytical methods

Quality assurance of applied analytical methods was achieved by preparation of blank samples and analysis of certified reference material samples. Subtraction of blank sample signal resulted in elimination of background corrections of measurements, as well as limit of detection, level of quantification and standard deviation were determined by using blank samples. Blank samples were prepared for every sample batch in the same mode as food or soil samples. Furthermore, each sample solution was made in triplicate, but certified reference sample solutions were made in fivefold. Mean characteristic values for metal detection with AAS are summarized in Table 2.1. Detection of such element as As, Cd, Cr and Pb quantity by AAS was limited due to the technical capability of apparatus; therefore the measurements done by ICP-MS were taken into account for further data statistical analysis.

Table 2.1

Characteristic values for quantitative metal detection by atomic absorption spectrometer *AANALYST 200* (Perkin Elmer)

Element	Limit of detection, mg/kg	Level of quantification, mg/kg
Ca	6.65	21.94
Cd	0.01	0.04
Cu	0.15	0.50
Fe	0.41	1.35
K	14.22	46.94
Mg	3.49	11.55
Mn	0.51	1.67
Na	3.29	10.84
Pb	0.18	0.59
Zn	0.32	1.06

Performance of the applied analytical methods was verified by comparative analysis of certified reference samples. Such reference materials were used as *CS-CR-2 Carrot root powder*, *NCS ZC73017 Apple powder*, *IAEA-336 Lichen*, *BCR-063R Skim milk powder* and *PT Red wine Chilian*. Certified values of element concentration of reference materials are summarized in Tables 2.2., 2.3., 2.4. and 2.5.

Table 2.2

Certified values and uncertainty of element concentration of reference material *BCR-063R Skim milk powder* (IRMM)

Element	Concentration ($\bar{x}$±s)[1], mg/kg	Element	Concentration ($\bar{x}$±s), mg/kg
Ca	13490±100	Mg	1263±24
Cl	9940±300	N	62300±800
Cu	0.602±0.019	Na	4370±31
Fe	2.32±0.23	P	11100±130
I	0.81±0.05	Pb	18.5±2.7
K	17680±190	Zn	49.0±0.6

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[1] Here and further $\bar{x}$ – mean value, s – standard deviation

Table 2.3

Certified values and uncertainty of element concentration of reference material *CS-CR-2 Carrot root powder* (LGC Standards)

Element	Concentration ($\bar{x}\pm s$), mg/kg
As	0.050±0.008
Cd	0.196±0.020
Hg	0.0043±0.0006
Pb	0.579±0.040
Zn	21.79±0.86

Table 2.4

Certified values and uncertainty of element concentration of reference material *NCS ZC73017 Apple powder* (Promochem)

Element	Concentration ($\bar{x}\pm s$), mg/kg	Element	Concentration ($\bar{x}\pm s$), mg/kg	Element	Concentration ($\bar{x}\pm s$), mg/kg
Al	70±10	Eu	0.0007*	Pb	0.084±0.032
As	0.020±0.004	Fe	16±2	Pr	0.0018±0.0003
B	19±3	Gd	0.00095±0.00011	Rb	5.0±0.6
Ba	2.5±0.3	Hg	0.002*	S	630±40
Be	0.001*	Ho	0.00025*	Sb	0.006*
Bi	0.0025*	I	0.12±0.04	Se	0.018*
Br	0.2*	K	7700±400	Si	50±13
Ca	490±10	La	0.014±0.004	Sm	0.0015±0.0005
Cd	0.0058±0.0012	Li	0.115±0.009	Sr	6.9±0.5
Ce	0.025±0.005	Mg	390±60	Th	0.004±0.0003
Cl	80*	Mn	2.7±0.2	Tl	0.0018*
Co	0.026±0.006	Mo	0.08±0.02	Tm	0.00012*
Cr	0.30±0.06	N	3100±300	U	0.0082±0.0018
Cs	0.02*	Na	1160±90	Y	0.008±0.002
Cu	2.5±0.2	Nd	0.006*	Yb	0.00066*
Dy	0.0011*	Ni	0.14±0.05	V	0.028*
Er	0.00065*	P	660±40	Zn	2.1±0.4

**- information value*

Table 2.5

Certified values and uncertainty of element concentration of reference material *IAEA-336 Lichen* (IAEA)

Element	Concentration $(\bar{x}\pm s)$, mg/kg	Element	Concentration $(\bar{x}\pm s)$, mg/kg	Element	Concentration $(\bar{x}\pm s)$, mg/kg
Al	680±110	Eu	0.023±0.004	Rb	1.76±0.22
As	0.63±0.08	Fe	430±50	Sb	0.073±0.010
Ba	6.4±1.1	Hg	0.20±0.04	Sc	0.17±0.02
Br	12.9±1.7	K	1840±200	Se	9.22±0.04
Cd	0.117±0.017	La	0.66±0.10	Sm	0.106±0.014
Ce	1.28±0.17	Lu	0.0066±0.0024	Sr	9.3±1.9
Cl	1900±300	Mn	63±7	Tb	0.014±0.002
Co	0.29±0.05	Na	320±40	Th	0.14±0.02
Cr	1.06±0.17	Nd	0.60±0.18	Yb	0.037±0.012
Cs	0.110±0.013	P	610±120	V	1.47±0.22
Cu	3.6±0.5	Pb	4.9±0.6	Zn	30.4±3.4

2.4. Reagents and laboratory equipment

Reagents used within the research:

- Concentrated analytically pure nitric acid (65 % w/v, suprapur grade, Scharlau, Penta or Merck).
- Concentrated analytically pure hydrogen peroxide (30 % w/v, suprapur grade, Merck).
- Deionised distilled water (<0.1 μS/cm, 18 MΩ/cm, Millipore Elix-3, Millipore Co).
- Certified reference material samples: *CS-CR-2 Carrot root powder* (LGC Standards); *NCS ZC73017 Apple powder* (Promochem); *BCR-063R Skim milk powder* (IRMM); *IAEA-336 Lichen* (IAEA); *PT Red wine Chilian* (LGC Standards).
- Standard solutions for element detection with ICP-MS: in 1 % HNO_3 (PerkinElmer); in 2 % HNO_3 (High-Purity Standards); in 3 % HNO_3 (Inorganic Ventures); in 7 % HNO_3 (Inorganic Ventures).
- Other reagents: hydrochloric acid; orthophosphoric acid; acetic acid; gallium solution (1 g/L Ga in 2 % HNO_3); potassium chloride; barium chloride; sodium hydroxide; potassium dichromate; ammonium ferrous sulphate; hydroxylamine hydrochloride; copper sulphate pentahydrate; cadmium acetate dihydrate; lead (II) nitrate; zinc sulphate heptahydrate; diphenylamine; silicone solution in isopropanole; solution of humic substances (30 g/L).

All used chemicals were of analytical grade or higher, provided for analysis of elements in trace levels.

Laboratory equipment exploited within the research:

- Inductively coupled plasma mass spectrometer *ELAN DRC-e* (Perkin Elmer):
- Atomic absorption spectrometer *AANALYST 200* (Perkin Elmer).
- Total reflection X-ray fluorescence spectrometer *Röntec PicoTAX* (Röntec GmbH).
- Water deionisator *Millipore Elix 3* (Millipore).

- Microwave digestion system *ETHOS One* (Milestone).
- Heating block *Thermoblock* (Biosan).
- Drying oven *Plus II Oven* (Labassco).
- Muffle furnace (t_{max}=1100 °C; Omron).
- Analytical balance ALJ 220-4 (m_{max}=220 g, d=0.1 mg; KERN).
- Technical balance (Kern).
- Vibro-homogeniser (Labassco).
- Mechanical shaker *Tachometer (RPM) PSU-20* (Biosan).
- Vacuum liophyliser *FreeZone* (Labconco).
- Ultrasonic bath (70 W, 42 Hz; Cole-Parmer).
- pH meter pH 213 (Hanna).
- Other laboratory equipment: membrane filters (0.45 μm); filter paper; glass, porcelain and polypropylene laboratory vessels such as beakers, flasks, cylinders, funnels and tubes; PTFE/TFM (polytetrafluoroethylene/TFM) tubes for microwave digestion; glass Petri plates; porcelain melting pots; porcelain mortar; glass pipettes; mechanical pipettes and micropipettes with disposable polypropylene thimbles; sieves of different size; ceramic knife.

For microelement analysis it is important to avoid any contact of samples with any contaminants, particularly metals. Therefore cutting, peeling and crushing of samples were done by using ceramic knife and ceramic mill but sample solutions were kept in polypropylene tubes. Only heating was performed in chemically persistent glass beakers.

Preparation of laboratory vessels. Quantitative analysis requires use of ultra clean vessels. Preparation of laboratory vessels was done as follows: 1) washing in hot water with use of detergent; 2) rinsing with a tap water; 3) demineralisation of vessels with concentrated HNO_3 holding for 20 minutes (or holding overnight, if 0.1 N HNO_3 were used); 4) accurate rinsing with tap water (not less than 4-5 times); 5) drying at room temperature avoiding contact with airborne particles; 6) clean and dry vessels were kept in hermetically closed disposable polyethylene bags.

All analysis were performed in the laboratories of the Department of Environmental Science and the Department of Analytical Chemistry of the University of Latvia.

2.5. Data statistical analysis

Statistical analysis of micro- and macroelement concentration analytical data was performed by using extended MS Excel data analysis tool QI Macros (QI Macros, 2013). For every data set the range of statistical parameters were calculated (e.g., standard deviation, mean, median, correlation, t-Tests etc.). If applicable, Pearson correlation was applied as follows: $r<0.5$ – slight correlation, $0.5<r<0.8$ – medium correlation, $r>0.8$ – strong correlation. For the comparison of data sets Student's tests were performed (t-Test: Two-Sample Assuming Equal Variance; t-Test: Two Sample Assuming Unequal Variances) as well as other tests were performed of necessity.

In some cases box-whisker plotting was chosen as appropriate descriptive statistical approach for the comparative assessment of element measurement data sets. This approach of data analysis allows easy determination not only of the routine statistical values within the data range but also allows detection of outliers. Box-plots show maximum, minimum and mean values of certain data sets as well as range between 25th and 75th percentiles.

3. RESULTS AND DISCUSSION

3.1. Assessment of the performance of analytical methods

3.1.1. Verification of analytical methods by analysis of certified reference samples

Samples of certified reference materials such as *BCR-063R Skim milk powder*, *CS-CR-2 Carrot root powder*, *NCS ZC73017 Apple powder*, *IAEA-336 Lichen* and *PT Red wine Chilian* were used for verification of applied analytical methods (TXRF, AAS/AES and ICP-MS).

While carrot root reference sample has been designed for measurements of five elements only, the analysis of apple reference sample supported characterization of accuracy and precision of measurements for more than fifteen elements. Obtained data revealed methodological distinctions, e.g., performance in respect to accuracy of measurements by TXRF was in range 65-105 %, AAS 36-101 % and ICP-MS 79-117 % (Table 3.1). Technical characteristics of used equipment did not allow equal detection of elements, for example, it was not possible to quantify concentration of Cd, Co, Mg, Na and Pb by TXRF, but quantification of such elements as Ca, Fe, K, Mg, Na and P was not possible by ICP-MS due to technical capability of exploited analytical equipment. In general, the highest accuracy and concentration compatibility with certified values were observed for measurements done by ICP-MS.

Table 3.1

Accuracy 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 ($\bar{x}$±*s*; n_m=5)[1] detected by corresponding analytical technique, mg/kg (Accuracy, %)		
		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)

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[1] Here and further n_m – number of measurements

Analysis of lichen reference sample revealed similar values of accuracy and additionally there were quantified such elements as As, Ba, Se and V (Table 3.2).

Table 3.2

Accuracy of applied analytical methods (TXRF, AAS and ICP-MS) detected by the analysis of certified reference sample *IAEA-336 Lichen*

Element	Certified value ($\bar{x}$±s), mg/kg	Concentration ($\bar{x}$±s; n_m=5) detected by corresponding analytical technique, mg/kg (Accuracy, %)		
		TXRF	AAS	ICP-MS
As	0.63±0.08	0.72±0.15 (115)	-	0.62±0.13 (98)
Ba	6.4±1.1	5.31±1.15 (83)	-	-
Cd	0.117±0.017	-	0.112±0.003 (94)	0.115±0.002 (98)
Co	0.290±0.050	-	0.201±0.002 (69)	0.253±0.011 (87)
Cr	1.06±0.17	<0.76 (-)	0.42±0.01 (40)	0.98±0.03 (93)
Cu	3.60±0.50	2.85±0.14 (79)	3.05±0.03 (85)	3.22±0.41 (90)
Fe	430±50	278±31 (65)	342±8 (80)	-
K	1840±200	1184±31 (64)	1544±57 (84)	-
Mn	63.0±7.0	52.9±0.8 (82)	56.98±0.52 (91)	-
Na	320±40	-	317±21 (99)	-
P	610±120	668±39 (113)	-	-
Pb	4.90±0.60	3.13±0.26 (64)	4.30±0.07 (88)	4.67±0.07 (95)
Se	9.22±0.04	<0.16 (-)	-	8.42±0.16 (91)
Sr	9.30±1.90	7.76±0.24 (83)	-	8.93±0.98 (96)
V	1.47±0.22	1.42±0.16 (97)	-	1.45±0.31 (99)
Zn	30.4±3.4	26.3±0.3 (87)	28.1±0.2 (92)	28.76±2.45 (95)

By analysis of skim milk powder reference sample it was possible to detect accuracy and precision for such elements as Ca, Fe, K, Mg, Na and Zn (Table 3.3). Wider range of data measurements was observed for TXRF (61-103 %) depending on certain element, but AAS performance (92-104 %) is quite comparable with ICP-MS measurements (88-98 %).

The main requirements for application of analytical methods include their sensitivity, selectivity and a high level of reliability. In case of analysis of food and beverage samples the most important limiting factor is the level of LOD (limit of detection) because several elements of interest (e.g., Cd, Co, Cr, Ni, Pb) in samples commonly are present in very low concentration, i.e., below the limit of detection (Aras and Ataman, 2006).

According to known certified values, analysis of red wine reference sample allowed to detect accuracy and precision of measurements only for two elements, Cu and Fe. Element content in red wine sample was analysed by TXRF with and without sample pretreatment, while analysis by AAS was applicable only for mineralized samples. Measured concentration of elements was in acceptable compliance with certified values (Table 3.4).

Table 3.3

Accuracy of applied analytical methods (TXRF, AAS and ICP-MS) detected by the analysis of certified reference sample *BCR-063R Skim milk powder*

Element	Certified value ($\bar{x}\pm s$), mg/kg	Concentration ($\bar{x}\pm s$; $n_m=5$) detected by corresponding analytical technique, mg/kg (Accuracy, %)		
		TXRF	AAS	ICP-MS
Ca	13490±100	8165±345 (61)	13350±250 (92)	13328±350 (98)
Fe	2.32±0.23	2.40±1.51 (103)	2.39±0.23 (103)	2.14±0.32 (92)
K	17680±190	13590±585 (77)	18400±220 (104)	16500±260 (93)
Mg	1263±24	-	1255±53 (99)	1170±65 (92)
Na	4370±31	-	4390±45 (100)	3870±200 (88)
Zn	49.0±0.6	34.6±11.3 (71)	48.1±2.2 (98)	46.2±3.1 (93)

Table 3.4

Accuracy of applied analytical methods (TXRF and AAS) detected by the analysis of certified reference sample *PT Red wine Chilian*, analysing directly or after mineralization

Element	Certified value ($\bar{x}\pm s$), mg/kg	Concentration ($\bar{x}\pm s$; $n_m=5$) detected by TXRF, mg/kg (Accuracy, %)		Concentration ($\bar{x}\pm s$; $n_m=5$) detected by AAS after mineralization, mg/kg (Recovery, %)
		Direct analysis	Analysis after mineralization	
Cu	0.12±0.06	0.08±0.01 (68)	0.11±0.02 (88)	0.083±0.006 (69)
Fe	3.38±0.33	3.24±0.15 (96)	3.64±0.06 (108)	3.43±0.02 (101)

Measurement of elements of low L lines (Na and Mg) by TXRF is problematic because signal of fluorescence is absorbed before it can be registered on spectra. Technical specifications of TXRF do not allow reliable measurements of Cd due to the parallel overlap of low energy Lα-lines with Kα-lines of Mo, Ca and K. Also precise Na detection is difficult as Kα-lines of Na may overlap with Lα-lines of Br and Zn. If Co concentration in analysed sample is low, but Fe concentration is high, it might influence accuracy of Co detection (Gruber et al., 2006; Klockenkamper, 1997; Stosnach and Gross, s.a.). However, many aspects of TXRF application (possibility to measure liquid samples without pretreatment) supports application of this method. In addition, although common methods such as AAS and ICP-MS have proved high sensitivity, the disadvantages of these methods involve time-consuming sample pretreatment steps with use of hazardous chemicals such as strong acids as well as high costs of exploitation of analytical equipment; therefore, TXRF can be assessed as eligible methodology for express analysis of environmental and biological samples.

3.1.2. Comparison of food sample analysis done by different analytical techniques

Apart from the analysis of certified reference samples, quality assessment of applied quantitative methodologies can be carried out with comparison of food sample analysis done by different methods. For example, analysis of a randomly selected cottage cheese sample revealed quite good compatibility between values obtained by AAS and TXRF (Figure 3.1).

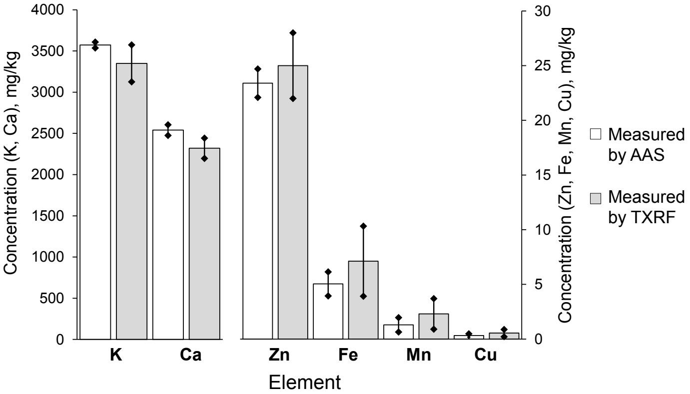

Figure 3.1. **Compatibility between measurements ($\bar{x}\pm s$; $n_m=5$) of element concentration done by AAS and TXRF for a randomly selected cottage cheese sample**

Analysis of fifteen randomly selected hen egg samples by AAS and TXRF revealed higher compatibility between measurements for macroelements, e.g., K and Ca, while greater deviation between the measurements were observed for microelements, e.g., Zn (Figure 3.2).

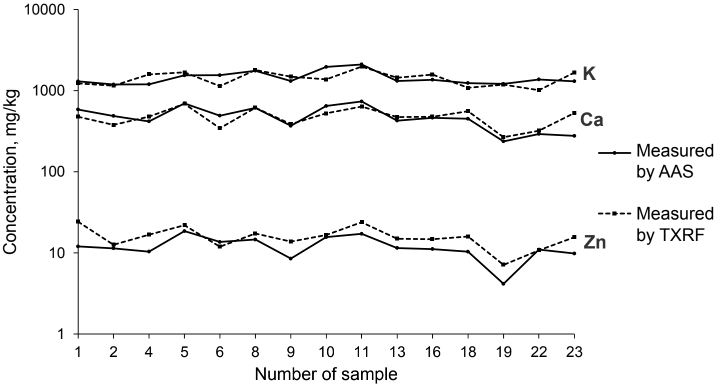

Figure 3.2. **Compatibility between measurements ($\bar{x}$; $n_m=3$) of K, Ca and Zn concentration done by AAS and TXRF for randomly selected hen egg samples ($n_s=15$)**

It was possible to compare obtained measurement data for solid consistency food samples and for liquid consistency samples. Measurements obtained from analysis of samples with solid consistency (honey, pollen, bee bread) by AAS/AES and TXRF revealed strong correlation for several elements. For instance, according to Pearson correlation coefficients, strong correlation between the applied methods can be attributed to such elements as Ca, Cu, Fe, K, Mn and Zn (Figure 3.3). Thus there are no many differences in the reliability of the applied analytical approach and the application quality yields rather good results.

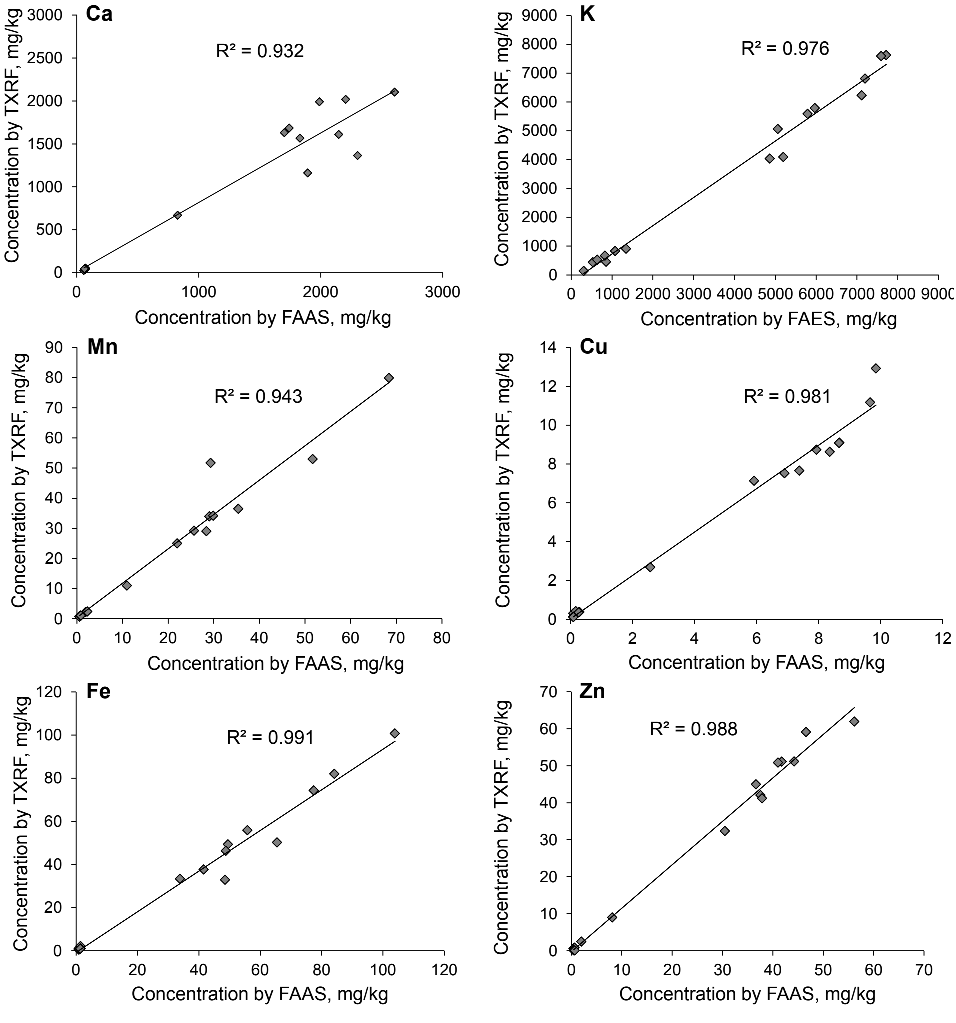

Figure 3.3. **Correlation between the element concentration values measured by TXRF and AAS in solid consistency food samples (honey, bee bread, pollen) for Ca, Cu, Fe, K, Mn and Zn**

For liquid consistency samples (e.g., apple wine and apple juice) assessment of measured values revealed no strong correlation for Cu, Zn, Fe and Mn (Figure 3.4.) while values detected for Ca and K correlated weakly. In the last case use of comparability with the values found for analysis of reference samples can be used to made decision about selection of best suitable analytical method. In case of some elements (e.g., Ni, Pb) interpretation of results was limited due to their low concentration in analysed samples.

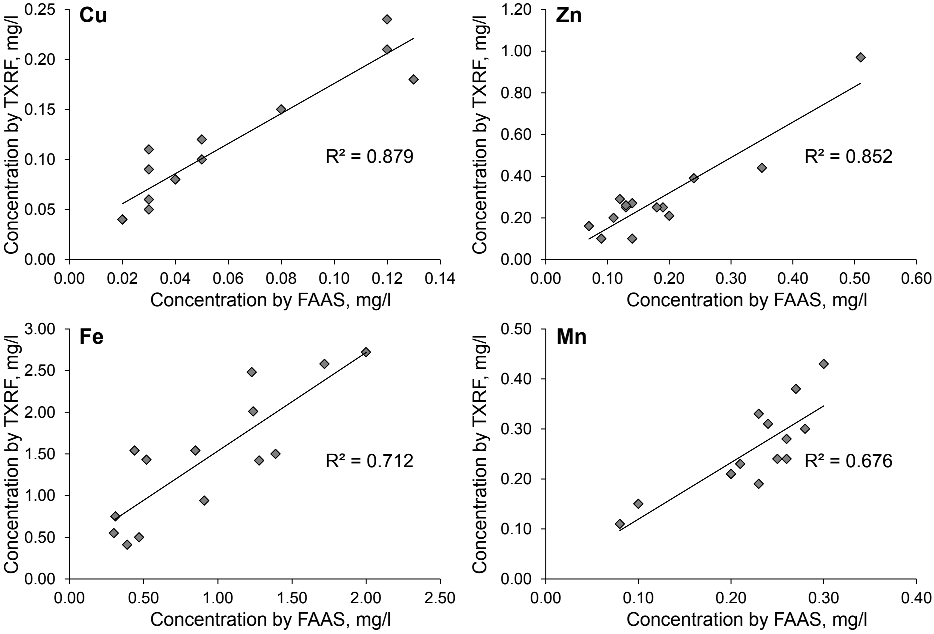

Figure 3.4. **Correlation between the element concentration values measured by TXRF and AAS in liquid consistency food samples (apple wine and apple juice) for Cu, K, Fe, Zn after direct analysis**

Slightly stronger correlation was detected for the analytical measurements of mineralised samples than for sample analysis without any pretreatment, e.g., Pearson correlation coefficients for Cu, Zn, Fe and Mn in solid consistency samples after mineralization were 0.922, 0.948, 0.714 and 0.606, respectively.

Statistical analysis of data showed that for several elements (e.g., Cu, Fe, Mn, Zn) obtained results are well comparable among the applied analytical methods; however, in case of elements with low concentration in samples methodological distinctions are of a greater impact. In the study in each case optimal analytical method was used.

3.1.3. Comparative evaluation of food sample pretreatment procedures

Sample pretreatment such as wet digestion or dry ashing has to be applied to destroy organic matrix of the biological and environmental samples that can influence the precision of measurements of micro- and macroelement quantitative detection by analytical techniques (Welna et al., 2011). As it was described in chapter *Materials and Methods*, one honey sample was treated in several treatment ways to assess the possible influence of sample matrix and the treatment procedures. In this case, high content of carbohydrates can influence the accuracy of detection of micro- and macroelement concentration. Comparative measurements were done by AAS and TXRF. Measurements done by TXRF showed that dry ashing helps to destroy sample matrix more efficiently as spectral intensity was detected in higher rate and background fluctuations of signal were at minimum; that allows more effective quantitative measurements of elements. On the contrary, analysis of honey sample water solution by TXRF revealed the disturbances caused by background influence. It can seriously affect quantitative detection of element content, especially, if concentration of elements is expected to be very low. Results revealed that wet digestion allows elimination of background influence caused by such organic matrix elements as C, N, O, H, S. Spectral analysis revealed that background influence is significantly lower after sample wet digestion than in case of samples in water solution. Results of analysis for several elements are summarized in Table 3.5.

Table 3.5

Influence of pretreatment procedure on precision of element concentration measurements in a randomly selected honey sample detected by TXRF and AAS

Element	Concentration ($\bar{x}$±*s; n_m=5*), mg/kg (Coefficient of variation, %)					
	Wet digestion		Water solution		Dry ashing	
	TXRF	AAS	TXRF	AAS	TXRF	AAS
Ca	48.9±5.5 (11)	74.7±2.3 (3)	69.8±9.2 (13)	57.7±1.9 (3)	92.5±11.3 (12)	161.2±3.7 (2)
Co	-	<0.004	-	0.005±0.001 (23)	-	0.005±0.001 (20)
Cr	<0.26	<0.01	<1.59	<0.01	-	0.020±0.005 (20)
Cu	0.42±0.05 (12)	0.17±0.01 (6)	0.34±0.05 (15)	0.13±0.02 (15)	0.95±0.14 (15)	1.47±0.28 (19)
K	905±69 (8)	1342±56 (4)	1356±209 (15)	1600±378 (24)	677±65 (10)	963±77 (8)
Mn	2.17±0.09 (4)	1.93±0.02 (1)	3.97±0.71 (18)	1.85±0.22 (12)	1.19±0.11 (9)	1.89±0.09 (5)
Na	-	5.75±0.59 (10)	-	8.67±1.19 (14)	-	123.32±22.16 (18)
Ni	0.32±0.05 (16)	<0.04	<0.43	0.11±0.01 (6)	0.04±0.01 (23)	0.10±0.02 (18)
Rb	1.94±0.05 (3)	-	0.83±0.09 (11)	-	0.84±0.08 (9)	-
Sr	<0.13	-	-	-	0.53±0.05 (9)	-
Zn	0.64±0.04 (6)	<0.47	0.74±0.09 (12)	0.35±0.03 (8)	0.43±0.05 (12)	0.63±0.11 (17)

Dry ashing and wet digestion can be assessed as more efficient sample pretreatment methods than sample dissolution in water which can result in more precise quantitative results. Although sample analysis after dry ashing revealed higher levels of elements, it cannot be assessed as the best method due to several limitations such as higher risk of sample contamination and losses of volatile elements. Therefore wet digestion can be estimated as the most optimal pretreatment procedure that also is affirmed by lower dispersion values of obtained results such as standard deviation and coefficient of variation than it was observed for other sample pretreatment procedures. However, values or coefficient of variation can be negatively affected by the fact that for some elements measured element concentration was close to the limit of detection of applied analytical methods.

3.2. Concentration of elements in studied food samples

3.2.1. Concentration of elements in food of plant origin

Root vegetables. Samples of onions *Allium cepa* ($n_s=98$), carrots *Daucus carota* ($n_s=81$) and potato tubers *Solanum tuberosum* ($n_s=55$) as well as samples of potato peel ($n_s=6$) were collected over the territory of Latvia as shown in schematic maps (Figures 3.5, 3.6 and 3.7).

Figure 3.5. **Origin of onion (*Allium cepa*) samples**[1]

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[1] Here und further number of a sample is indicated on the map

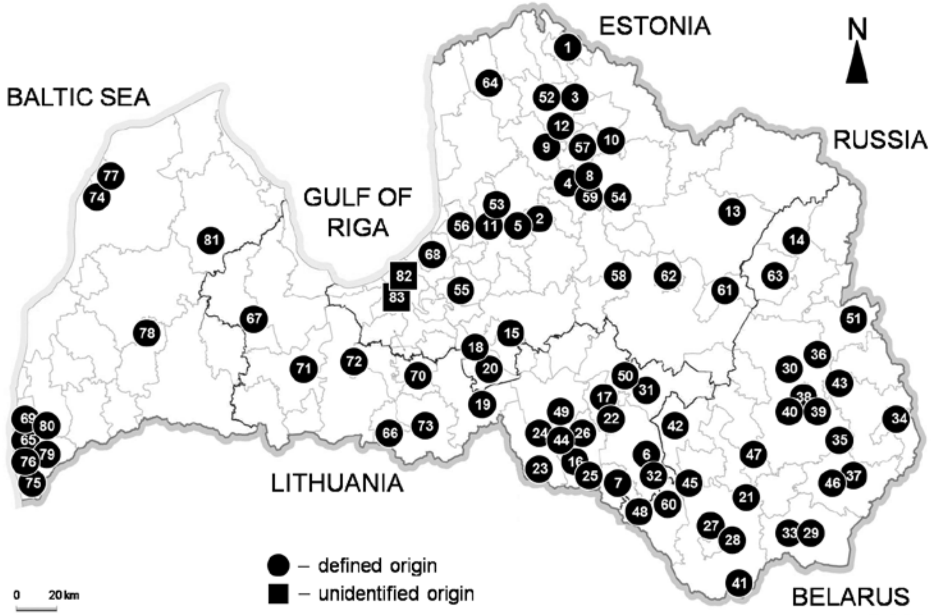

Figure 3.6. **Origin of carrot (*Daucus carota*) samples**

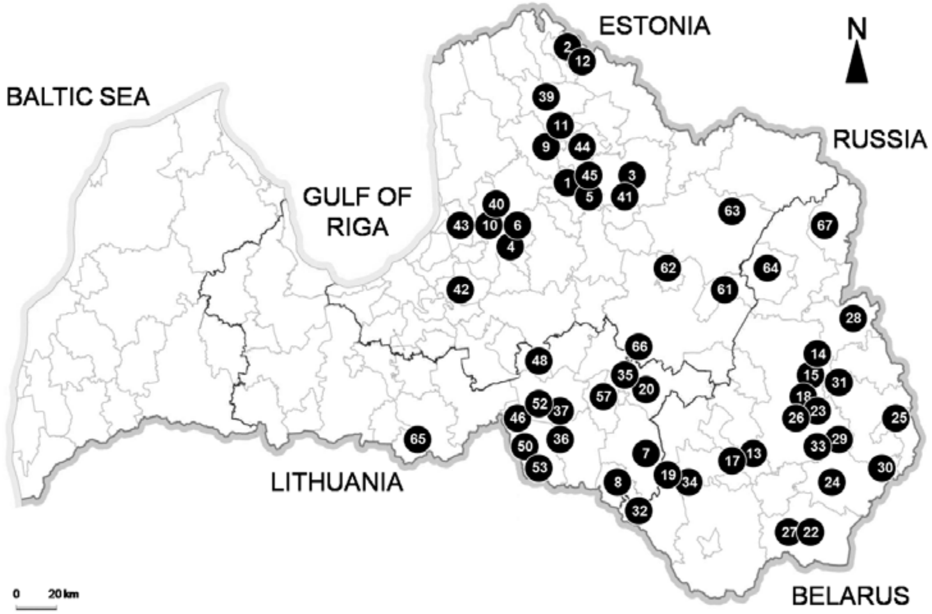

Figure 3.7. **Origin of potato (*Solanum tuberosum*) samples**

Nine microelements (As, Cd, Co, Cr, Cu, Ni, Pb, Se and Zn) were quantified, concentration is expressed as mg/kg of dry weight (DW), if not stated otherwise. Mean moisture content of samples was determined to be 90 % for onion bulbs, 91 % for carrot roots and 78 % for potatoes.

The sequence of analyzed microelements in edible parts of root vegetables grown in Latvia was detected as follows: Zn >Cu >Ni >Pb >Cr >Cd >Co >As >Se (based on mean values). Zn was the element detected in the highest concentration. The widest range of Zn concentration was discovered for onion bulbs and carrot roots, 8.11-24.38 mg/kg (mean 14.80 mg/kg) and 2.88-21.01 mg/kg (mean 9.02 mg/kg), respectively (Figure 3.8). However, one outlier appeared among the samples of onion bulbs up to 40.66 mg/kg. Potato tubers contained the lowest content of Zn (mean 6.35 mg/kg), while values for potato peel were at medium level (mean 8.36 mg/kg).

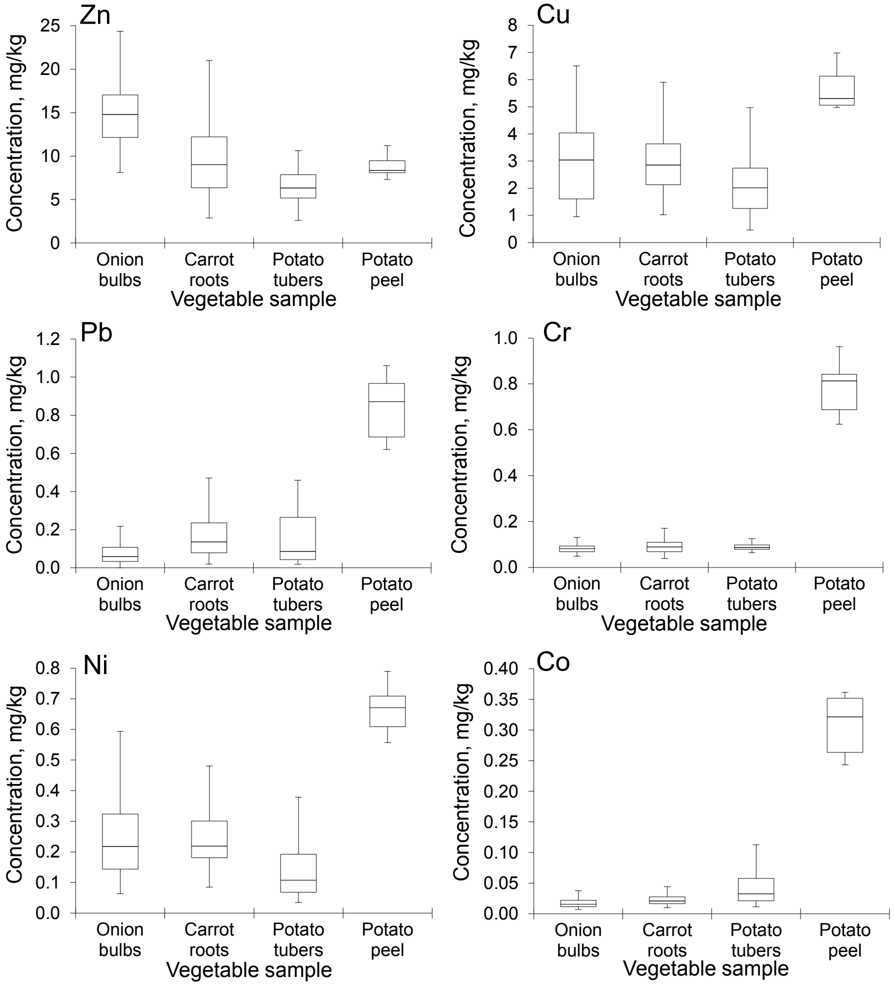

Figure 3.8. **Concentration of Zn, Cu, Pb, Cr, Ni and Co detected in samples of root vegetables**

Literature data show that in root vegetables collected in Finland comparable Zn concentration has been detected: in onion bulbs 13-22 mg/kg, in carrot roots 21-23 mg/kg and in potato tubers 10 mg/kg (Ekholm et al., 2007). Also data from study of vegetables in Egypt were similar: mean concentration of Zn detected in onions was 11.4 mg/kg, in carrots 7.69 mg/kg and in potatoes 7.16 mg/kg (Radwan and Salama, 2006).

Cu concentration in root vegetables grown in Latvia varied in similar range (range of mean values 2.01-3.04 mg/kg), while potato peel contained the highest levels of copper (mean 5.14 mg/kg). Pb is one of the toxic elements that may cause significant adverse effects for human health (Hashmi et al., 2007; Kumar et al., 2007). Lowest concentration of Pb was detected in onion bulbs. Carrot roots and potato tubers contained similar concentration of Pb (from 0.02 to 0.47 mg/kg), but potato peel samples contained about 10 times higher concentration (range 0.62-1.06 mg/kg and mean 0.81 mg/kg) of Pb than any mean values for edible parts of analyzed root vegetables (Figure 3.8). Also a study in Denmark revealed that vegetables with peel contained much higher concentration of Pb than without peel. If vegetables were grown in contaminated soil, i.e., Pb content in potatoes with peel reached up to 0.226 mg/kg WW (wet weight), while concentration of Pb in potatoes without peel was only 0.013 mg/kg WW (Samsoe-Petersen et al., 2002). Potato tubers of different cultivars grown in Spain contained 1.76-5.60 mg/kg of Zn and 0.23-2.29 mg/kg of Cu (Rivero et al., 2003), but in a study of organically grown potatoes in Denmark the content of Zn was 1.98-7.50 mg/kg WW, Cu 0.37-1.51 mg/kg WW and Pb 0.0025-0.024 mg/kg WW (Bibak et al., 1998). Finnish scientists comparing microelement content in vegetables grown in Finland between 1970s and 2000s found that concentration of such elements as Co, Cu, Ni and also Zn has a tendency to decrease by 25 %, while concentration of Se and Pb in 2000s was detected higher (Ekholm et al., 2007).

Wide range of Ni concentration was observed for all analyzed root vegetables (from 0.034 mg/kg in potato tubers up to 0.594 mg/kg in onion bulbs). Cr and Co were detected in comparably low amounts in edible parts of root vegetables. In comparison with edible parts of vegetables potato peel contained the exaggeratedly high values of Ni (mean 0.60 mg/kg), Cr (mean 0.65 mg/kg) and Co (mean 0.35 mg/kg) (Figure 3.8). A Finnish study showed that carrots grown in Finland contained similar amounts of Ni and Co with the current study, respectively, 0.48-0.60 mg/kg and 0.03-0.04 mg/kg, (Ekholm et al., 2007). The data from a study with carrots grown in industrial area of Greece showed that carrot roots can contain very high levels of elements, e.g., Cr up to 8.62 mg/kg and Co up to 3.29 mg/kg (Voutsa and Samara, 1998), while other study from agricultural areas of Greece revealed that carrots contain Cr 0.062-0.160 mg/kg WW and Co 0.009-0.023 mg/kg WW (Stalikas et al., 1997).

Results regarding As were similar to those obtained for Ni, Cr and Co where edible parts of vegetables contained significantly lower concentration than potato peel. Cd content in the widest range was detected in carrot roots (0.030-0.324 mg/kg), but the highest average value referred to potato peel (mean 0.147 mg/kg) (Figure 3.9).

Other studies revealed different ranges of Cd concentration in vegetables. For example, vegetables grown in Egypt contained 0.012-0.029 mg/kg, 0.006-0.018 mg/kg and 0.015-0.026 mg/kg of Cd, respectively, onions, carrots and potatoes (Radwan and Salama, 2006); but results from Finnish study showed the following mean values of Cd concentration: in

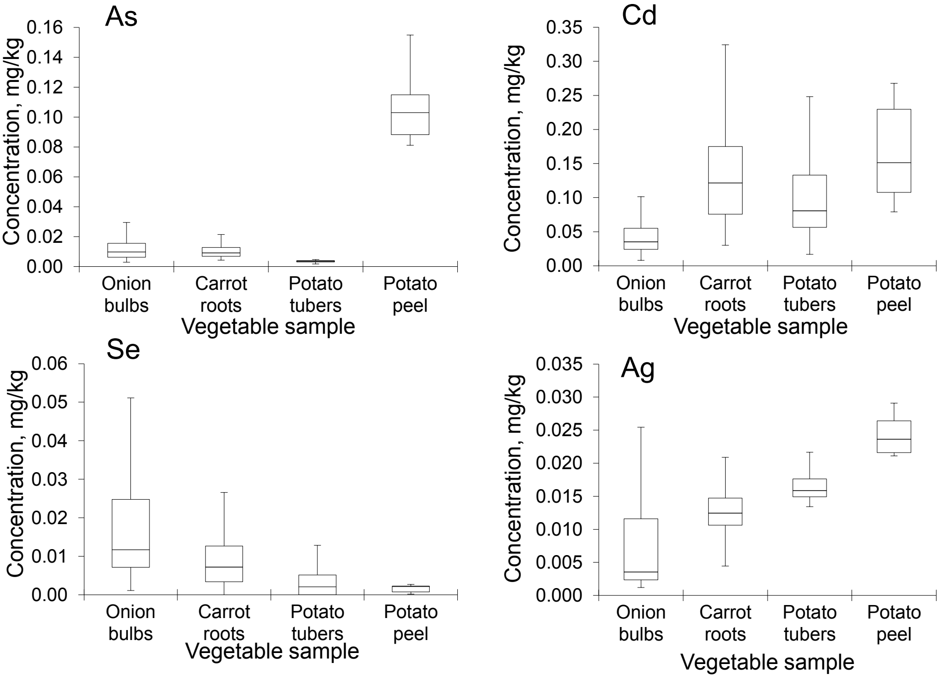

Figure 3.9. **Concentration of As, Cd, Se and Ag detected in samples of root vegetables**

onions 0.03-0.15 mg/kg, in carrots 0.12-0.28 mg/kg and in potatoes 0.07 mg/kg (Ekholm et al., 2007). Other study in Romania revealed that carrot roots may contain Cd up to 3.39 mg/kg (Soceanu et al., 2007), but Cd content in carrot roots grown near zinc plant in China reached up to 9 mg/kg (Zheng et al., 2007). Thus, the impacts of the basic soil composition, soil contamination level in each study site as well as agricultural practices (for example, compostion and application of fertilizers) may have major impact on the metal accumulation. Organically grown potatoes contained very low concentration of Cd (0.006-0.040 mg/kg WW) (Bibak et al., 1998).

Different results were detected for Se. Onion bulbs were richest in Se (range 0.001-0.051 mg/kg), followed by carrot roots (a range from less than LOD to 0.027 mg/kg) and potato tubers (a range from less than LOD to 0.013 mg/kg), but potato peel contained the lowest concentration of Se (<0.003 mg/kg) (Figure 3.9.), thus indicating the element behaviour and speciation form importance on its accumulation.

It has been reported in the past that soil in Latvia contained Se 0.054-0.340 mg/kg and was estimated as selenium deficient soil. There are some plant species such as *Allium sp.* that are tended to accumulate selenium (Duma et al., 2011; Zegnere and Alsina, 2008). Current study also revealed that the highest concentration of Se was detected in onion samples. Se enrichment of soils nowadays is applied in agriculture practice worldwide (Ekholm et al., 2007; Hawkesford and Zhao, 2007); however, there were no information available of possible Se enrichment of soils in Latvia.

As and Se in vegetables have been detected only in few studies. For example, onion bulbs analyzed in Spain contained 0.039 mg/kg of As and 0.010 mg/kg of Se but carrot roots 0.241 mg/kg of As and 0.059 mg/kg of Se (Matos-Reyes et al., 2010). As and Se concentration in carrots grown in an industrial area in Greece was 0.02-0.05 mg/kg of As and 0.02-0.63 mg/kg of Se (Voutsa and Samara, 1998), while in carrot samples from agricultural areas of Greece As and Se were detected below the detection limits (Stalikas et al., 1997). The study in Bangladesh revealed that in a case of As and also some metals, soil characteristic parameters are of importance, e.g., moisture content of soil organic matter, pH, soil texture and oxidation/reduction properties (Alam et al., 2003).

Within the European legislation there were maximum levels set for some metals in root vegetables and peeled potatoes: for Pb 0.10 mg/kg WW and for Cd 0.10 mg/kg WW (EC Regulation 1881, 2006). Recalculation of characteristic values obtained within the current study from units of dry weight to units of wet weight revealed that maximum levels of certain contaminants in analyzed root vegetable samples were not exceeded. Only potato peel may contain Pb above 0.10 mg/kg WW; however, peel is not assessed as edible part of vegetables (Table 3.6.), but still this parameter can be used for environmental monitoring purposes.

Table 3.6

Concentration of potentially toxic elements Cd and Pb detected in samples of root vegetables, recalculated to mg/kg wet weight

Sample	Concentration (x_{min}-x_{max} ($\bar{x}$))[1], mg/kg WW	
	Pb	Cd
Onion bulbs	0.0000-0.0324 (0.0081)	0.0008-0.0201 (0.0049)
Carrot roots	0.0018-0.0898 (0.0172)	0.0026-0.0322 (0.0119)
Potato flesh	0.0041-0.0992 (0.0316)	0.0036-0.0612 (0.0208)
Potato peel	0.1342-0.1745 (0.2290)	0.0318-0.0578 (0.0171)

Analysis of macroelements in root vegetables revealed that K and Ca are the most abundant elements. Data showed that carrots contained twice more of K and Ca than onions. Also the concentration of Na, Mg and Fe in carrot roots was significantly higher than in onion bulbs (Table 3.7). The comparison of element concentration in potato peel and edible parts of vegetables revealed that there is significantly higher concentration of elements in peel, for example, Fe concentration in potato peel was more than 30 times higher and Mn concentration more than 7 times higher than in potato flesh that confirms the barrier function of peel (Samsoe-Petersen et al., 2002).

The observed concentration sequence of macroelements K >Ca >Mg >Na in onions grown in Latvia refers to literature data where onion cultivars grown in United Kingdom (Chope and Terry, 2009) and Finland (Ekholm et al., 2007) were analyzed. However, in the research done by A.E. Mohamed with colleagues (2003), where was investigated element concentration in vegetable samples from Saudi Arabia, the macroelements ranked

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[1] Here and further x_{min} – minimal value, x_{max} – maximal value

Table 3.7

Concentration of macroelements detected in samples of root vegetables

Element	Concentration (x_{min}-x_{max} ($\bar{x}$)), mg/kg			
	Onion bulbs (n_s=98)	Carrot roots (n_s=81)	Potato bulbs (n_s=55)	Potato peel (n_s=6)
Ca	543.98-2850.18 (1344.39)	2042.76-5154.75 (3327.41)	83.64-458.72 (186.70)	597.03-1383.89 (861.67)
Fe	8.77-45.66 (17.98)	9.71-460.43 (30.86)	5.96-22.89 (15.87)	462.79-850.64 (593.20)
K	9598.32-28417.55 (17457.06)	7906.00-63475.66 (29499.53)	13780.49-27600.68 (20878.39)	31725.69-42023.05 (38093.00)
Mg	455.19-1458.50 (791.92)	461.65-3097.23 (1407.51)	587.47-1458.94 (1047.67)	1412.30-2063.95 (1631.66)
Mn	4.52-33.56 (10.89)	2.35-47.54 (9.06)	2.68-15.43 (5.50)	28.34-46.49 (37.42)
Na	8.70-1204.41 (153.59)	150.40-13928.48 (2082.48)	0.56-46.46 (11.48)	16.14-76.55 (53.04)

in a different sequence, i.e., Ca >K >Mg >Na. Conditions in Saudi Arabia differ much from those in Latvia, therefore, the detected differences obviously confirm that vegetable and plant composition is dependent on site specific conditions as climate regime and soil composition.

In general, the macroelement content of root vegetables grown in Latvia was comparable with results from other countries with similar climatic conditions, e.g., carrots in Finland contained K 23300-26500 mg/kg, Ca 2140-2250 mg/kg, Mg 1210-1500 mg/kg and Fe 30-34 mg/kg (Ekholm et al., 2007).

Leafy vegetables. Lettuce *Lactuca sativa* samples, randomly selected samples grown in Latvia (n_s=7) and samples grown in contaminated soil (n_s=3) were analysed to detect quantitative concentration of elements (Figure 3.10).

Concentration of elements detected in lettuce samples grown in contaminated soil is not included in overall assessment, but it is discussed in the next chapter in the context of impact of pollution on element concentration in food.

Twelve microelements (As, Ba, Cd, Co, Cu, Mn, Ni, Pb, Rb, Se, Sr, Zn) and five macroelements (Ca, Fe, K, Mg, Na) were quantified. In higher concentration there were detected such elements as Mn, Zn, Cu, Sr of which mean concentration was near or above 20 mg/kg (Figure 3.11.), while the concentration of other microelements varied but in average were in lower concentration.

In comparison with other studies currently detected concentration of such microelements as Zn and Rb was in good compatibility, but concentration of Mn, Cu and Sr in other studies of lettuce was detected lower. For example, in a study done by D. Kelly and A.S. Bateman (2010) in the UK concentration of Mn in lettuce samples was detected about 7-27 mg/kg, Zn 20-43 mg/kg, Cu 4-11 mg/kg, Sr 1.8-16.0 mg/kg and Rb 0.1-35.0 mg/kg.

Among the macroelements the highest concentration in analysed lettuce samples was detected for K and Ca, followed by Mg, Na and Fe, based on the mean values (Table 3.8).

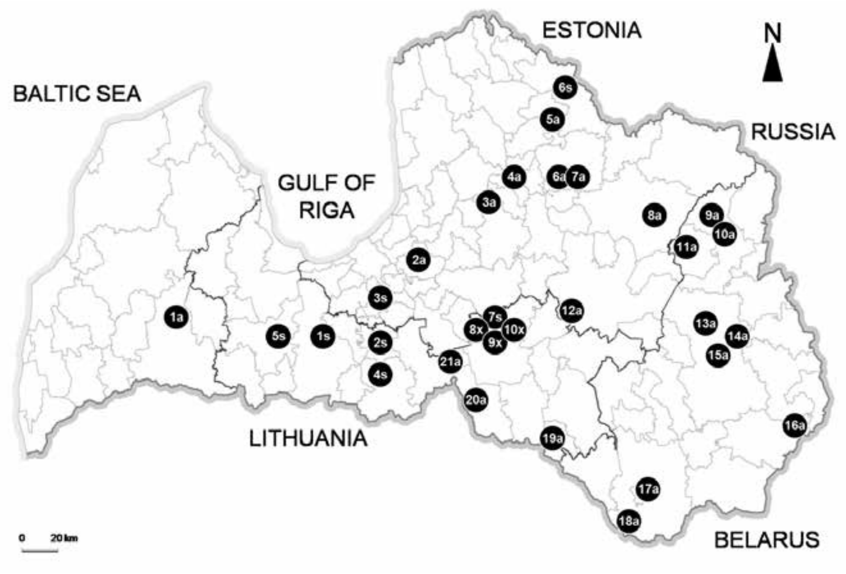

Figure 3.10. **Origin of collected lettuce (*Lactuca sativa*) samples (s) and samples grown in contaminated soil (x); origin of apple (*Malus domestica*) fruit samples (a)**

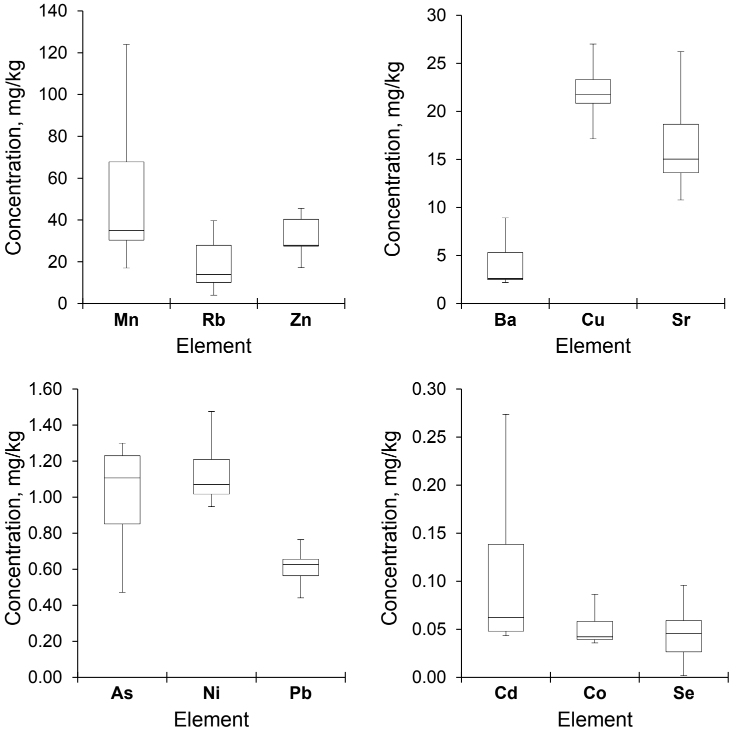

Figure 3.11. **Concentration of microelements detected in samples of lettuce**

Table 3.8

Concentration of macroelements detected in samples of lettuce

Element	Concentration (x_{min}-x_{max} ($\bar{x}$); n_s=7), mg/kg	
Ca	7163.32-13 232.29	(10 291.54)
Fe	35.67-53.20	(43.86)
K	59 513.35-103 944.14	(75 368.14)
Mg	2405.17-4896.56	(3650.26)
Na	613.14-4228.94	(1545.67)

Concentration of macroelements detected in the current study was higher in comparison to other studies, but the tendencies of element distribution were similar. In the study done in the UK concentration of macroelements in lettuce samples was measured in following ranges: about 10-1600 mg/kg Na, 1500-2500 mg/kg Mg, 26 000-42 000 mg/kg K, 500-3700 mg/kg Ca and 25-77 mg/kg Fe (Kelly and Bateman, 2010).

Fruits. Apple tree *Malus domestica* fruit samples (n_s=21) collected over the territory of Latvia (Figure 3.10) were analysed. Fifteen microelements (Ag, As, Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, Rb, Se, Sr, V, Zn) and five macroelements (Ca, Fe, K, Mg, Na) were quantitatively detected in peeled apple fruit flesh and in peel samples (n_s=3).

In apple fruit flesh the highest concentration was detected for such elements as Rb, Cu, Mn, Zn, Sr and Ba which mean concentration was near or above 1 mg/kg (Figure 3.12.), while the concentration of other microelements was lower.

In the study of apple fruit analysis done in Croatia concentration of microelements in apple fruit flesh was detected as follows: 0.84-7.79 mg/kg Zn, 0.29-1.27 mg/kg Sr, but Mn and Cd concentration was below the limit of detection (Cindric et al., 2012). Concentration of these elements detected in the current study are quite similar for Zn and Sr (0.56-2.16 mg/kg and 0.29-2.54 mg/kg, respectively), but Mn and Cd concentration was in range 1.20-4.50 mg/kg and <LOD-0.003 mg/kg, respectively. I.J. Cindric with colleagues (2012) detected that Mn concentration in peel (4-6 mg/kg) was 2-3 times higher compared to whole apple (0.7-1.7 mg/kg), but Cd was found only in peel, in the concentration range of 0.4-1.1 mg/kg. In samples of apple fruit peel from Latvia higher concentration was detected for several elements, if compared with apple fruit flesh. Mean concentration of these microelements in apple fruit peel/flesh was following: 1.72/1.04 mg/kg for Sr, 1.84/0.91 mg/kg for Ba, 0.47/0.18 mg/kg for Ni, 0.30/0.16 mg/kg for Cr, 0.027/0.010 mg/kg for V, 0.009/0.007 mg/kg for Co and 0.006/0.002 mg/kg for As.

Among the macroelements the highest concentration in analysed apple fruit flesh samples was detected for K, Ca and Mg, followed by Na and Fe, based on the mean values. Concentration of Na was in range from 8.18 mg/kg up to 480.28 mg/kg, but concentration of other macroelements was not so variable (Table 3.9).

Mean macroelement concentration in apple fruit flesh samples from other study done in Croatia was 38 400 mg/kg for K, 8430 mg/kg for Na, 4040 mg/kg for Ca and 2710 mg/kg for Mg (Cindric et al., 2012) which can be assessed as much higher values than detected in average for apple fruit flesh samples in Latvia. Macroelement concentration quantified in apple fruit peel in average was slightly higher than in fruit flesh, respectively,

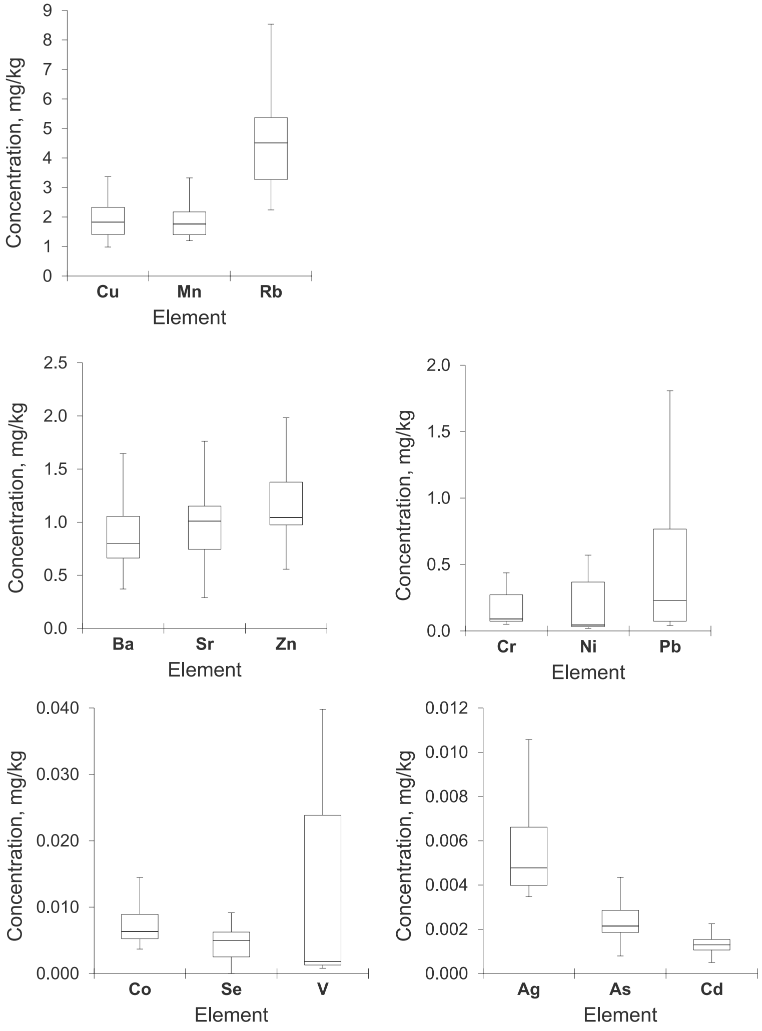

Figure 3.12. **Concentration of microelements detected in samples of apple fruits**

Table 3.9

Concentration of macroelements detected in samples of apple fruits

Element	Concentration (x_{min}-x_{max} ($\bar{x}$±s); n_s=*21*), mg/kg
Ca	158.38-608.33 (332.29±95.67)
Fe	2.80-8.53 (4.86±1.41)
K	7142.86-12 111.31 (9323.55±1392.00)
Mg	256.97-408.04 (315.29±47.23)
Na	8.18-480.28 (39.86±101.16)

544.52 mg/kg for Ca, 6.38 mg/kg for Fe, 10 469.83 mg/kg for K, 321.06 mg/kg for Mg and 31.89 mg/kg for Na.

Cereal products. Samples of cereal meals, i.e., cereal mixtures for porridge preparation were collected within the current study. It should be remarked that due to product specifics only some of the samples were produced in Latvia; however, overall comparison of element concentration in products available for consumption for consumers in Latvia is important issue within the food safety field. Collected products were divided in four subgroups: a) mixed cereal meals (n_s=*10*) containing two or more types of cereals; b) rice meals (n_s=*10*); c) wheat meals (n_s=*12*); d) buckwheat meals (n_s=*11*).

The highest concentration of microelements were detected for Mn, Zn, Cu and Rb. Ranges of concentration varied widely, for example, the highest variation of measured concentration of Mn, Zn and Cu were observed for wheat meal samples (2.31-70.60 mg/kg, 2.54-45.00 mg/kg, and 1.13-9.97 mg/kg, respectively) while the narrowest variation range of Mn, Zn and Cu in average can be attributed to rice meal samples (6.82-13.26 mg/kg, 8.44-13.78 mg/kg, 1.02-4.08 mg/kg, respectively). At the same time some outlier values were detected for rice meal samples, e.g., in two samples Mn concentration was detected up to 58 mg/kg, in one sample 59 mg/kg of Zn and 9 mg/kg of Cu. Amongst mean values the highest were detected in mixed cereal meal samples for Mn and Zn, and in buckwheat meal samples for Cu and Rb (Figure 3.13).

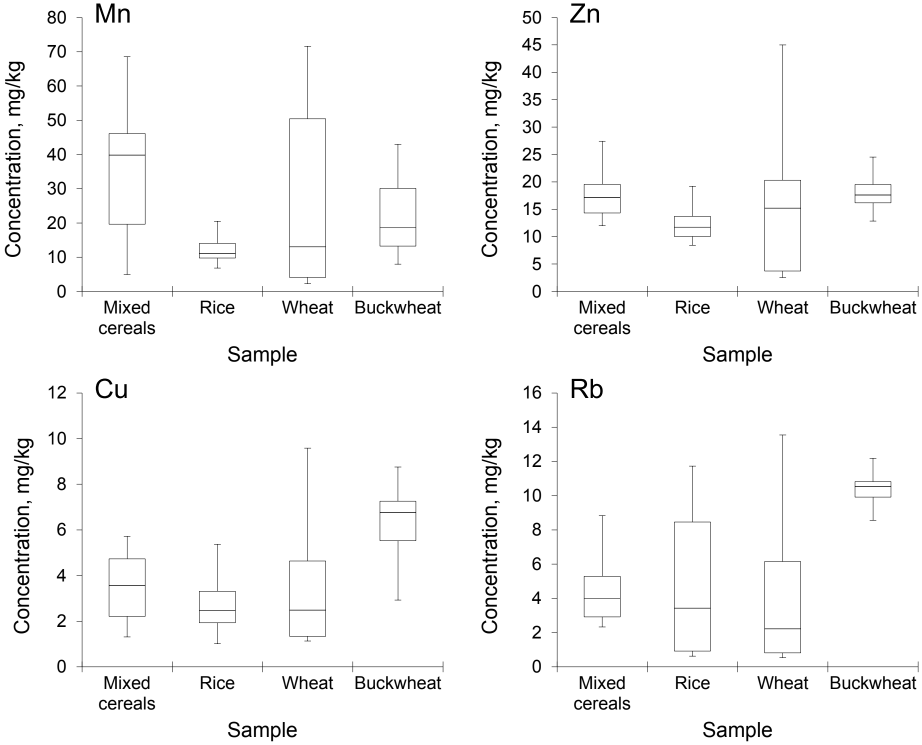

Figure 3.13. **Concentration of Mn, Zn, Cu and Rb detected in samples of cereal meals**

Ni, Se, As, Co, Cd and Pb in cereal meal samples were detected in lower concentration (Figure 3.14). While Se and Co in certain amounts are essential elements, As, Ni, Cd and Pb are elements of concern, especially if detected in food produced for infants and children. Also in literature it is reported that in comparison with milk based infant food, cereal based infant food can contain higher amounts not only of essential elements, but also of toxic elements, such as As, Cd, Sb (Ljung et al., 2011). There is not much information available about As or other microelement concentration in wheat products produced for infants and children, but some comparison can be done. For example, in Spain, infant food with wheat as predominant component contained up to 0.02 mg/kg of total As (Hernandez-Martinez and Navarro-Blasco, 2013). In Sweden, in such organic wheat containing products as spelt flour and semolina intended for infants, As concentration was less than 0.003 mg/kg (Ljung et al., 2011).

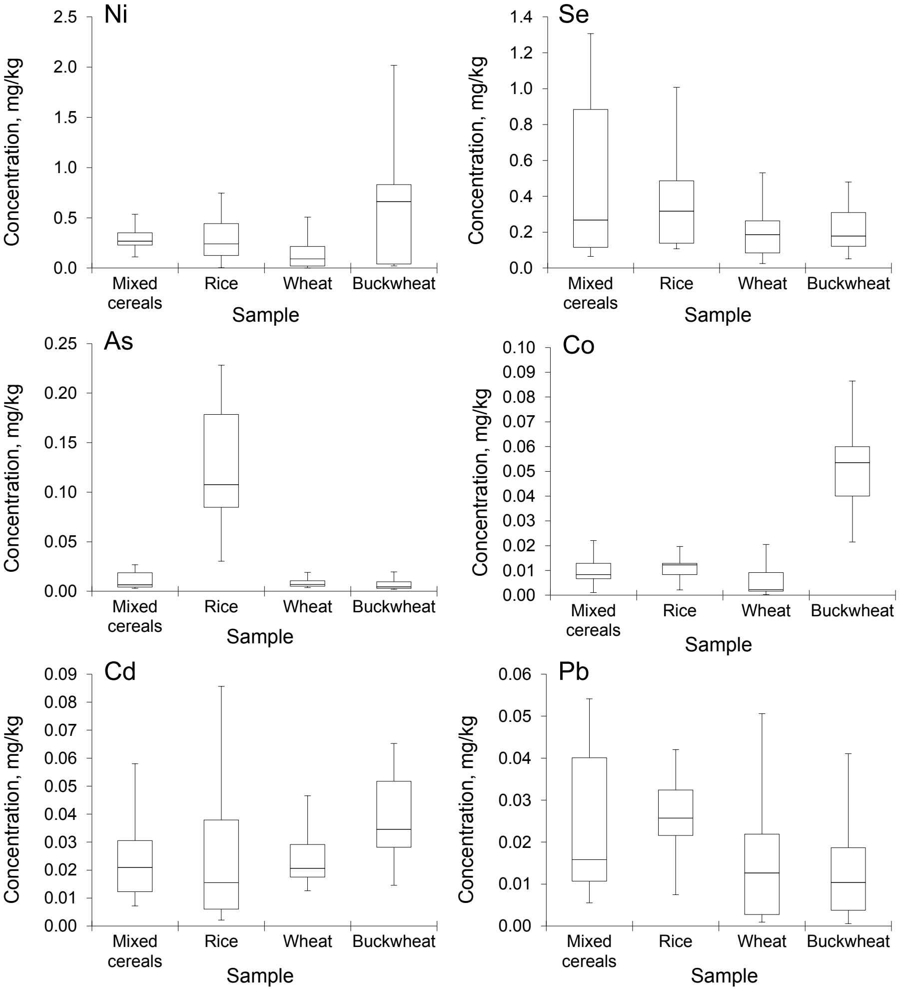

Figure 3.14. **Concentration of Ni, Se, As, Co, Cd and Pb detected in samples of cereal meals**

For the comparison with other food analysis results from a study done in Canada, it can be mentioned that the highest levels of total arsenic were detected in fish (>1 mg/kg), while meat, bakery products and cereals contained lower content of As (0.02-0.03 mg/kg) (Dabeka et al., 1993).

Regular intake of essential elements, minerals and vitamins is very important for human organism, especially, in childhood when growth and development is rapid. Therefore the element entity in diet should be balanced and it is important to avoid the presence of potentially toxic elements in food (Carbonell-Barrachina et al., 2012; Melo et al., 2008).

Among the macroelements the highest concentration was detected for K, Mg and Ca, followed by Na and Fe (Table 3.10).

Table 3.10

Concentration of macroelements detected in samples of cereal meals

Element	Concentration (x_{min}-x_{max} ($\bar{x}$)), mg/kg			
	Mixed cereals (n_s=10)	Rice (n_s=10)	Wheat (n_s=12)	Buckwheat (n_s=11)
Ca	91.86-3487.72 (842.82)	1.00-2849.67 (509.06)	5.90-2102.65 (386.09)	27.40-2418.26 (553.05)
Fe	23.99-90.41 (36.15)	1.85-104.01 (26.10)	3.61-394.40 (54.92)	18.81-102.52 (37.59)
K	3453.75-8654.74 (4555.37)	699.20-5283.40 (2247.83)	1019.89-4972.37 (3065.96)	3078.26-6372.72 (4296.42)
Mg	403.22-994.05 (781.50)	109.31-1656.66 (466.37)	113.65-1755.80 (731.68)	909.33-2403.27 (1659.66)
Na	1.93-2151.79 (457.17)	0.80-1464.52 (261.30)	0.94-1119.16 (178.67)	0.84-1081.62 (189.03)

Mixed cereal meal samples contained higher concentration of Ca, K and Na in average, but wheat cereal meal samples contained significantly higher concentration of Fe. Mg concentration was detected the highest for buckwheat meal samples. Rice meal samples contained lowest mean concentration of Mg and Fe.

3.2.2. Concentration of elements in food of animal origin

Cottage cheese. Samples of cottage cheese (n_s=27) were purchased from randomly selected individual dairy farms and supermarkets in Latvia (Figure 3.15).

All samples chosen were labelled as cottage cheese derived from whole milk, i.e., cottage cheese with content of fat not lower than 9 %. In total it was possible to determine quantitatively seven microelements (Cr, Cu, Fe, Mn, Ni, Pb, Zn) and four macroelements (Ca, K, Mg, Na) in analyzed cottage cheese samples.

The highest concentration was detected for Zn and Fe, 15.34-95.32 mg/kg and 0.51-23.16 mg/kg, respectively; followed by Cu, Mn, Pb, Ni and Cr (Table 3.11).

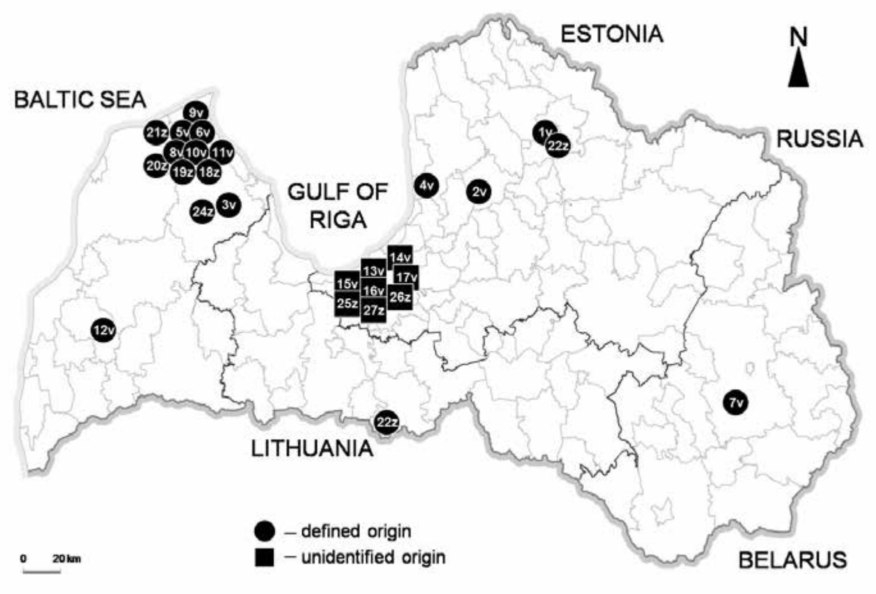

Figure 3.15. **Origin of cottage cheese samples collected over summer season (v) and winter season (z)**

Table 3.11

Concentration of microelements detected in samples of cottage cheese

Element	Concentration (x_{min}-x_{max} ($\bar{x}$±s); n_s=27), mg/kg
Cr	0.023-0.251 (0.086±0.066)
Cu	0.13-1.69 (0.87±0.42)
Fe	0.51-23.16 (5.88±4.75)
Mn	0.15-1.31 (0.56±0.25)
Ni	0.017-0.710 (0.177±0.164)
Pb	0.013-1.065 (0.409±0.333)
Zn	15.34-95.32 (30.52±15.17)

Too high amount of possibly toxic microelements (Pb, Ni, Cr) in cottage cheese arise qualms of potential risk for consumer safety while these elements can bring harmful effects for human health especially after long term intake. There are no maximum contamination levels set for heavy metals in milk products except for Pb. Taking into account the legal regulations of European Commission, the limit for concentration of Pb in raw milk, heat-treated milk and milk for manufacture of milk-based products is set 0.02 mg/kg WW (EC Regulation 1881, 2006).

Most abundant macroelements quantified in cottage cheese samples were Ca and K followed by Na and Mg (Table 3.12).

Table 3.12

Concentration of macroelements detected in samples of cottage cheese

Element	Concentration (x_{min}-x_{max} ($\bar{x}$±s); n_s=27), mg/kg	
Ca	1379.37-12291.22	(4124.44±2016.00)
K	752.98-8865.97	(4512.09±1559.65)
Mg	129.63-533.08	(326.88±89.68)
Na	233.67-1777.05	(970.35±335.11)

As it was not possible to find any previous studies about element content in cottage cheese due to the regional specifics of this foodstuff, obtained results were compared with average content of micro- and macroelements in milk. Numerical outcomes discovered about threefold distinctions among average macroelement content for Ca, K and Mg in favour of cottage cheese. For example, concentration of macroelements in milk are 1120 mg/L for Ca, 1360 mg/L for K, 110 mg/L for Mg and 530 mg/L for Na (Cashman, 2006). In general, content of elements in dairy products mostly is dependent on the composition of elements dairy animal feed (Ayar et al., 2009; Lante et al., 2006) as well and can reveal the content of elements in soil, water and vegetation.

Hen eggs. Samples of hen eggs (n_s=33) were collected from different housing types of poultry farms over the territory of Latvia as well as 24 samples over a year were collected for detection of seasonality impact on element concentration in eggs (Figure 3.16).

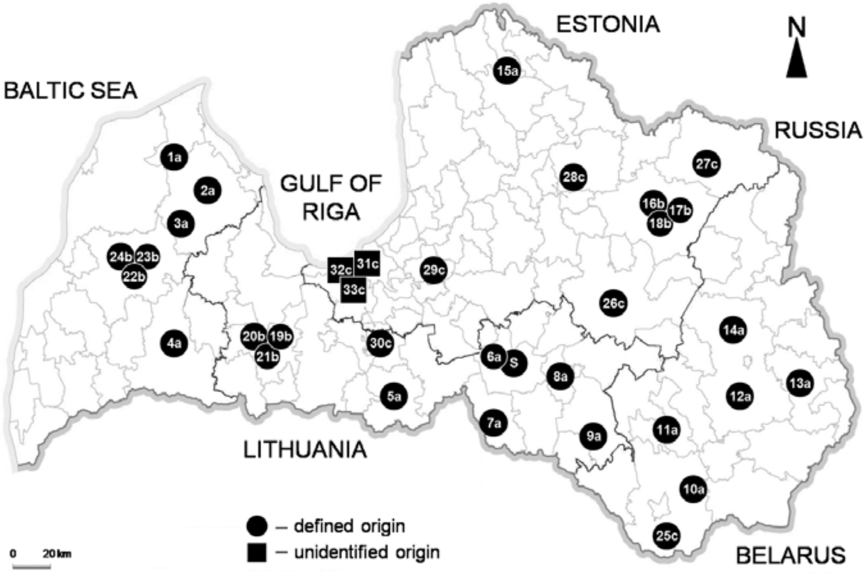

Figure 3.16. **Origin of hen eggs from domestic farms (a), organic farms (b), large-scale poultry farms (c) and samples for seasonality detection (s)**

In overall, twelve microelements (Ba, Cu, Cr, Fe, Mn, Ni, Pb, Rb, Se, Sr, Zn, V) and four macroelements (Ca, K, Mg, Na) were quantitatively detected in egg albumen and egg yolk samples. Element concentration for analysed egg samples are expressed in mg/kg wet weight (WW).

There were detected significant distinctions between element concentration in egg yolk and egg albumen samples. Concentration of Fe, Zn, Cu and Mn was much lower in egg albumen samples (mean values 1.8 mg/kg, 0.5 mg/kg, 0.4 mg/kg and 0.2 mg/kg, respectively) than in egg yolk samples (mean values 59 mg/kg, 39 mg/kg, 1.6 mg/kg and 0.7 mg/kg, respectively). Concentration of Ba and Rb varied in wide amplitude but in average was higher for egg albumen samples (Figure 3.17).

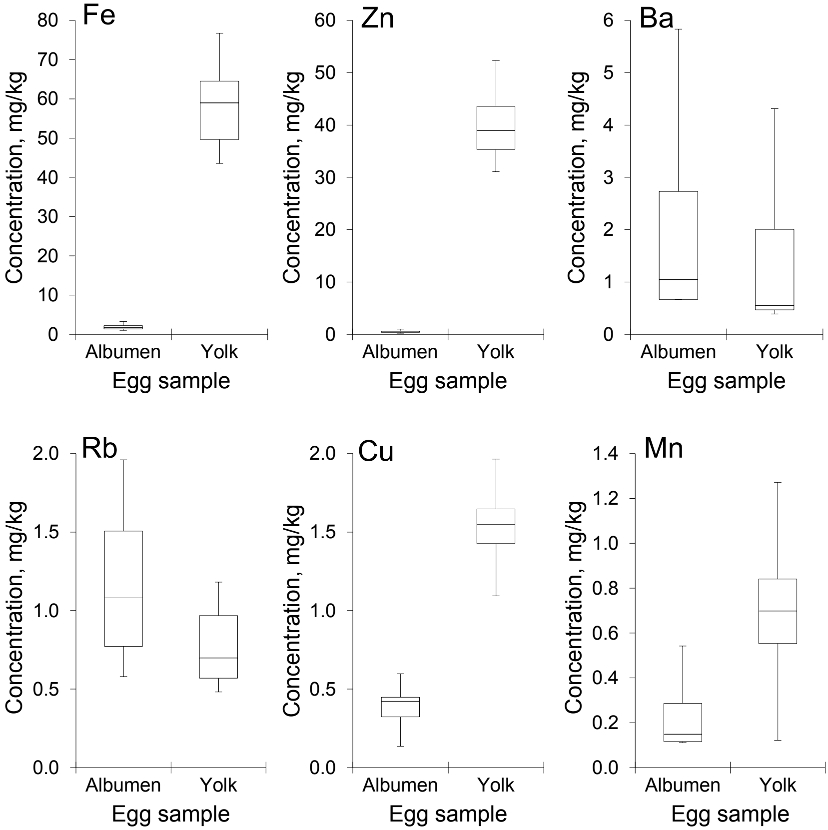

Figure 3.17. **Concentration of Fe, Zn, Ba, Rb, Cu and Mn detected in samples of hen eggs**

Detected concentration of Sr, Cr, Ni, Se, V and Pb also varied according to analysed sample type. While concentration of Sr and Se was significantly lower in egg albumen, concentration of Cr and Pb was comparable in both groups of samples. But such elements as Ni and V were not detected in egg yolk and only quantified in egg albumen samples (Figure 3.18).

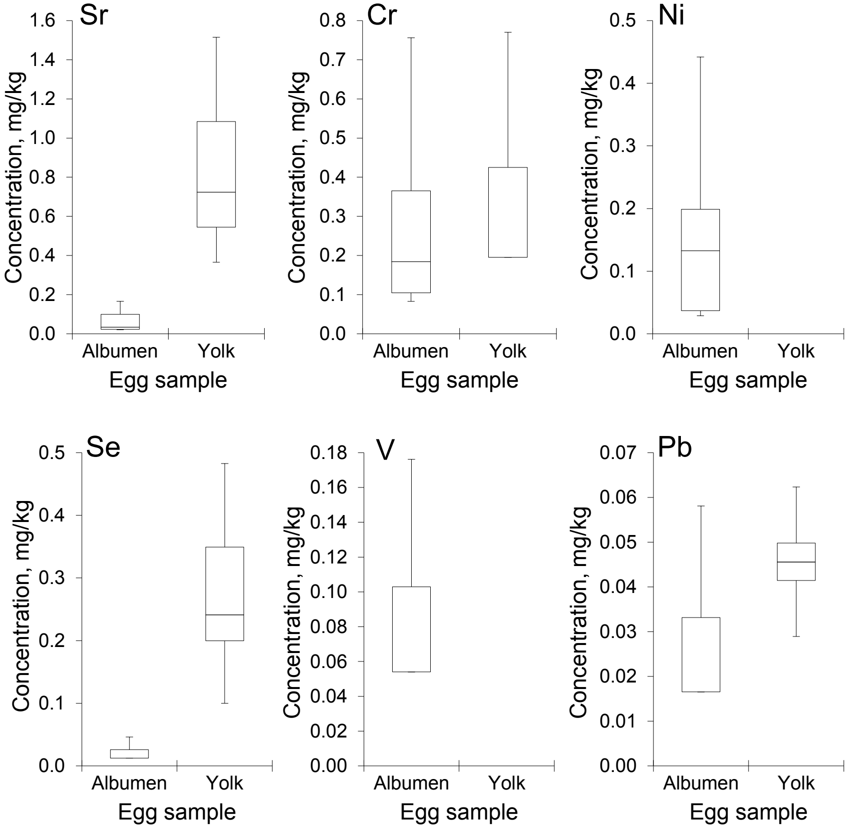

Figure 3.18. **Concentration of Sr, Cr, Ni, Se, V and Pb detected in samples of hen eggs**

In comparison with values from other studies it was observed that obtained data are in good compliance with overall tendencies. Higher concentration of Cr was detected in egg samples from Belgium, Pb in samples from Italy, but Fe concentration was similar in egg samples from countries with southern climatic conditions such as Brazil, Italy and Turkey (Table 3.13).

Table 3.13

Average concentration of several microelements in samples of hen eggs from different countries

(after Briggs and Wahlqvist, 1998; Waegeneers et al., 2009b)

Country	Sample type	Concentration, mg/kg							
		Co	Cr	Cu	Fe	Mn	Pb	Se	Zn
Belgium	Whole egg	-	0.485	-	-	-	0.099	-	19.8
Brazil	Whole egg	-	-	-	110.9	-	-	-	68.6
Greece	Egg albumen	0.0011	0.068	0.25	-	0.035	-	0.066	1.4
	Egg yolk	0.0049	0.090	1.28	-	0.705	-	0.217	21.2
Italy	Egg yolk	-	-	-	119.1	-	0.260	-	77.6
Latvia*	Egg albumen	-	0.152	0.39	1.9	0.121	0.006	0.004	0.7
	Egg yolk	-	0.071	1.54	58.7	0.588	0.076	0.272	40.0
	Whole egg	-	0.052	0.95	26.5	0.278	0.072	0.113	14.6
Poland	Egg albumen	0.0016	0.022	0.24	0.2	0.047	-	0.087	0.2
	Egg yolk	0.0044	0.235	1.65	70.3	0.648	-	0.327	43.0
Turkey	Whole egg	-	-	2.70	112.0	-	0.061	-	67.5

** Current research*

The highest macroelement concentration was detected in egg albumen for Na, while egg yolk contains more Ca. Such elements as Mg and K in average were distributed roughly equally in egg yolk and egg albumen samples (Table 3.14).

Table 3.14

Detected concentration of macroelements in egg samples

Element	Concentration (x_{min}-x_{max} ($\bar{x}$); n_s=33), mg/kg	
	Egg albumen	Egg yolk
Ca	36.83-60.97 (49.72)	814.37-1461.14 (1063.27)
K	839.85-1255.12 (1098.30)	704.57-1495.86 (973.92)
Mg	81.39-179.26 (114.77)	47.14-129.24 (108.20)
Na	1053.08-2677.95 (1621.20)	211.71-706.76 (546.32)

In comparison with the data found in food fact sheets (USDA, s.a.) it can be observed that element distribution in egg yolk and albumen is similar (Figure 3.19.)

In general, egg yolk samples are richer in micro- and macroelement than egg albumen samples.

Bee products. Within the group of bee products honey (n_s=80), pollen (n_s=5) and bee bread (n_s=5) samples were collected over the territory of Latvia (Figure 3.20).

Quantitative analysis of bee products allowed detection of concentration for ten microelements (Cd, Co, Cr, Cu, Mn, Ni, Pb, Rb, Sr, Zn) and seven macroelements (Ca, Fe, K, Mg, Na, P, S). Concentration of elements for analysed bee product samples is expressed in mg/kg wet weight (WW).

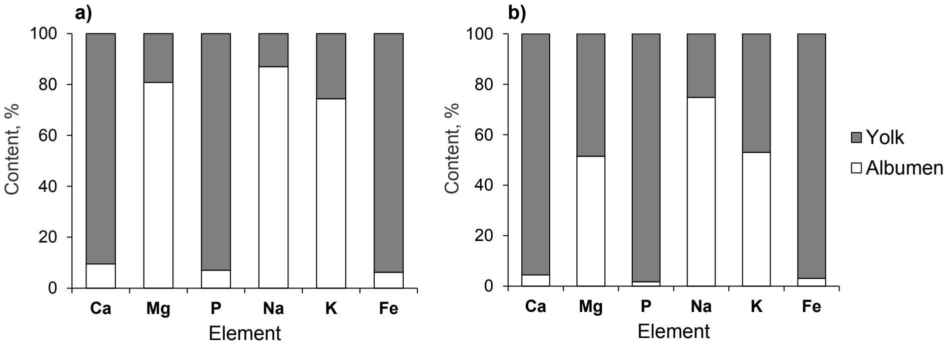

Figure 3.19. **Comparison of distribution of some elements in egg yolk and albumen: a) after data from literature (USDA, s.a.); b) current research**

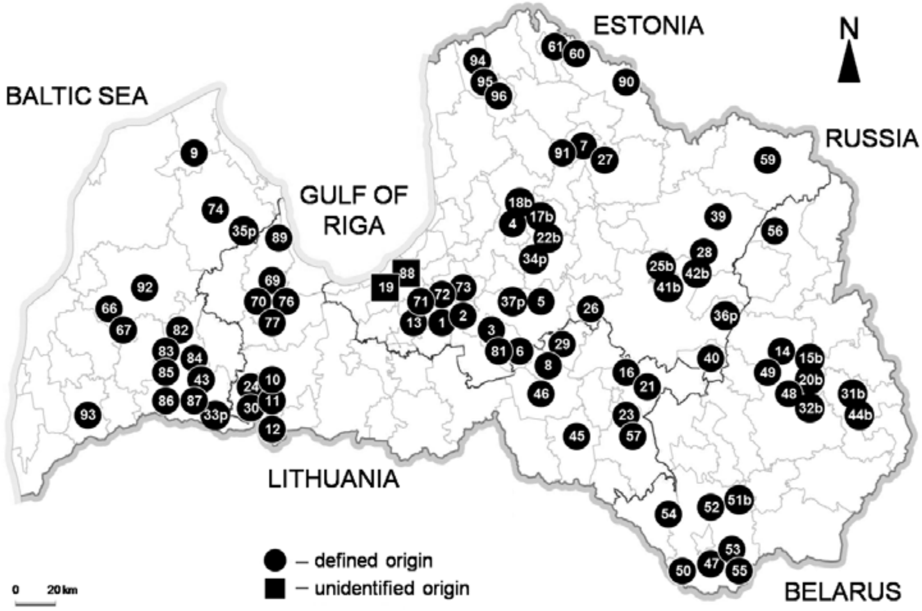

Figure 3.20. **Origin of bee products: pollen and bee bread (p), and honey, including samples from organic farms (b)**

In general, pollen and bee bread samples contained significantly higher element concentration than honey samples. For example, Cd concentration in pollen was 33 times higher, Cu – 29 times higher, Ni – 8 times higher and Pb – 15 times higher than detected in honey samples (Table 3.15). Presence of such elements as Cd and Pb in the samples of bee products suggests the important influence of environmental conditions. Studies done in other countries reveal that content of Cd may vary from concentration near the limit of detection in honey samples, e.g., from Hungary, Poland, Lithuania, Switzerland and Czech Republic from (<LOD-1.55 μg/kg) up to 270-350 μg/kg in samples from Macedonia and Italy, respectively (Buldini et al., 2001; Stankovska et al., 2008; Vincēviča-Gaile, 2010). The lowest concentration of Pb was detected in honey samples from Poland, Lithuania and Switzerland (<LOD-3 μg/kg), but significantly higher concentration of Pb was detected in samples from Slovenia – up to 79.1 mg/kg (Vincēviča-Gaile, 2010), while Pb and Cd concentration in honey samples from Latvia are tended to be very low (mean 0.03 mg/kg and 0.008 mg/kg, respectively).

Table 3.15

Concentration of microelements in analysed bee products

Element	Concentration (x_{min}-x_{max} ($\bar{x}$)), mg/kg		
	Honey (n_s=80)	Pollen (n_s=5)	Bee bread (n_s=5)
Cd	0.002-0.150 (0.008)	0.09-0.62 (0.27)	0.02-0.12 (0.06)
Co	0.005-0.122 (0.011)	0.03-0.10 (0.05)	0.01-0.03 (0.02)
Cr	0.015-0.314 (0.175)	0.06-0.08 (0.07)	0.08-0.75 (0.22)
Cu	0.06-1.43 (0.28)	5.92-12.92 (8.19)	2.57-11.17 (7.86)
Mn	0.08-13.58 (2.44)	22.01-79.88 (39.43)	11.01-53.12 (32.01)
Ni	0.03-0.51 (0.06)	0.18-0.96 (0.47)	0.22-1.16 (0.71)
Pb	0.01-0.15 (0.03)	0.11-1.24 (0.46)	0.12-1.96 (0.50)
Rb	0.17-9.43 (1.34)	4.76-17.65 (9.69)	1.89-11.27 (6.25)
Sr	0.03-1.22 (0.12)	0.90-2.09 (1.31)	1.03-2.21 (1.48)
Zn	0.15-18.89 (1.56)	37.57-61.93 (48.82)	8.14-51.16 (33.61)

The legislation of European Union indicates maximum allowable limits for some potentially toxic metals in several foodstuffs. For example, limits for Pb are 0.02-1.50 mg/kg in certain food of animal origin and 0.05-0.30 mg/kg in certain food of plant origin and for Cd 0.05-1.00 mg/kg and 0.05-0.20 mg/kg, respectively. Limits for Hg and Sn are set for certain types of food (EC Regulation 629, 2008; EC Regulation 1881, 2006). However, within the lists of contaminants or products regulated there is no honey or other bee products included. Before the joining of Latvia in the EU there were restrictions for some heavy metal content (e.g., for Pb and Cd) in honey set by the Cabinet of Ministers (Dimiņš, 2006).

Similarly as observed for microelements also the highest macroelement concentration was detected in pollen and bee bread samples (Table 3.16).

Table 3.16

Concentration of macroelements in analysed bee products

Element	Concentration (x_{min}-x_{max} ($\bar{x}$)), mg/kg		
	Honey (n_s=80)	Pollen (n_s=5)	Bee bread (n_s=5)
Ca	17-272 (63)	1565-2205 (1836)	669-2606 (1668)
Fe	0.2-21.6 (4.0)	32.9-55.9 (43.8)	46.3-104.0 (73.4)
K	161-2314 (772)	5058-7715 (6417)	438-7592 (4608)
Mg	7-95 (23)	618-830 (756)	296-979 (700)
Na	4-285 (25)	40-54 (47)	113-223 (159)
P	*Not analysed*	13 125-15602 (14 447)	657-12 535 (7402)
S	*Not analysed*	7310-9418 (8116)	509-7844 (4691)

Range of Ca concentration was observed from <LOD in honey samples from Poland up to 409 mg/kg in honey from Italy. Concentration of Na in different honey samples is similar and not much dependent on botanical origin, while concentration of Mg, Ca, Mn and Zn are variable due to the botanical origin (Chudzinska and Baralkiewicz, 2010; Fernandez-Torres et al., 2005; Silva et al., 2009).

3.2.3. Element concentration in beverages

Samples of beverages collected in Latvia and analysed within this study were apple juice (n_s=9), apple wine (n_s=5) and birch sap (n_s=10); all samples were of local origin (Figure 3.21).

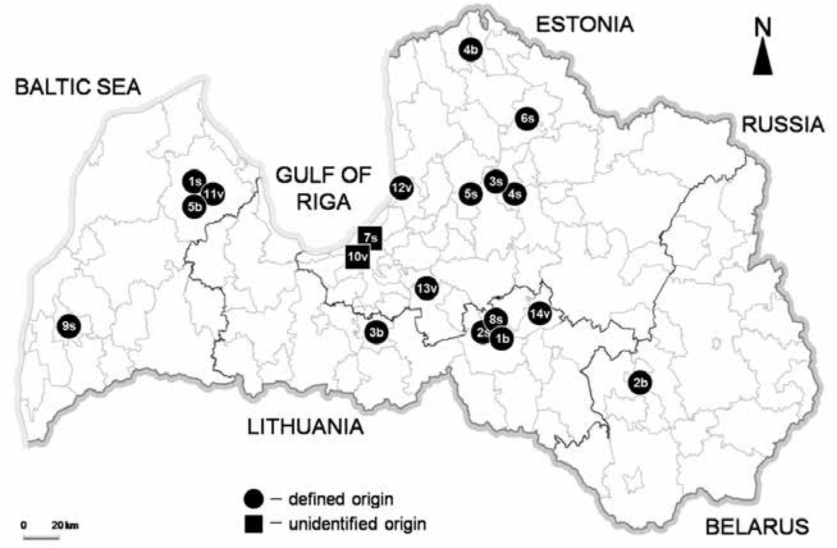

Figure 3.21. **Origin of beverage samples: apple juice (s), birch sap (b) and apple wine (v)**

Quantitative analysis of beverages allowed detection of concentration for ten microelements (Cd, Co, Cr, Cu, Fe, Mn, Ni, Rb, Sr, Zn) and six macroelements (Ca, K, Mg, Na, P, S). Element concentration for analysed beverages is expressed in mg/L.

In comparison with other analysed food microelement concentration in beverages was very low. The highest concentration was detected for Fe, Rb, Mn and Zn, but concentration of such microelements as Cd, Co and Cr was detected near limit of detection (LOD) (Table 3.17). Apple juice samples contained higher concentration of Cu and Fe, but in samples of apple wine higher levels of Ni and Sr were measured, while concentration of Ni and Sr in juice was below LOD.

Table 3.17

Concentration of microelements in analysed samples of beverages

Element	Concentration (x_{min}-x_{max} ($\bar{x}$)), mg/L		
	Apple juice (n_s=*9*)	Apple wine (n_s=*5*)	Birch sap (n_s=*10*)
Cd	0.0001-0.0011 (0.0004)	0.0002-0.0006 (0.0003)	<LOD
Co	0.0003-0.0032 (0.0007)	0.0003-0.002 (0.0011)	<LOD-0.046 (0.009)
Cr	<LOD-0.0010 (0.0004)	0.004-0.110 (0.0535)	<LOD
Cu	0.03-0.24 (0.11)	0.02-0.08 (0.04)	0.019-0.029 (0.025)
Fe	0.31-2.72 (1.24)	0.30-2.58 (1.10)	0.05-0.29 (0.13)
Mn	0.10-0.38 (0.24)	0.08-0.43 (0.24)	0.11-6.16 (2.55)
Ni	<LOD	0.01-0.09 (0.03)	0.02-0.16 (0.09)
Rb	0.21-0.97 (0.48)	0.51-1.14 (0.75)	0.02-0.28 (0.14)
Sr	<LOD	0.04-0.43 (0.17)	0.02-0.28 (0.12)
Zn	0.09-0.97 (0.25)	0.07-0.44 (0.23)	0.90-4.96 (2.03)

Information about element concentration in apple wine is very scarce, but it was possible to summarize information about average microelement concentration derived in several studies of apple juice worldwide. The limiting factor for adequate data comparison is use of different analytical techniques and sample pretreatment methods; however, overall trends in element content can be assessed. Highest concentration of Fe and Mn was detected in apple juice samples from Latvia, but other element concentration was similar or lower in comparison of literature data (Table 3.18).

Among macroelements the highest concentration of Ca was detected in birch sap samples, but K and Mg in apple juice and apple wine. Such elements as S and P were not detected in apple juice but only in apple wine revealing influence of fermentation process on element changes in beverages; also in birch sap P and S were quantified (Table 3.19).

Table 3.18

Concentration of elements quantified in apple juice from different countries

(after Farid and Enani, 2010; Magdas et al., 2012; Onianwa et al., 1999)

Country	Concentration, mg/L								
	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Brazil	-	-	-	0.336	-	-	-	-	0.69
France	-	-	0.016	-	-	-	-	-	-
Iran	-	-	-	-	-	-	-	-	0.56
Korea	-	0.0300	-	-	-	-	-	-	-
Latvia*	0.0004	0.0007	<LOD	0.110	1.240	0.240	<LOD	<LOD	0.25
Nigeria	-	-	0.010	0.535	0.416	0.056	0.013	-	0.47
Romania	0.0050	0.0008	0.056	0.315	-	-	0.030	0.0027	0.16
Saudi Arabia	-	0.0084	0.007	0.331	0.338	0.024	0.007	-	0.55
Spain	-	-	0.008	-	-	-	-	-	-
USA	-	-	-	-	0.1-0.7	-	-	-	-

* *Current research*

Table 3.19

Concentration of macroelements in analysed samples of beverages

Element	Concentration (x_{min}-x_{max} ($\bar{x}$)), mg/L		
	Apple juice (n_s=9)	Apple wine (n_s=5)	Birch sap (n_s=10)
Ca	10-70 (30)	8-83 (35)	42-150 (94)
K	206-1390 (777)	117-1195 (617)	54-142 (87)
Mg	39-51 (43)	19-84 (51)	*no data*
Na	1-25 (6)	7-26 (15)	*no data*
P	<LOD	17-106 (43)	3-41 (16)
S	<LOD	9-210 (75)	5-12 (7)

3.3. Conditions influencing element concentration in analysed food samples

3.3.1. Impact of seasonality on element concentration in food

Cottage cheese. Comparison of micro- and macroelement concentration in cottage cheese samples collected in Latvia over two seasons, summer and winter (Figure 3.15), showed evidence of recognizable impact of environmental conditions on element occurrence in the final product of milk processing.

Content of all detected macroelements in cottage cheese derived in winter season was higher than in samples from summer season especially concerning Ca and K (Figure 3.22.) which can be explained by animal feed and breeding distinctions between seasons. Dairy animals are fed by supplemented fodder during a winter season and this factor can be most relevant for the increase of macroelement content in subsequently derived food products such as milk and also cottage cheese.

Impact of seasonality is obvious also regarding concentration of microelements. Obtained results revealed that potentially toxic elements such as Pb and Ni prevailed over in the samples derived in summer season that can be associated with an impact of environmental pollution on food chain *soil-feed-milk*.

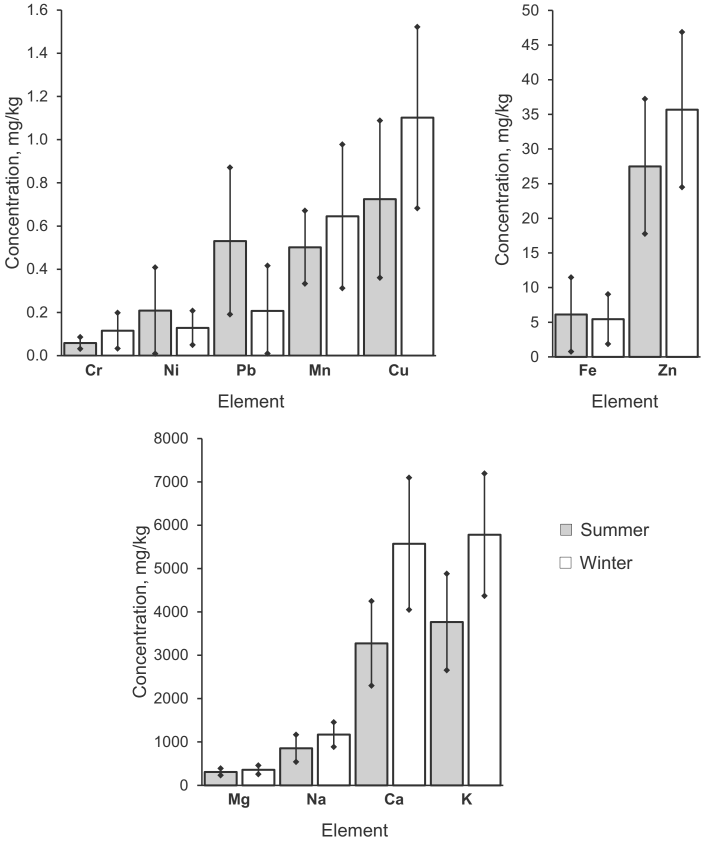

Figure 3.22. **Average concentration of elements in cottage cheese depending on season**

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 (n_s*=24*) were collected each month from April, 2011 to March, 2012 in a courtyard farm at Aizkraukle, Latvia (Figure 3.16.) 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. Determination of seasonal impact was done within four seasons: winter, spring, summer and autumn. In overall, differences in concentration of micro- and macroelements in hen egg samples affected by seasonality were observed. Transfer and concentration of elements can be influenced by several factors associated with seasonality: specific climatic conditions, morphological and hydrological conditions, environmental pollution (Brekken and Steinnes, 2004).

The highest mean concentration of microelements Fe, Zn and Mn was observed in the egg yolk samples collected in summer, while in egg albumen element concentration seasonaly varied unevenly (Figure 3.23). Considering the detected concentration of microelements in the current study in comparison to studies in Greece and Belgium, the mean concentration of Zn in egg yolk was obtained higher in our study, but egg albumen contained lower concentration of Zn (Giannenas et al., 2009; Waegeneers et al., 2009a; Waegeneers et al., 2009b). The research in Belgium revealed seasonal Zn and Cu differences in whole egg samples between samples from spring and autumn seasons: Zn concentration varied from 19.2 mg/kg in spring to 20.3 mg/kg in autumn and from 0.52 mg/kg to 0.43 mg/kg for Cu, respectively (Waegeneers et al., 2009a). In natural environment the essential element Zn can be strongly enriched by precipitation and is uptaken in food chain by plants and birds (Brekken and Steinnes, 2004).

The lowest concentration of Se in egg yolk was detected in samples from autumn (0.08 mg/kg) but the highest in winter (0.13 mg/kg). Se mostly was detectable in samples of egg yolk, while in egg albumen Se was detected only in samples collected during winter season (0.02 mg/kg). These differences can be related to poultry feeding specifics as inclusion of nutritionally enriched complex food in winter. Concentration of Se in egg yolk samples in detected in studies from Greece and Turkey was higher as it is reported in the current study (Nisianakis et al., 2009; Uluozlu et al., 2009). The highest concentration of Mn in egg yolk samples was detected in spring and summer season (0.35 mg/kg). In egg albumen concentration of Mn increased in spring-summer seasons (mean 0.30 mg/kg) but lowered in autumn-winter (mean 0.03 mg/kg). Also Ni concentration higher was detected in summer season in egg albumen samples (mean 0.20 mg/kg) (Figure 3.24). In addition, Ni dominated in egg albumen samples, except samples from spring season, when Ni was detected also in egg yolk. Similar tendencies of Ni distribution in egg yolk and egg albumen were observed in the study done in Greece (Nisianakis et al., 2009).

Concentration of Pb in both, egg yolk and albumen, was significantly higher in summer season (mean 0.13 mg/kg for yolk and 0.17 mg/kg for albumen) in comparison with spring period (mean 0.03 mg/kg for yolk and 0.10 mg/kg for albumen). In samples from winter and autumn seasons Pb was not detected.

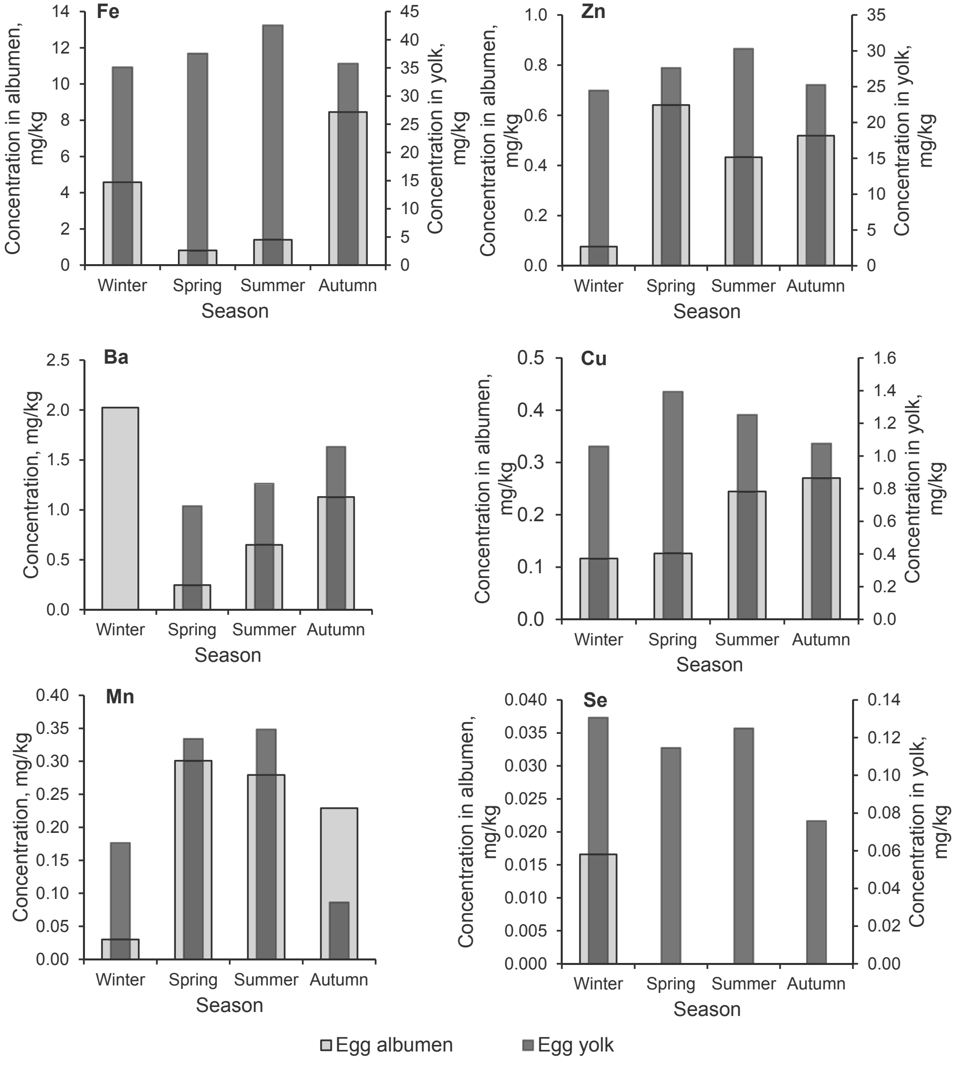

Figure 3.23. **Seasonal differences in concentration of Fe, Zn, Cu, Ba, Mn and Se in hen egg samples**

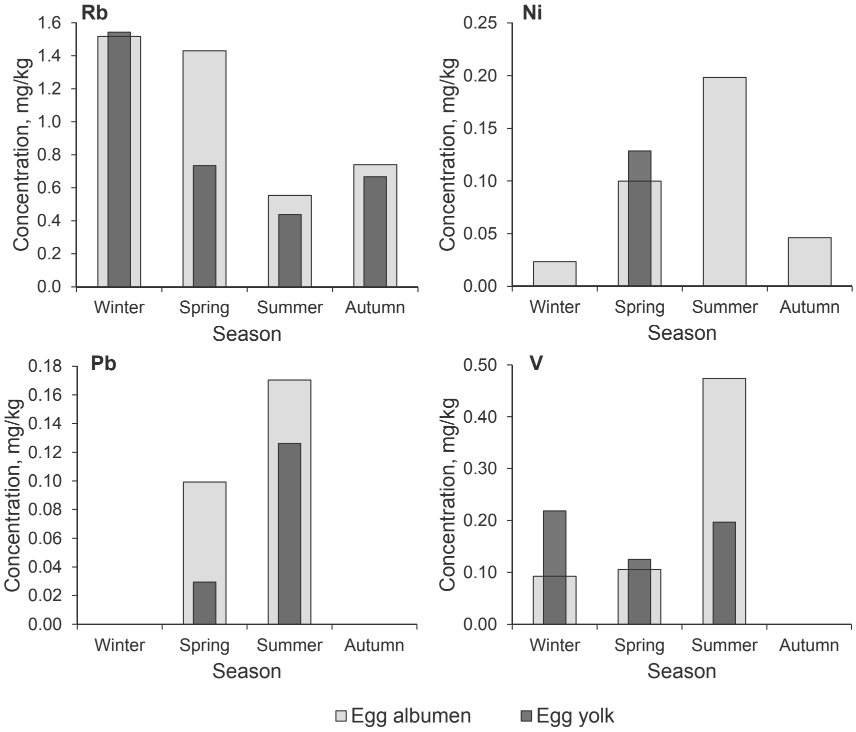

Figure 3.24. **Seasonal differences in concentration of Rb, Ni, Pb and V in hen egg samples**

This can be associated with impact of free range conditions on hen breeding during spring and summer, due to the higher possibility to uptake potentially toxic elements from rainwater, soil and air. Soil properties (e.g., soil pH, clay and organic matter content) can influence element bioavailability not only for plants but also in upper food chain segments (Brekken and Steinnes, 2004; Diez et al., 2009; Kabata-Pendias, 2004). Lower probability to contact with outdoor environment and subsequently with potentially toxic elements for poultry breed in free range is in winter season due to their breeding under the caged conditions.

Observing seasonal tendencies of macroelement concentration ranges in hen egg samples derived in Latvia, K and Ca in higher concentration was detected in samples from winter season (Figure 3.25). The concentration of Ca and K lowered in summer period collected hen egg samples (mean Ca 857 mg/kg and K 953 mg/kg for egg yolk and 33 mg/kg and 1177 mg/kg for albumen, respectively).

In comparison with the study done in Slovenia (Stibilj et al., 2002), current research revealed higher content of macroelements in egg samples. That can be related to poultry feeding specifics: in summer season the poultry was fed with seasonal food predominantly (grass, fresh vegetables and fruits), but in the autumn-winter season nutritionally enriched complex poultry feed is fed. In overall, the tendency of increased microelement

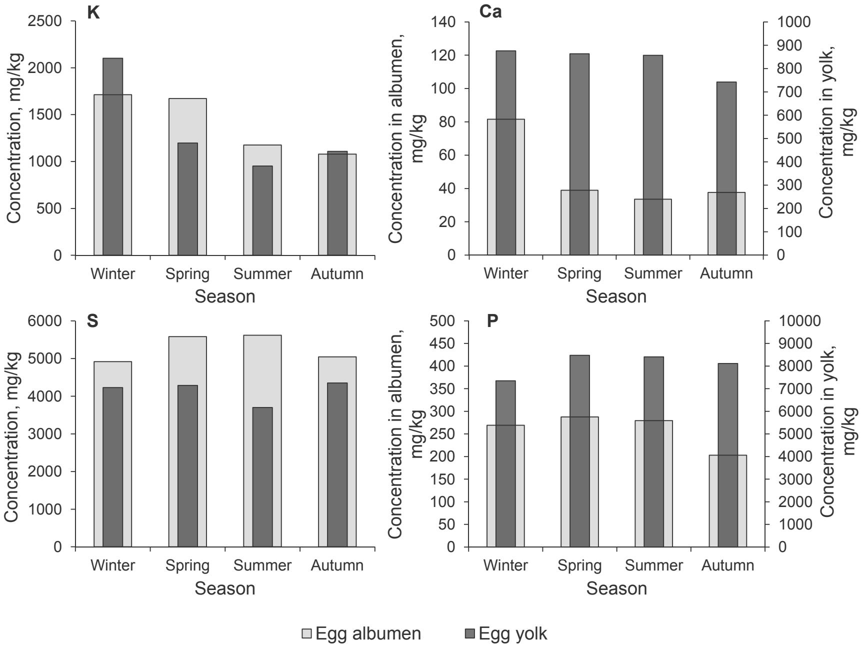

Figure 3.25. **Seasonal differences in concentration of K, Ca, S and P in hen egg samples**

concentration in summer season was detected in contrary to concentration of macroelements, revealing the relation with poultry feeding and free range conditions (Kucukyilmaz et al., 2012).

3.3.2. Impact of site-specific conditions on the concentration of elements in food

Honey. For the assessment of site-specific conditions and geographical distribution of elements in honey the samples were divided into sets based on the regional geological information of Latvia (Juškevičs, 2000; Nikodemus, 2004). Arrangement of sample sets was also tightly associated with historical regions of Latvia, i.e., Kurzeme, Zemgale, Vidzeme and Latgale. Geochemical background of Latvia in details have been studied by A. Gilucis (2007) who states that in Latgale region geochemical background of Pb, Cd, Sb, Ag, Se, As and S concentration is lower than in other areas of Latvia, but concentration of Ni, Co, Fe, La, K and Ga in Latgale and east of Vidzeme is heightened. Comparison of micro- and macroelement content of honey in-between selected sets revealed that only for Cu, Fe, Mg and V there are no substantial differences. Taking into account the known geochemical distribution of elements, the interconnections of element content in honey detected in current research cannot be unambiguously linked to the geochemical background regionally. More influence on element content of honey can be attributed to site-specific anthropogenic activities, such as traffic intensity, agricultural and agrochemical actions or other ways of environmental pollution. Deeper and more specific studies taking into account site-specific impacts should be carried out.

Birch sap. Birch sap is a specific beverage derived in early spring from birch trees *Betula* sp. It is consumed widely in the northern countries, including Latvia directly after collection from trees or after fermentation as well as used for preparation of syrup. After the literature data the most abundant elements in birch sap are Ca, Mg, P, Mn and Zn detectable in concentration usually above 1 mg/L. It has been detected that element composition of birch sap can reflect geochemical background of such elements as Ag, Cd, Pb and Zn, therefore, the analysis of samples with known origin can be used as a tool for biogeochemical prospecting (Harju and Hulden, 1990).

As the origin of birch sap samples was known it was possible to compare detected concentration of micro- and macroelements mutually and also with available data from other studies done in Latvia and Lithuania (Table 3.20 and 3.21).

Table 3.20

Concentration of macroelements in birch sap

(data from current research and after Kuka et al., 2013; Viskelis ir Rubinskiene, 2011)

Origin of sample	Concentration of element, mg/L						
	Ca	Cl	K	Mg	Na	P	S
Jelgava	53	-	41	-	-	2.1 (as $PO_4)^{3-}$	36 (as $SO_4)^{2-}$
Ozolpils	41	9	66	-	-	2.4 (as $PO_4)^{3-}$	34 (as $SO_4)^{2-}$
Azkraukle*	42	6	61	-	-	7	<LOD
Iecava*	50	16	54	-	-	3	7
Preiļi*	150	8	87	-	-	6	5
Sēļi*	86	6	92	-	-	25	6
Stende*	142	7	142	-	-	41	12
Lithuania	57	-	115	22	15	-	-

* *Current research*

Table 3.21

Concentration of microelements in birch sap

(data from current research and after Kuka et al., 2013; Viskelis ir Rubinskiene, 2011)

Origin of sample	Concentration of element, mg/L										
	As	Ba	Co	Cr	Cu	Fe	Mn	Ni	Rb	Sr	Zn
Jelgava	-	-	-	-	0.04	0.10	0.50	-	-	-	-
Ozolpils	-	-	-	-	-	-	0.52	0.03	-	-	-
Azkraukle*	-	-	-	-	0.02	0.10	0.11	-	0.03	0.02	1.70
Iecava*	-	0.07	-	-	0.03	0.11	0.14	0.08	0.02	0.07	0.90
Preiļi*	-	0.67	-	-	0.03	0.29	1.77	0.16	0.18	0.12	1.69
Sēļi*	-	0.26	-	-	-	0.05	6.16	0.02	0.19	0.11	0.90
Stende*	0.01	0.48	0.05	-	0.03	0.08	4.57	-	0.28	0.28	4.96
Lithuania	-	-	-	0.02	0.09	0.67	1.17	-	-	-	1.49

* *Current research*

Observed differences among the values element concentration can be assessed as quite notable, but it is very complicated to make unified conclusions on impacts influencing element content. According to data it is obvious that for example birch sap collected in Preiļi and Stende contain higher concentration of elements but further studies are needed to detect site-specific impacts influencing element content in food.

3.3.3. Impact of botanical origin on element concentration in food

Honey. For the statistical data analysis with the aim to detect impact of botanical origin on the concentration of elements in honey samples they 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 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*). Honey is known as the easily contaminable product if stored or processed by inappropriate, mostly metal alloys, equipment (Joudisius ir Simoneliene, 2009) as well as a biological product that can reflect environmental pollution or geochemical specifics of area where bees collect nectar (Fodor and Molnar, 1993; Pohl, 2009). 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.

Taking into account the botanical origin of honey collected in Latvia several differences in concentration of potentially toxic metals were detected among the species. The highest variability of zinc concentration was observed for commercially manufactured honey mixtures (0.28-11.60 mg/kg), followed by heather / forest blossom honey and polyfloral honey samples, while rape / spring blossom honey contained the lowest concentration of this element (Figure 3.26). Some outliers appeared in the group of polyfloral honey samples, i.e., one sample contained 18.89 mg/kg of Zn. Honey analysis in the neighbour country Lithuania revealed obvious honey contamination with Zn up to 41.25 mg/kg in a case when honey sample were kept in a vessel covered with zinc (Joudisius ir Simoneliene, 2009). That approves the importance of equipment materials used for honey storage and processing. Although the widest spread of aluminium concentration was detected for polyfloral honey (0.09-1.15 mg/kg), the highest mean concentration refer to the honey mixtures (0.62 mg/kg) and heather / forest blossom honey (0.49 mg/kg). For comparison, nectar honey samples collected in Czech Republic contained Al in higher levels (0.61-5.49 mg/kg) (Lachman et al., 2007). Other studies showed that rape honey in Poland may contain Al up to 11 mg/kg but buckwheat honey in less levels (up to 2.27 mg/kg) (Chudzinska and Baralkiewicz, 2010).

The highest ranges of variability as well as the highest mean concentration of Cu was detected for heather / forest honey samples (0.35 mg/kg) and buckwheat / clover honey samples (0.25 mg/kg). Regarding the botanical origin in the study by Spanish

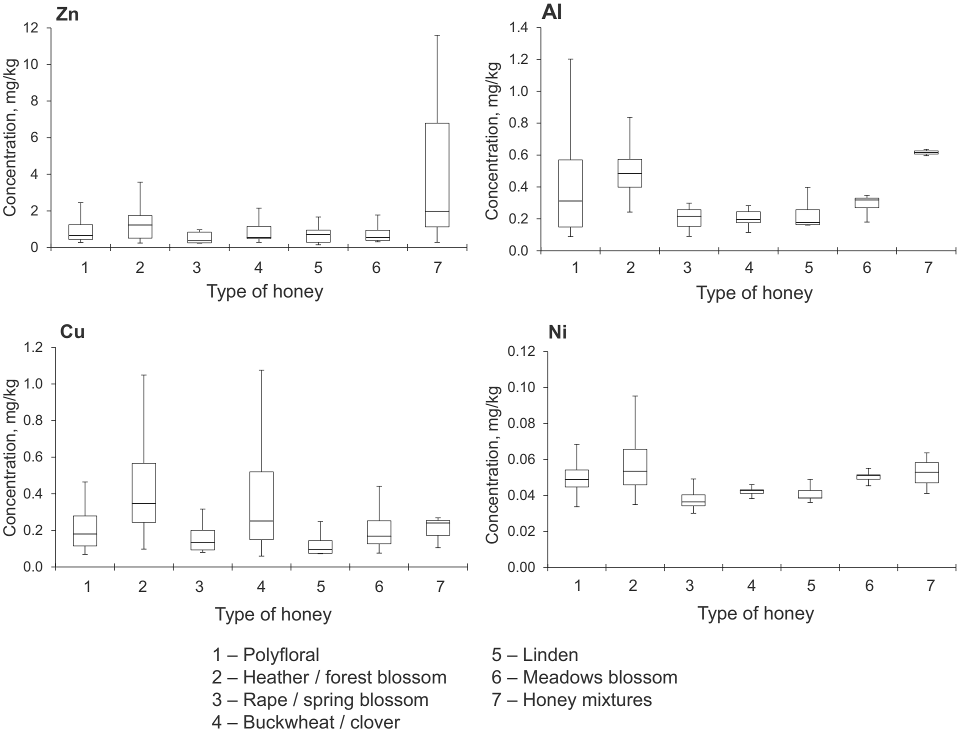

Figure 3.26. **Concentration of Zn, Al, Cu and Ni in honey samples of different botanical origin**

scientists it has been found out that orange blossom honey may contain much higher values of Cu (42.59-90.90 mg/kg) than other honey types (Fernandez-Torres et al., 2005), while mean (and maximum) values for rape and buckwheat honey in Poland were 0.17 mg/kg (1.69 mg/kg) and 0.91 mg/kg (1.55 mg/kg), respectively (Chudzinska and Baralkiewicz, 2010).

Range of Ni concentration within the groups of honey samples was not as variable as for other elements. The highest mean content of nickel was detected in heather / forest blossom honey (0.054 mg/kg). However, detected values of Ni are much lower than detected in Lithuanian honey samples 0.206-0.350 mg/kg (Joudisius ir Simoneliene, 2009) and in nectar honey from Czech Republic 0.06-0.40 mg/kg (Lachman et al., 2007).

Different results were gained for lead. The highest levels of Pb were detected in linden honey (mean 0.014 mg/kg) (Figure 3.27.) as well as in this group was detected one outlier with Pb concentration of 0.147 mg/kg.

Contamination of linden honey with Pb might be connected with the possible impact of pollution because linden trees widely grow in urban areas or near the roadways. In Hungarian study Pb concentration was detected 0.024-0.163 mg/kg for polyfloral honey and 0.017-0.144 mg/kg for acacia honey (Ajtony et al., 2007). But in Italian study lead was detected 0.047-0.053 mg/kg for clover honey and 0.028-0.304 mg/kg for polyfloral honey

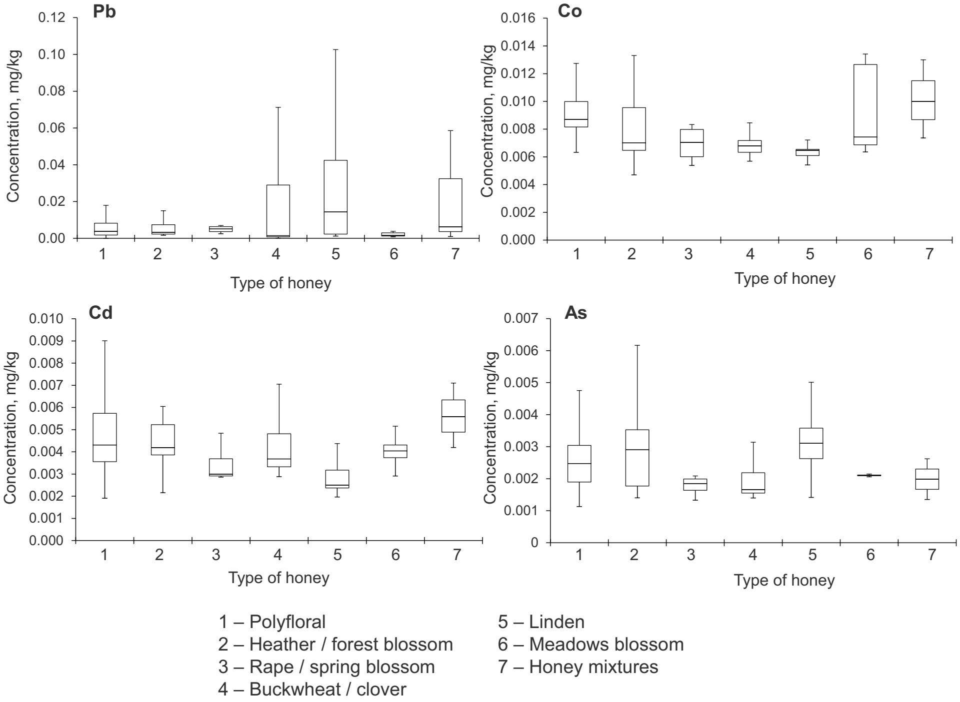

Figure 3.27. **Concentration of Pb, Co, Cd and As in honey samples of different botanical origin**

(Pisani et al., 2008). Lead is an element which in long term can easily accumulate in living organisms and may cause serious adverse effects (Kabata-Pendias and Mukherjee, 2007), therefore, its presence in foodstuffs should be kept under regular control.

In many samples chromium was detected below the detection limit (<0.02 mg/kg) therefore it was not possible to make a box-whisker plot for this element. However, in ones sample of meadows blossom honey Cr was found 0.31 mg/kg and in one linden honey sample 0.18 mg/kg, that might be resulted from traffic pollution taking into account the site-specific conditions or geographical origin of these samples. Other studies reveal that Cr might be found up to 0.09 mg/kg in polyfloral honey and up to 0.11 mg/kg in acacia honey in Hungary (Ajtony et al., 2007) as well as 0.005-0.093 mg/kg in rape honey in Poland (Chudzinska and Baralkiewicz, 2010). Cr contamination can be connected with pollution created by anthropogenic activities.

The lowest concentration of Co was detected in linden honey but the highest variability for the heather / forest blossom (0.005-0.013 mg/kg) honey and meadows blossom honey (0.006-0.013 mg/kg) while the highest mean was detected for manufactured honey mixtures.

The widest range of Cd concentration was observed for polyfloral honey while the highest mean value refers to commercially manufactured honey mixtures (0.006 mg/kg). In the group of polyfloral honey some outlier values were detected with concentration of

Cd 0.027 mg/kg and 0.012 mg/kg. Other studies show that concentration of Cd in honey can be detected in higher levels, e.g., for rape honey up to 0.082 mg/kg and for buckwheat honey 0.003-0.030 mg/kg in Poland (Chudzinska and Baralkiewicz, 2010).

Wide variability of arsenic concentration was detected for heather / forest blossom honey, followed by linden and polyfloral honey groups. The highest mean concentration refer to linden honey and heather / forest blossom honey (0.003 mg/kg). Arsenic has been quantified in acacia honey up to 0.013 mg/kg and up to 0.006 mg/kg in polyfloral honey in Hungary (Ajtony et al., 2007) and 0.0046-0.0055 mg/kg in clover honey and 0.0028-0.0111 mg/kg in polyfloral honey in Italy (Pisani et al., 2008).

Impact of botanical origin on the content of potentially toxic metals in honey is obvious. Overall average concentration was detected lower than in similar studies worldwide; however, due to appearance of outliers significant contamination risks remain in some cases. Taking into account 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.

According to detected variability between the groups of honey samples and quantified elements, impact of botanical origin on element content in honey can be connected with the growing conditions of the floral plant species. For example, some elements were detected in higher levels in linden honey (Pb and As) and it is known that linden trees are widely grown in urban areas or near the traffic lines that can be a source of element contamination. Agricultural activities and use of agrochemicals and fertilizers also can become a source of contaminants for some types of honey such as rape honey or buckwheat honey.

Honey storage and processing equipment can be assessed as one of the honey contamination ways, especially for such elements as Al, Cu and Zn. This fact can be attributed to commercially manufactured honey mixtures that might be processes with inappropriate equipment.

3.3.4. Impact of processing or agricultural practice on the concentration of elements in food

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 support 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.

An assessment of major element content in root vegetables was performed to draw a comparison between the samples of species grown in allotment gardens versus the samples of species grown in farmlands. Taking into account the comparison of variances by Fisher's criteria and the results of performed appropriate t-tests for samples of onion bulbs, only the content of sodium was significantly different in selected subgroups. The mean score for the subgroup of samples grown in farmlands ($M=186.59$, $n_s=17$) was significantly higher than the scores for the subgroup of samples grown in allotment gardens ($M=87.55$, $n_s=13$) using the two-sample t-test for unequal variances ($p=0.04$). The data of the major element content of carrot roots revealed significant differences for two major elements between subgroups: content of K ($M=1641.64$, $n_s=12$) and Mg ($M=31643.9$, $n_s=12$) in the subgroup of samples grown in allotment gardens was significantly higher than in the subgroup of samples grown in farmlands where the mean scores for Mg ($M=1180.9$, $n_s=18$) and for K were $M=25302.9$, $n_s=18$ detected by t-tests for unequal variances and t-test for equal variances, respectively. Results of statistical data analysis confirm the hypothesis that element uptake during plant development is to a great extent dependent on botanical properties of species as it is also revealed in related studies (Kabata-Pendias, 2004).

In overall, comparison of selected subgroups of vegetable samples grown in farmlands versus samples grown in allotment gardens revealed that amounts of several elements (Cd, Co, Na, Ni, Se, Sr) were significantly higher in the subgroup of onion samples grown in farmlands while the same samples contain significantly less amount of Rb. For carrots significantly higher amounts of some elements (K, Mg, Mn, Rb, Zn) are contained in samples from allotment gardens. 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. Subsequently, a risk of food plant contamination by potentially harmful chemicals, e.g., potentially toxic metals can be posed in both cases. However, onion and carrot samples within the current study were collected mainly in rural areas. Therefore, the influence of industry or heavy traffic on vegetables grown in allotment gardens cannot be reliably assessed. Differences between selected subgroups may arise as well as entailed by natural geochemical background peculiarities as from use of soil fertilizers that can influence content of major elements or use of pesticides regarding some trace elements. Therefore further studies are needed and certain regional geochemical background of the origin place of samples should be taken into account within the assessment.

Cottage cheese. As the provenance of the cottage cheese samples was established at the moment of purchasing it was enough easy to compare content of micro- and macroelements in cottage cheese produced by individual dairy farms with those obtained from supermarkets where dairy products comes from large-scale manufacturers. The results revealed considerable interconnections. Firstly, range of macroelements did not varied significantly but it showed stable tendency that macroelements, especially Ca, prevailed in cottage cheese samples from individual dairy farms (Figure 3.28).

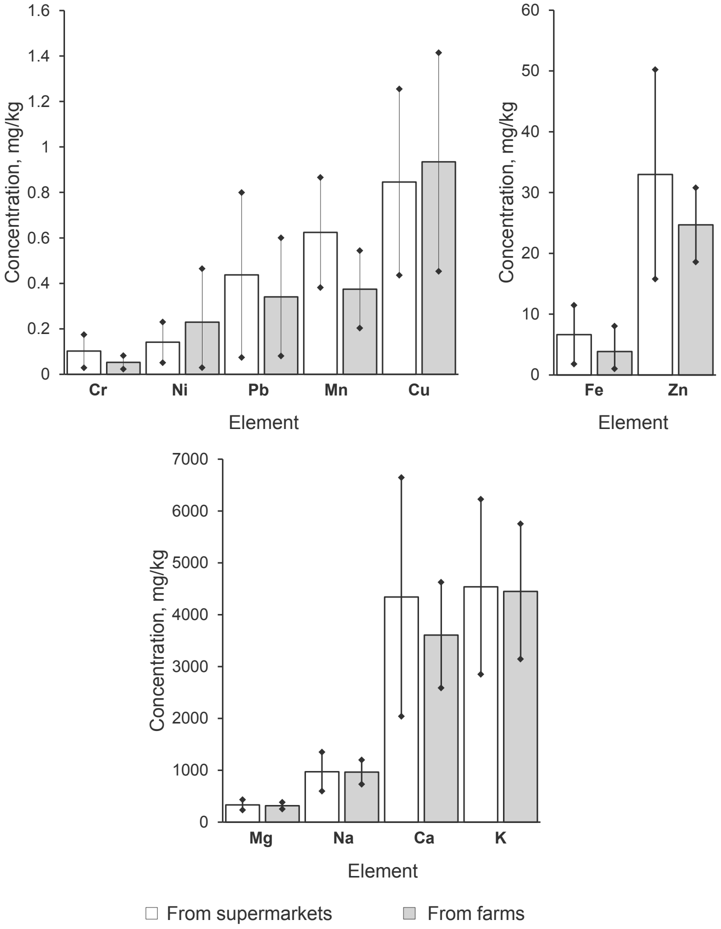

Figure 3.28. **Concentration of elements in cottage cheese depending on producer**

Secondly, concerning microelements all except Ni and Cu were also detected in higher amount in cottage cheese samples from individual dairy farms. These coherences indicate of both, better dairy animal breeding conditions in small individual dairy farms as well as higher possibility to contaminate the product with potentially toxic elements. Conversely, animals in large-scale dairy farm complexes mostly have less possibility to contact with environmental pollutants and they get more balanced supplemented fodder equally all over the year. Another assumption for these distinctions can be related to milk processing equipment and manufacturing practice asset while in large-scale farms cottage cheese production process is organized in more closed processing chains by applying automation which allows to avoid an unexpected contamination.

Comparison between element concentration in milk and cottage cheese (Table 3.22.) revealed impact of processing.

Table 3.22

Comparison of average concentration of micro- and macroelements in milk (after Cashman, 2006) **and cottage cheese** (data from current study)

Element	Concentration, mg/kg* or mg/L**	
	Cottage cheese*	Milk**
Ca	4120	1120
Cr	0.090	0.002
Cu	0.87	0.09
Fe	5.88	0.50
K	4510	1360
Mg	330	110
Mn	0.56	0.03
Na	970	530
Ni	0.180	0.026
Pb	0.41	-
Zn	30.52	3.90

Data discovered about threefold distinctions between average macroelement content for Ca, K and Mg in favour of cottage cheese. Such differences can be associated mostly with the impact of milk fermentation and cottage cheese manufacturing peculiarities. But this assumption could be verified only if the whole process of cottage cheese making would be investigated step by step according to quantitative analysis of intermediate products. Unlike the determined content of macroelements elevated levels of microelements in cottage cheese can be explained by possible contamination during milk collection and transport, and contamination during production by technical equipment used which may contain details made from heavy metals and their alloys. It can be assumed that also impact of site-specific environmental conditions is of a great importance for microelement appearance in final product. Dairy animal breeding under outdoor conditions, as it is typical for small individual dairy farms, can result in excess of contamination with heavy metals.

Hen eggs. Quantitative analysis of hen egg samples from different poultry housing types in Latvia (Figure 3.16.) was done to reveal the impact of agricultural practice on element concentration in eggs. The highest content was detected for Fe, Zn, Cu and Mn in egg samples from organic farms (Figure 3.29). Also Pb concentration was detected the highest in egg samples from organic farms. Other elements were detected in lower concentration. In addition, Pb was not detected in any of egg samples derived from large-scale poultry farms.

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

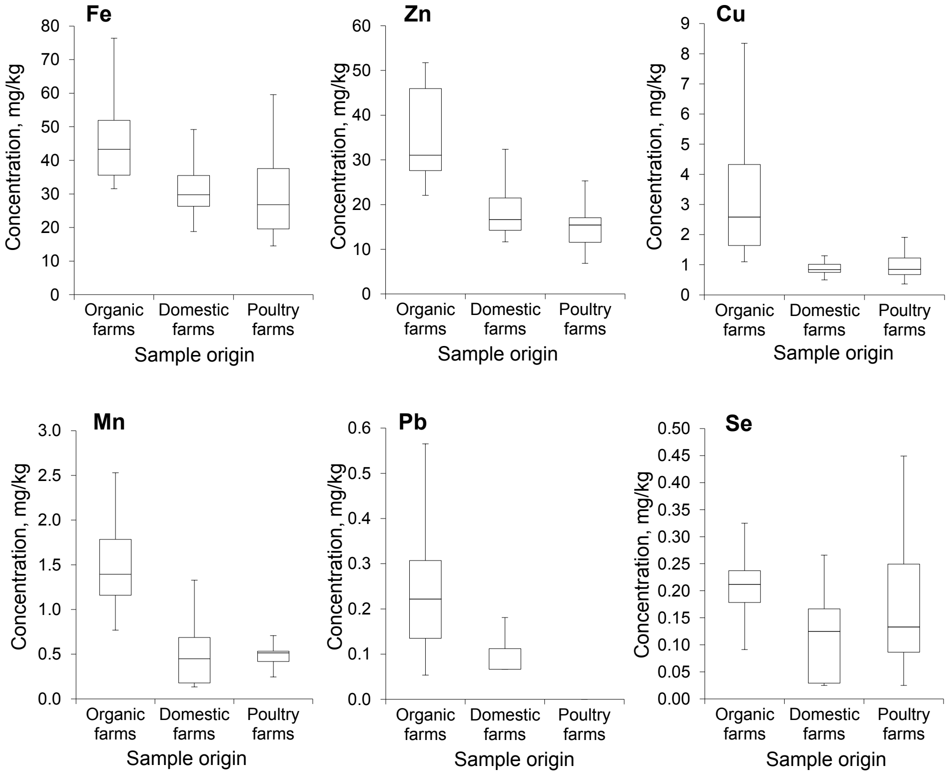

Figure 3.29. **Concentration of Fe, Zn, Cu, Mn, Pb and Se detected in hen egg samples from different poultry housing types**

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 conditions on element content of egg samples, likely in relation to potential environmental contaminants (e.g., Cu, Pb, Zn).

Although organic farming is known as more clean and healthy food production than conventional farming, obtained results within the present study regarding microelement concentration in hen eggs were not in favour with this common assumption.

The differences among the hen eggs derived in different housing systems have been detected also in previous studies. For example, it has been discovered that hen eggs derived from poultry farms equipped with cage systems may have lower nutritional value and inferior taste compared to eggs from domestic farms and organic farms. Feed, mineral supplements and water composition as well as impact of environmental conditions such as indoor and outdoor conditions are assessed as the main influencing factors (Dobrzanski et al., 2007; Giannenas et al., 2009; Kucukyilmaz et al., 2012) that may lead to food chain contamination with potentially toxic elements. P.S. Holt with colleagues (2011) mentioned that hen eggs of free-range housing systems may become contaminated also through veterinary medicine that is given to protect hens against diseases and parasites.

Comparison of macroelement concentration revealed tendency that higher concentration are detectable in egg samples from organic farms (Figure 3.30). Only for Na and Mg mean values were higher for samples from poultry farms that can be associated in lower quality feed containing higher content of common salt.

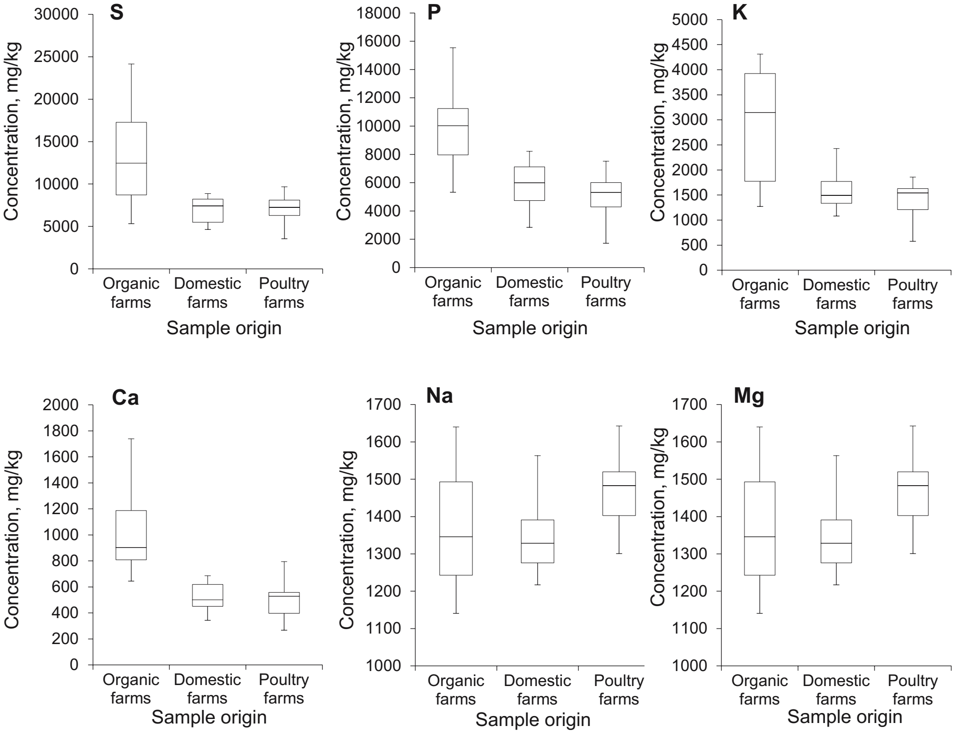

Figure 3.30. **Concentration of S, P, K, Ca, Na and Mg detected in hen egg samples from different poultry housing types**

The highest values and most variable range of concentration of microelements were determined for egg samples derived from organic farms, while egg samples from domestic farms and large-scale poultry farms mostly contained lower content of elements. That can be attributed not only to poultry feed specifics within different housing types but also to the impact of environmental conditions such as indoor and outdoor conditions. Such environmental contaminant as Pb was not detected in egg samples from large-scale poultry farms where hen breeding is not affected by outdoor conditions. In general, the results confirmed the importance of the analysis of food composition that should be implemented by taking into account specific conditions of food production and applied agricultural practice.

3.4. Assessment of element bioavailability

Bioavailability of elements in food chain segments *soil-plant* and *plant-human* from food of plant origin is a complex system involving complicated biochemical processes and transfer reactions that are dependent on biogeochemical behaviour of corresponding element, plant physiology and soil properties as well as are influenced by environmental conditions. Sequestration, soil weathering, pH, oxidation-reduction potential are just some attributes that are of importance (Alexander et al., 2006; Chojancka et al., 2005; Kabata-Pendias, 2004). In this chapter the results of experimental growing of food crops in contaminated soil and speciation analysis of soil and lettuce samples are discussed.

3.4.1. Characteristics of soil samples

Accumulation of metallic elements and metalloids in plants can be affected by soil properties such as pH, cation exchange capacity, content of organic matter and the texture of soil (Malandrino et al., 2011; Salazar et al., 2012; Walker et al., 2003; Xu et al., 2013; Zheng et al., 2007). Within the present study five soil samples were used to evaluate soil contamination effect. Soil contamination, analysis and the experiment of food crop growth was done in a way described in details under the chapter *Materials and Methods*. The analysis of soil samples involved determination of soil type and texture, pH (pH_{H2O} and pH_{KCl}), content of humic substances, cation base saturation, total element content in soil prior contamination, and detection of element concentration in soil samples after spiking.

a) Soil type and texture of mineral soil samples was primary detected in field conditions (FAO, 2006; Pansu and Gautheyrou, 2006) and then approved by laboratory methods as pipetting and wet sieving (Van Reeuwijk, 1995). At the beginning soil type and texture was identified in the field conditions as follows: 1 sample of fen peat soil and 4 samples of sod-podzolic soil (with higher or lower content of organic matter and clay content) (Kārkliņš u.c., 2009; Nikodemus, 2011), but precise soil type was identified at the laboratory: 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; Regulation 804, 2005). Characteristic soil texture of analysed mineral soil samples is shown in Figure 3.31).

b) Soil pH value can be considered as one of the most significant influencing factors affecting element mobility and total bioavailability (Alloway et al., 2004). The highest pH value was detected for fen peat soil S1, but the lowest value for sod-podzolic / sandy clay loam soil S5, respectively, pH_{H2O} 5.31 and 4.61 in water solution and pH_{KCl} 5.06 and 4.11 in KCl solution (Table 3.23).

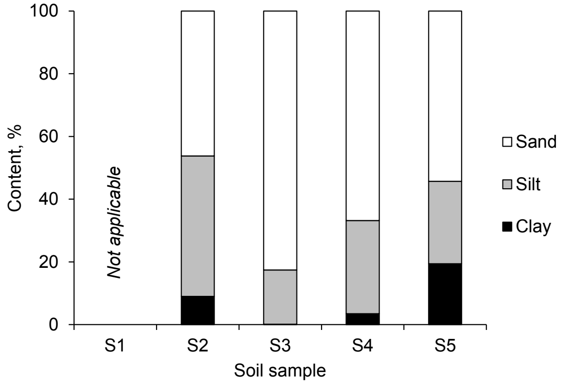

Figure 3.31. **Soil texture of analysed mineral soil samples (S1 – fen peat soil; S2-S5 – sod-podzolic soil)**

Table 3.23

Detected pH of analysed soil samples

Soil sample description			pH_{H2O}	pH_{KCl}
Soil type	Soil texture	Abbreviation		
Fen peat	*Not applicable*	S1	5.31	5.06
Sod-podzolic	Sandy loam	S2	4.93	4.38
Sod-podzolic	Sand	S3	5.05	4.56
Sod-podzolic	Loamy sand	S4	5.01	4.65
Sod-podzolic	Sandy clay loam	S5	4.61	4.11

In overall, according to the values obtained of soil sample water solution analysis, it can be assessed that all soil samples are related to be of acidic media (Fan et al., 2009). Metal mobility is proposed to be higher in acidic media than in alkaline media (Tao et al., 2003), as well, it is in agreement with the average soil pH values (pH 4-8) corresponding to temperate climatic zone conditions (Malandrino et al., 2011). It is suggested that plant uptake of anions is more intensive from soils of acidic media while cations are taken up more rapidly from soils of neutral and alkaline media (Tao et al., 2003).

c) Soil organic matter expressed as content of humic substances in soil samples was detected prior soil contamination and addition of humic substances and it varying in a wide range from 2.9±0.15 % to 4.2±0.4 % in sod-podzolic soil (S2-S5) up to 29.3±8.6 % in fen peat soil (S1) (Figure 3.32).

Obtained data corresponds with literature information as in average organic matter content in sod-podzolic soil does not exceed 10 % and those can be named *mineral* soils, while peat soil is naturally rich with high content of organics and can be attributed to *organic* soils (Gilucis, 2007; Kārkliņš u.c., 2009; Nikodemus, 2008).

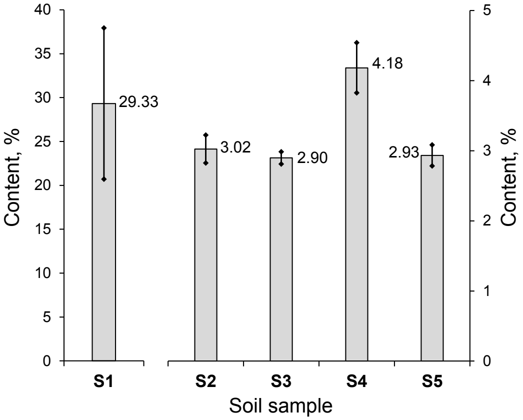

Figure 3.32. **Soil organic matter expressed as content of humic substances ($\bar{x}\pm s$; $n_m=3$) in analysed soil sample (S1 – fen peat soil; S2-S5 – sod-podzolic soil)**

d) Cation base saturation and cation exchange capacity (CEC) in a great extent is dependent on the organic matter content in soil and soil pH. Surface electric charge increases with increasing pH and as a result sorption capacity of metallic elements and metalloids increases, but element bioavailability reduces. On the contrary, if pH values decrease and soil medium becomes more acidic, then anion sorption increases (e.g., in case of metalloid As), but sorption of cations decreases. Cation base saturation and CEC influence on bioavailability in food chain segment *soil-plant* is well explored for such element as Zn (Fairbrother et al., 2007).

In analysed mineral sod-podzolic soil samples (S2-S5) cation base saturation varied from 3.13 to 8.17 cmol/kg, that corresponds to soils of light structure with high level of sand (Grant et al., 1998; Nikodemus, 2008). Significantly higher value (142.29 cmol/kg) was determined for fen peat soil (S1) in comparison with other soil samples that can be attributed to the naturally high content of organic matter (Table 3.24).

Table 3.24

Detected cation concentration and cation base saturation for analysed soil samples

Soil sample	Cation concentration, cmol/kg				Cation base saturation, cmol/kg
	Ca^{2+}	K^+	Mg^{2+}	Na^+	
S1	124.53	0.46	16.57	0.72	142.29
S2	4.18	0.39	0.86	0.27	5.71
S3	2.37	0.18	0.26	0.31	3.13
S4	5.82	0.62	0.98	0.61	8.04
S5	5.78	0.56	1.29	0.53	8.17

Although it is known that pH influences cation base saturation values, in the current study weak correlation (*r<0.5*) between these parameters was detected.

The value of cation base saturation and CEC can be used for soil fertility description, as it is stated that soils with high fertility contain calcium 60-80 % from total CEC and other cations 20-50 % (Hodges, s.a.). Detected values revealed that Ca^{2+} content varies from 71 % of cation base saturation for sod-podzolic soil / sandy clay loam S5 to 88 % of cation base saturation for fen peat soil S1 (Figure 3.33).

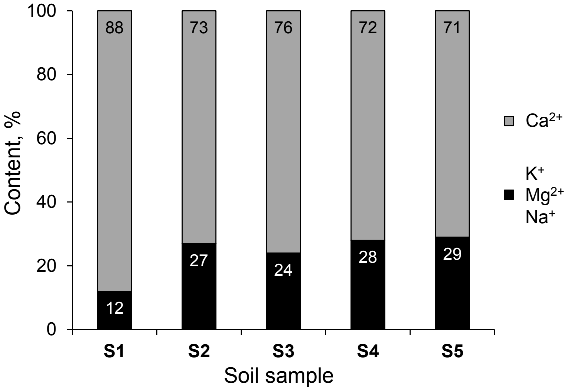

Figure 3.33. **Ratio of cation content (Ca^{2+} versus sum of K^+, Mg^{2+} and Na^+) in analysed soil samples (S1 – fen peat soil; S2-S5 – sod-podzolic soil)**

Thereof it can be assessed that selected soil samples belong to soils of high fertility and are applicable for crop cultivation, including experimental growth of crops.

e) Total element content of soil samples was measured prior the soil contamination procedure with the aim to detect natural geochemical background levels of elements. Results revealed that in fen peat soil S1 the highest concentration of such elements as Ca, Cd, Cu, Fe, Ni and Pb were detectable (Table 3.25.) that corresponds to assumption that some element associations in soil are tightly connected with the organic matter content (Gilucis, 2007). Highest concentration of Mn and Zn was detected for sod-podzolic soils S4 and S5.

Sod-podzolic soil / sandy clay loam S5 contained significantly higher concentration of Cr, Ni and Pb that can be associated with stronger sorption of elements on clay particles, as this soil sample was most rich in clay (Gilucis, 2007). Strong positive correlation (*r>0.8*) was detected for such element pairs as Zn with Ca, Co, Cr, Fe, K, Ni, Mg; K with Cu, Pb; Ca with Co, Mn.

f) Element concentration in soil samples after contamination procedure. Before crop growing experiment soils were contaminated with substances containing metallic elements as it was described in details previously in chapter *Materials and Methods*.

Table 3.25

Concentration of elements in studied soil samples prior contamination

Element	Soil sample				
	S1	S2	S3	S4	S5
	Element concentration ($\bar{x}\pm s$; $n_m=3$), 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 ($\bar{x}\pm s$; $n_m=3$), 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

Measurements of actual concentration of Cu in soil samples after the contamination with copper sulphate pentahydrate $CuSO_4\times5H_2O$ solution at target contamination concentration of Cu 40, 70, 100, 130 and 200 mg/kg revealed tendency of hyperaccumulation in case of fen peat soil S1 (Table 3.26.) at all Cu target concentrations. Slight hyperaccumulation of Cu was observed also for sod-podzolic soil / sandy clay loam S5 that contains higher amount of clay.

Table 3.26

Concentration of Cu in soil samples after contamination with $CuSO_4$ at different target Cu concentration

Element	Target concentration of Cu, mg/kg	Actual concentration ($\bar{x}\pm s$; $n_m=3$) of Cu in soil sample, mg/kg				
		S1	S2	S3	S4	S5
Cu	40	138±1	49±3	44±2	53±2	60±2
	70	220±12	70±2	71±4	86±8	77±1
	100	298 ±3	95±1	100±8	116±5	118±5
	130	408±24	137±4	126±4	150±12	243±50
	200	654±1	195±1	205±3	218±1	224±2

Also after soil sample contamination with mixture of compounds containing metallic elements Cd, Cu, Pb and Zn, hyperaccumulation was obvious for fen peat soil S1. On the contrary, lowest concentration of elements was detected in sod-podzolic soil / sandy loam S2 and sod-podzolic soil / sand S3 (Table 3.27).

Table 3.27

Element concentration in soil samples after contamination with metal 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 indicated tight relationship between soil contamination rate and organic matter content in soil as well as soil texture is important if soil contains high amount of clay.

3.4.2. Accumulation of elements in experimentally grown food crops

The primary route of microelements, including metals, and transfer of them into the food chain is realised through the *soil-plant* interaction within the certain ambient environment. Sustainable micronutrient cycling is an important issue not only in case of essential element transfer but also for the assessment of possible human health risks caused by contamination of daily nutrition with potentially toxic elements (Yang et al., 2007).

To detect provisional bioavailability of elements and rates of element accumulation, the quantitative content of elements was analysed in selected experimentally grown food crops: radish *Raphanus sativus* L. ‘Saxa 2’, leafy lettuce *Lactuca sativa* L. ‘Grand Rapids’ and dill *Anethum graveolens* L. ‘Mammut’. Food crops were grown soil samples described previously: 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 with or without addition of humic substances. Contamination of soil samples in five target concentration of Cu as well as contamination with a mixture of compounds containing Cd, Cu, Pb and Zn at certain target concentration was applied as it was described previously. Control samples of food crops were obtained by growing them in uncontaminated soils. It should be remarked that it was not possible to harvest all food crop samples due to probably low tolerance of certain species or possible contaminant phytotoxicity, i.e., within the current experiment it was possible to harvest dill samples only grown in soils enriched with solution of humic substances. Radish samples were not harvested from contaminated soils at highest Cu target concentration (200 mg/kg). However, obtained data were sufficient for overall assessment of element transfer from soil to plant.

a) Copper concentration in experimentally grown food crops. Cu concentration was measured in lettuce, radish and dill samples grown in contaminated and control soils.

Radish samples grown in control soils containing in average 3.42±0.27 mg/kg of Cu, while the highest concentration was about 40 times higher than the control (up to 123.60 mg/kg at Cu 130 mg/kg target concentration in soil) and it was detected for samples grown in sod-podzolic soil / sand S3 at all target copper contamination concentration (Figure 3.34). Cu concentration in samples grown with or without addition of humic

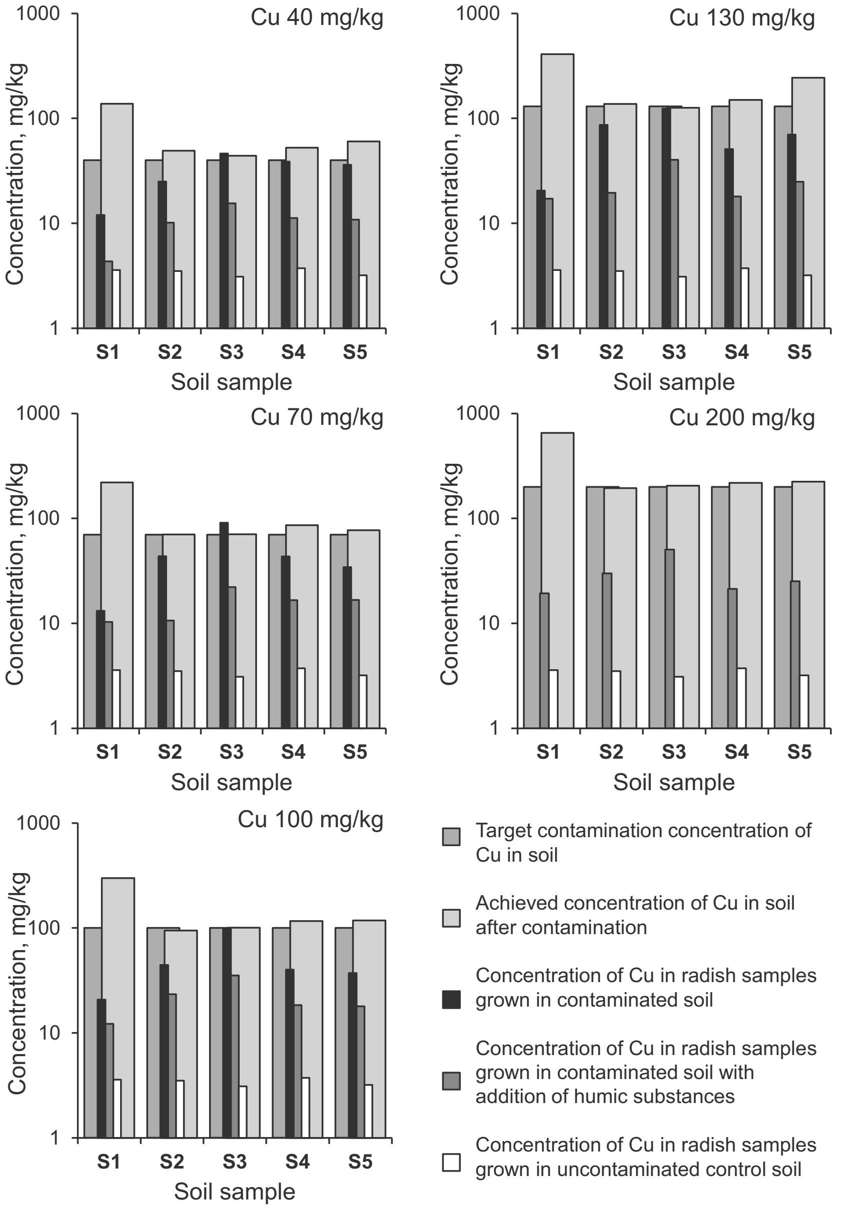

Figure 3.34. **Concentration of Cu in radish samples grown in control and contaminated soils with different target concentration with or without addition of humic substances (S1 – fen peat soil; S2 – sod-podzolic soil / sandy loam; S3 – sod-podzolic soil / sand; S4 – sod-podzolic soil / loamy sand; S5 – sod-podzolic soil / sandy clay loam)**

substances differed significantly. If in some cases there were detected Cu hyperaccumulation in radish samples grown in contaminated soils then in samples grown in soils with enrichment of humic substances Cu concentration was detected up to 4 times lower. Hyperaccumulation of metals in edible parts of plants can be linked to possible risks for consumers, e.g., high doses of Cu in daily nutrition may lead to acute toxicity of human organism (ATSDR, s.a.; Fraga, 2005). Regarding consumers, obtained results of element content in food crops can be considered as worst case as concentration of elements are expressed on dry weight (DW).

The lowest concentration of Cu was detected for radish samples grown in fen peat soil S1. It has been described that natural complex forming substances (e.g., humic acids or humic substances) and synthetic solvents (e.g., ethylenediamine tetraacetic acid EDTA or diethylenetriamine pentaacetic acid DTPA) used as chelators may influence metal accumulation in plants and can be used for metal removal from polluted soils (Inaba and Takenaka, 2005). However, treatments by humic acids, if compared with synthetic chelators, in case of copper contamination showed higher potential to reduce copper toxicity by involving metal ions in complex compounds in plants (Heemsbergen et al., 2010; Inaba and Takenaka, 2005).

It was not possible to harvest radish samples from soils contaminated with Cu at target concentration 200 mg/kg. Burden growth of radish at high contamination of soil can be associated with possible phytotoxic effects as copper is among the metals that induces plant phytotoxicity as 20-100 mg/kg of Cu is excessive or toxic concentration for plants depending on species (Kabata-Penidas and Mukherjee, 2007). Phytotoxic effects of Cu excess in soils especially affect roots inducing defects in root system, reduced root growth or damage of epidermal cells of plant roots (Chojnacka et al., 2005; Guala et al., 2010; Lin et al., 2003).

Although lettuce samples grown in control soils contained in average 5.07±0.45 mg/kg that is higher level than detected in radish control samples, in general Cu concentration in lettuce samples (Figure 3.35) was detected lower than for radish thus approving that element accumulation in roots generally is more intensive than in leaves (Alloway et al., 2004). Leafy vegetables such as spinach or lettuce are among the food crops with tendency to accumulate higher amounts of elements than other vegetables (Alexander et al., 2006). In a study done by P.D. Alexander with colleagues (2006) quite similar results has been obtained for lettuce as in the current research. Lettuce samples of different varieties were grown in soil contaminated with target concentration 130 mg/kg of Cu. Copper concentration in lettuce was detected in range 6.73-12.55 mg/kg (control values 4.19-7.07 mg/kg) but no significant differences were statistically detected among different lettuce cultivars.

The lowest copper concentration was found in lettuce samples grown in fen peat soil S1 and sod-podzolic soil / loamy sand S4, soils with naturally higher content of organic matter. The tendency of humic substances to reduce metal content in plants was clearly detectable, e.g., for lettuce samples grown in sod-podzolic soil / sandy loam S2 with target Cu 200 mg/kg concentration copper content was about 11 times lower in samples grown in soil enriched with humic substances than without.

As it is reflected in figures, excess of Cu uptake by lettuce was observed for samples grown in sod-podzolic soils S2 and S5, which contain higher amounts of clay particles.

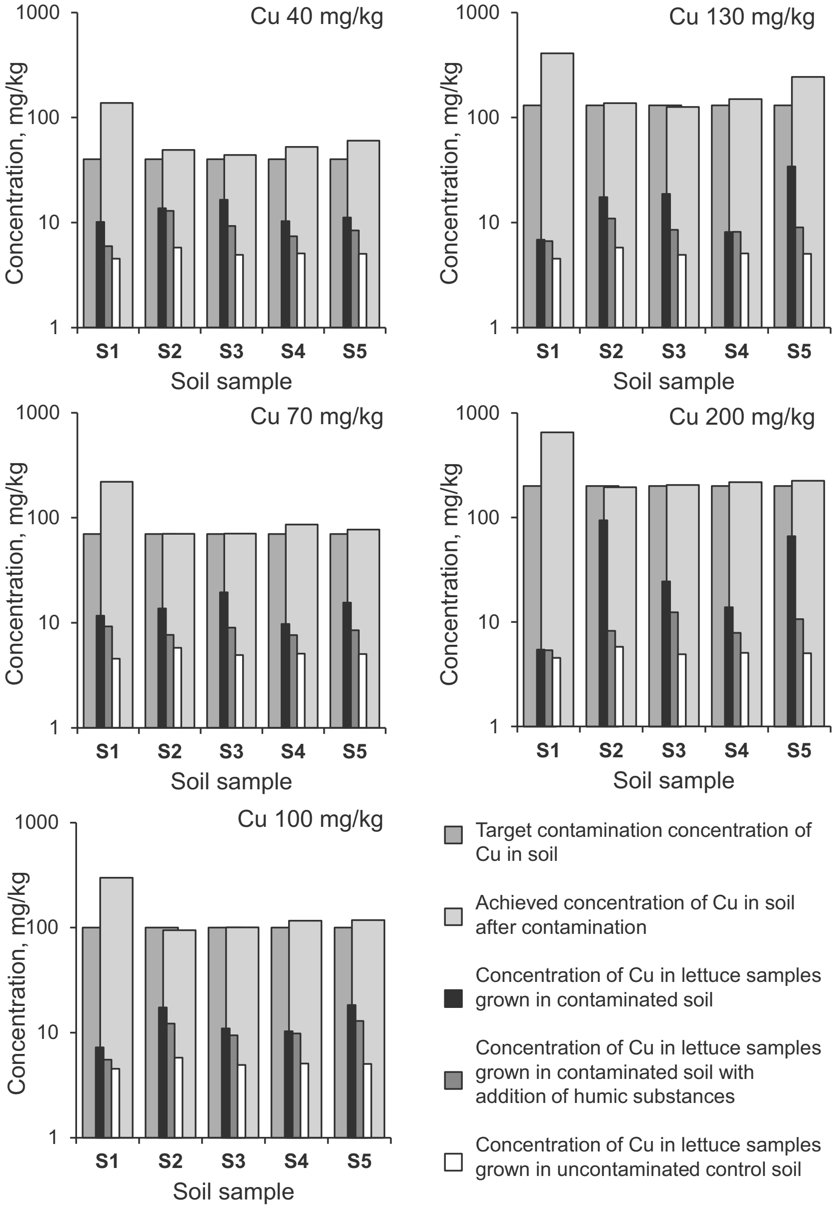

Figure 3.35. **Concentration of Cu in lettuce samples grown in control and contaminated soils with different target concentration of Cu with or without addition of humic substances (S1 – fen peat soil; S2 – sod-podzolic soil / sandy loam; S3 – sod-podzolic soil / sand; S4 – sod-podzolic soil / loamy sand; S5 – sod-podzolic soil / sandy clay loam)**

Major part of Cu in soils can be found in such chemical compounds that are tended tightly to bind organic substances and other soil colloids, and therefore are not easily accessible for plants (Lin et al., 2003); therefore more active accumulation in soils S2 and S5 in this case is not linked to soil texture of the samples as these soils had higher content of clay which can be a basis for colloid aggregation with trace metals. It is possible that in this case plant uptake of elements from soil is affected by pH because sod-podzolic soils S2 and S5 have slightly lower pH values than other soils.

Analysis of dill samples revealed that this is the crop with the lowest tolerance to metal contaminants, especially due to the fact that it was not possible to harvest samples from contaminated soils without addition of humic substances (Figure 3.36). Dill samples grown in control soils contained in average 4.28±0.35 mg/kg of Cu. The highest concentration of Cu in dill samples was detected mostly for sod-podzolic soil / sand S3, but the lowest for fen peat soil S1, similarly as observed for radish samples. At high contamination levels in soil the uptake of Cu by dill plants was more extensive as, for example, in dill samples grown in soils with Cu 200 mg/kg target contamination detected Cu concentration was 13-25 times higher than in control dill samples from the same soil types.

b) Cd, Cu, Pb and Zn concentration in experimentally grown food crops. After soil contamination with mixture of compounds containing Cd, Cu, Pb and Zn at different target concentration (respectively, Cd 6 mg/kg, Cu 130 mg/kg, Pb 750 mg/kg and Zn 300 mg/kg) several food crop samples were obtained. Multielement contamination negatively affected plant growth as not all crop samples were possible to harvest. For example, radish samples were harvested only from contaminated soils with addition of humic substance, but dill sample was obtained only one (from fen peat soil S1). Toxic effects in plants can be observed at such concentration of elements: Cd 5-30 mg/kg, Cu 20-100 mg/kg, Pb 30-300 mg/kg and Zn 100-300 mg/kg depending on species tolerance (Kabata-Pendias, 2011; Kabata-Pendias and Mukherjee, 2007), therefore, burdensome growth of crops can be related with possible phytotoxicity of studied microelements. Only lettuce samples were resistant to pollution and thus harvesting in all contaminated soil types at all target contaminations was possible.

Obtained results revealed different tendencies. It is known that not only Cu, as mentioned before, but also such elements as Co, Cr, Hg, Ni, Pb, Sb, Se and Zn may be soil contaminants and subsequently may be hyperaccumulated in plant leaves (Wuana and Okieimen, 2011). Within the present study, in lettuce samples grown in soils contaminated with the element salt mixture and with addition of solution of humic substances, obvious hyperaccumulation of Zn, Cd and Cu was detected for several samples (Figure 3.37). For example, in sod-podzolic soil / sand S3 Zn concentration in lettuce reached 4125.43 mg/kg and in sod-podzolic soil / loamy sand S4 4091.06 mg/kg while control samples of lettuce grown in uncontaminated soils contained only 62.50 mg/kg and 79.35 mg/kg, respectively. Addition of humic substances into these soils resulted in lower Zn concentration in lettuce 654.48 mg/kg and 597.78 mg/kg, respectively; however, anyway exceeding true Zn concentration detected in soil.

Taking into account different target concentration of contaminants, the sequences of analysed metals in plants were detected as follows: Zn >Cd >Cu >Pb, based on mean results.

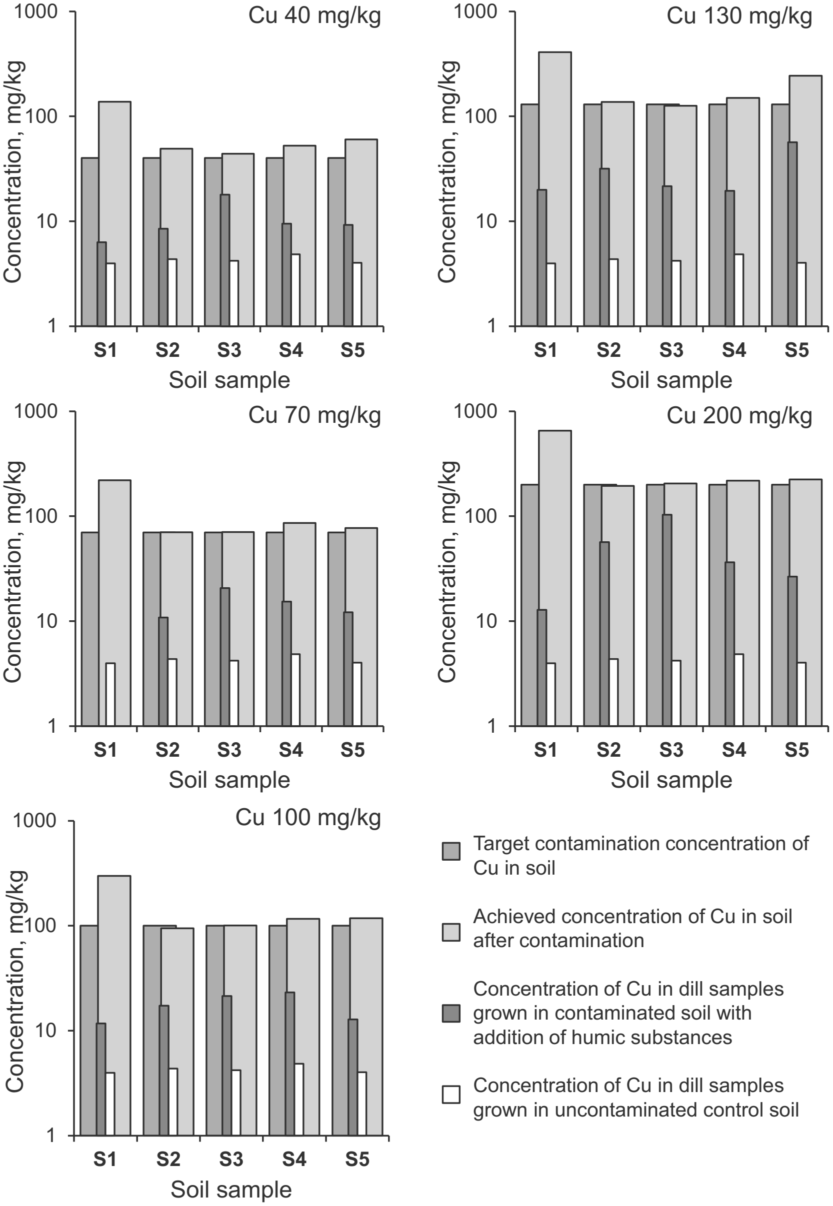

Figure 3.36. **Concentration of Cu in dill samples grown in control and contaminated soils with different target concentration of Cu with addition of humic substances (S1 – fen peat soil; S2 – sod-podzolic soil / sandy loam; S3 – sod-podzolic soil / sand; S4 – sod-podzolic soil / loamy sand; S5 – sod-podzolic soil / sandy clay loam)**

Such metals as Cd, Cu and Pb are well known pollutants of environment and agricultural soils. Element uptake in large amounts can lead to toxic effects in plants and subsequently in animals and humans. At the same time Cu and Zn are essential micronutrients for plants but Pb and Cd are not involved in biological functions, but can be taken up by plants in different intensity depending on element content in soils and plant species (Zheljazkov et al., 2006).

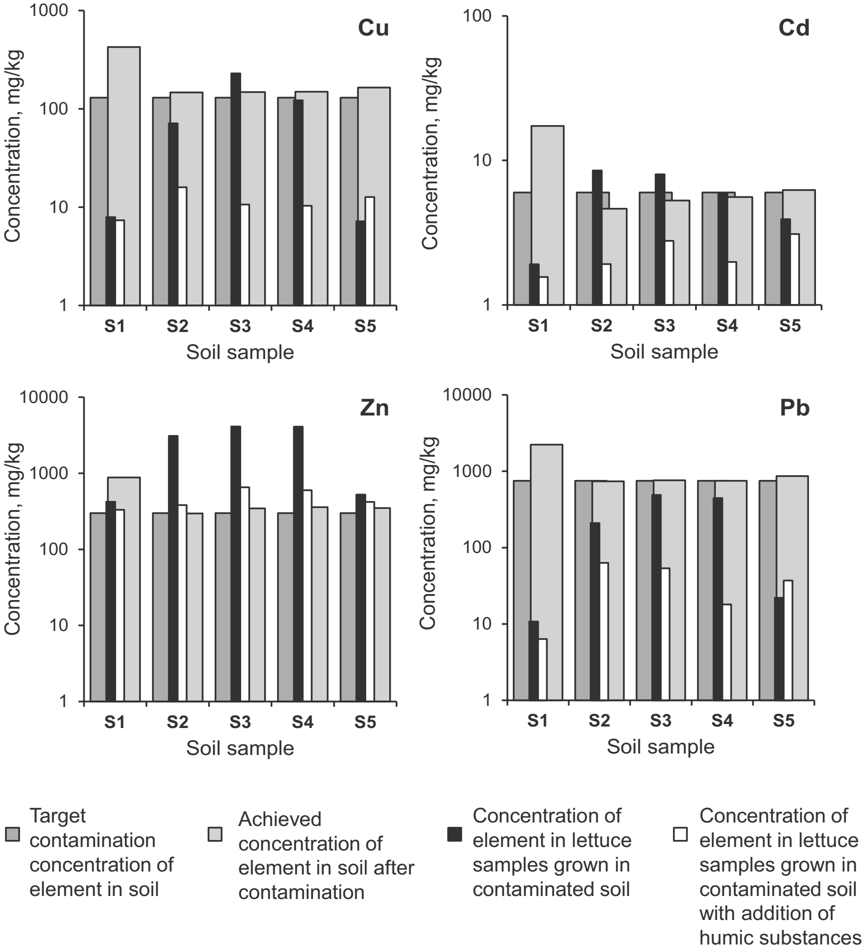

Figure 3.37. **Concentration of Cd, Cu, Pb and Zn in lettuce samples grown in soils contaminated with element salt mixture, with or without addition of humic substances (S1 – fen peat soil; S2 – sod-podzolic soil / sandy loam; S3 – sod-podzolic soil / sand; S4 – sod-podzolic soil / loamy sand; S5 – sod-podzolic soil / sandy clay loam)**

Radish sample analysis also revealed Zn hyperaccumulation tendency (Figure 3.38). Highest content of contaminants mostly was detected for radish samples grown in sod-podzolic soils S3 and S5 while samples grown in soils with higher content of organic matter contained relatively lower concentration of elements, e.g., for fen peat soil S1 and sod-podzolic soil / loamy sand S4.

Average natural concentration of elements in plants, as it was mentioned in literature, has been estimated as follows: Cd 0.01-0.2 mg/kg, Cu 5-30 mg/kg, Pb 5-10 mg/kg and Zn 25-150 mg/kg (Kabata-Pendias, 2011; Kabata-Pendias and Pendias, 2007). That is in agreement with element concentration in crop samples grown in uncontaminated control soils, e.g., concentration of elements in radish samples was: Cd 0.06-0.15 mg/kg, Cu 4.54-5.87 mg/kg, Pb <1 mg/kg and Zn 4.54-5.78 mg/kg.

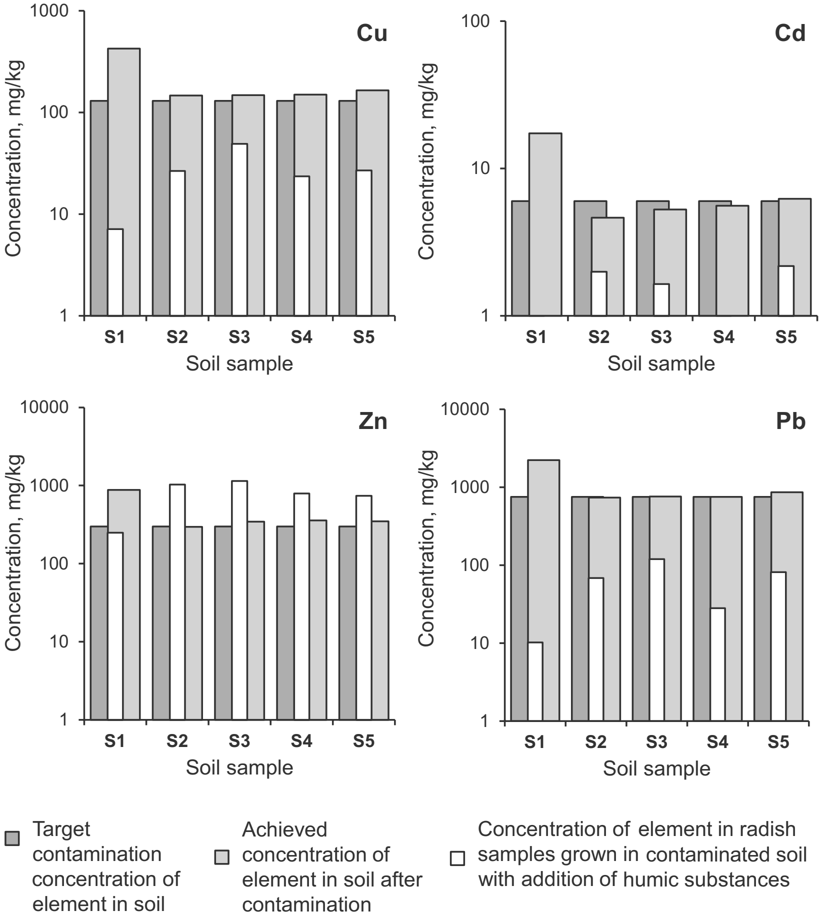

Figure 3.38. **Concentration of Cd, Cu, Pb and Zn in radish samples grown in soils contaminated with element salt mixture, with addition of humic substances. (S1 – fen peat soil; S2 – sod-podzolic soil / sandy loam; S3 – sod-podzolic soil / sand; S4 – sod-podzolic soil / loamy sand; S5 – sod-podzolic soil / sandy clay loam)**

Metal transfer from soil to plants is dependent on various chemical processes such as chelation, absorption and desorption, precipitation and dissolution. Z.L. He with colleagues (2005) defined that *'chelation is the process during which trace elements form stable complexes with organic or inorganic ligands'*. It is supposed that chelation is the main factor that affects copper accumulation in lettuce grown in soils added with solutions of humic substances. In several studies it was described that characterization of quantitative transfer of metals from soil to plants can be estimated by so called transfer factor (TF) or soil-plant partition coefficient. Transfer factor reveals the ratio of contaminant concentration C_{plant} in plants versus contaminant concentration C_{soil} in soil (Alexander et al., 2006; Chojancka et al., 2005). Higher values of transfer factor reflect greater ability of plants to accumulate metal whereas lower values of transfer factor show the intensity of sorption of metal ions to soil colloidal particles (Hao et al., 2009). Transfer factor can be variable due to several influencing factors; however, A. Kloke with colleagues (1984) have suggested mean transfer factor values for some metals, e.g., 0.01-1.00 for Cu and Pb, 1-10 for Zn, to be used for the assessment of metal transfer from soil to food and feed plants. Calculated values for theoretical transfer factor in this study fall within the suggested mean boundaries. Such soil properties as low pH and low content of organic matter as well as metal depositions from atmosphere and anthropogenic activities can lead to high values of transfer factor in case of Cu in ambient environment (Hao et al., 2009; Kloke et al., 1984).

Transfer factor calculation was performed for lettuce and radish samples grown in selected soils contaminated with compound mixture containing Cd, Cu, Pb and Zn. Results revealed the highest TF values for Zn (>10) for lettuce grown in some sod-podzolic soils (S2-S4) without enrichment of humic substances, while significantly lower TF values were detected for lettuce and radish grown in soils with addition of humic substances thus highlighting organic matter importance in element transfer from soil to plants (Table 3.28).

Table 3.28

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

Comparing individual elements, the lowest TF values were observed for Pb. TF is higher for plant roots than for leaves.

It was calculated that Cu in interaction with other metals (Cd, Pb, Zn) accumulates in lettuce up to 32 % more than if soils are contaminated with one element, if soils are additionally enriched with humic substances. If no humic substances are added, accumulation of elements can reach up to 93 %. In radish samples accumulation rate is lower – 27 % for plants grown with addition of humic substances.

3.4.3. Assessment of element bioavailability in food chain segment soil-plant

Tentative assessment of provisional bioavailability of elements in different soil samples was performed by speciation analysis to understand the possible tendencies in element accumulation in soil and following uptake by plants. Speciation analysis allowed detection of element distribution in five selected fractions of soil sample extracts as follows: 1) fraction of water soluble compounds; 2) fraction of acid soluble compounds; 3) fraction of compounds in reduced forms; 4) fraction of compounds bound with organics; 5) fraction of compounds bound with sulphides (Arthur et al., 2007; Malandrino et al., 2011; Tessier et al., 1979).

Distribution of elements in fractions after speciation analysis revealed some differences among soil samples, mainly between fen peat soil S1 and sod-podzolic soils (S2-S5) in general. Largest fraction of elements in reduced forms of compounds corresponded to fen peat soil S1 and sod-podzolic soil / loamy sand S4, respectively, 41% and 35 % – the soils containing high content of organic matter. The largest fraction of elements bound in sulphide compounds was detected for sod-podzolic soil / sand S3 (39 %), but it did not much differed among other soil samples, respectively, 27-35 % (Figure 3.39).

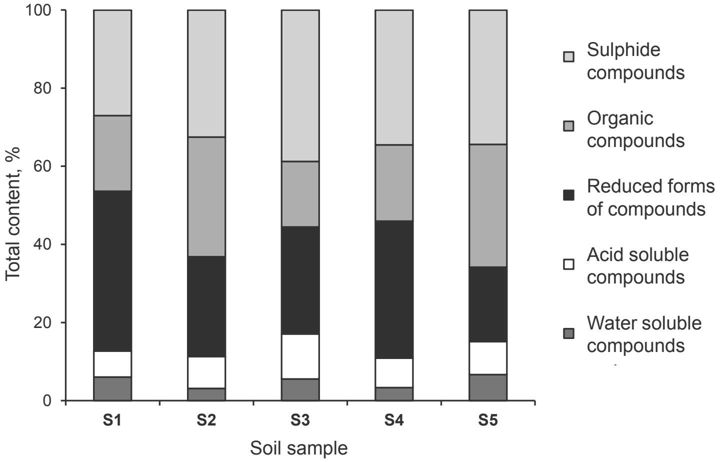

Figure 3.39. **Distribution of elements by fractions in analysed soil samples (S1 – fen peat soil; S2 – sod-podzolic soil / sandy loam; S3 – sod-podzolic soil / sand; S4 – sod-podzolic soil / loamy sand; S5 – sod-podzolic soil / sandy clay loam)**

Fraction of water soluble compounds was the smallest (3-7 %) followed by fraction of acid soluble compounds (7-12 %). It suggests that only small amount of total content of elements in soils can be taken up by plants and used in biochemical processes, while the major part of elements are bound in fractions of compounds with significantly lower bioavailability.

It was possible to detect 10 elements (As, Cd, Co, Cu, Ni, Pb, Rb, Sr, V and Zn) in soils samples by fractions. Distribution of individual elements by fractions among soil samples differed widely. For fen peat soil S1 in fraction of water soluble compounds the highest content was detected for Cu, followed by Sr, Ni and Zn (Figure 3.40).

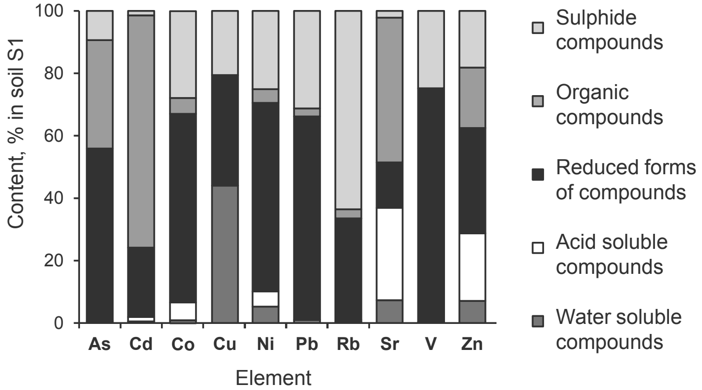

Figure 3.40. **Element distribution by fractions in fen peat soil (S1)**

In fraction of acid soluble compounds Sr, Zn, Ni and Co was found in considerable concentration, while such elements as As, Pb, Rb and V mostly were bound in other fractions suggesting their lower bioavailability.

Also in sod-podzolic soils (S2-S5) in fraction of water soluble compounds Cu was the only element found in considerable concentration. However, for soil S5 (sandy clay loam) also Zn was found in relatively high concentration in form of water soluble compound (Figure 3.41).

In sod-podzolic soils (S2-S5) Cd and Sr were the most abundant elements of the fraction of acid soluble compounds, while the greatest part of elements (e.g., As, Ni, Pb, Rb, V, Zn) mostly were bound with sulphides suggesting their low solubility and, respectively, expecting lower rate of bioavailability.

In fraction of water soluble compounds highest rates were attributed to such elements as Cu, Cr and Zn. D.A. Heemsbergen with colleagues (2010) have outlined that Cu availability for plants is dependent on speciation of substance applied, i.e., is it salt or not; however, copper solubility can be increased by complex formation with dissolved organic matter but bioavailability in this case can be not changed or even can be reduced.

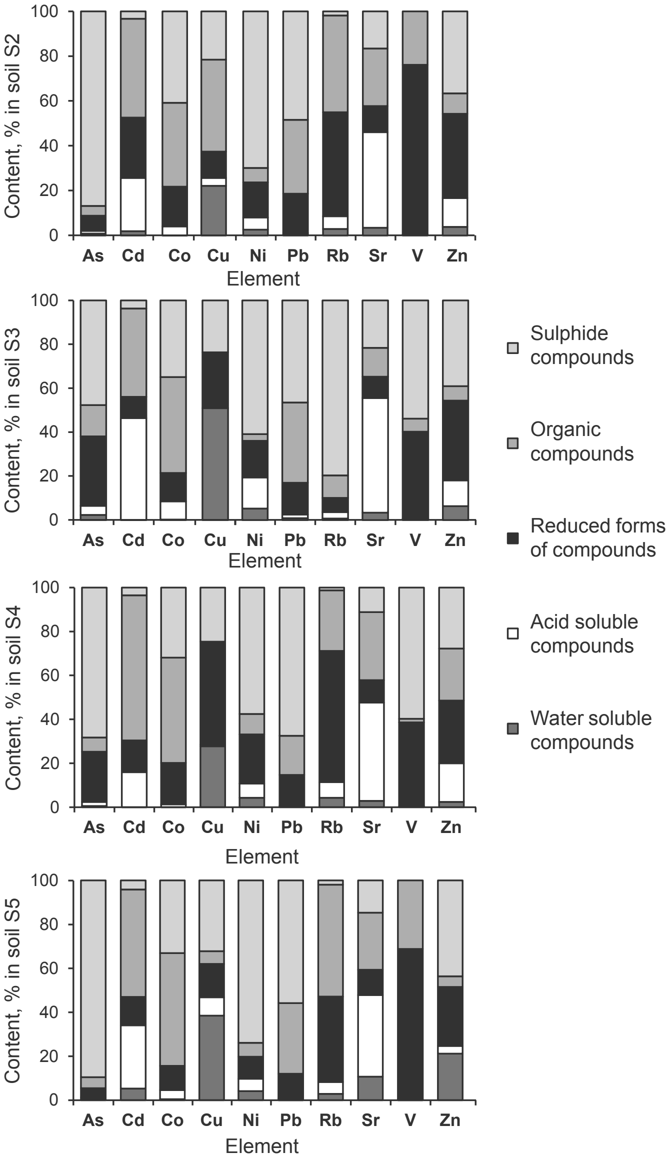

Figure 3.41. **Element distribution by fractions in sod-podzolic soils (S2-S5)**

Taking into account values of Cd, Cu, Pb and Zn content, as these there were elements exploited in the soil contamination and crop growing experiment, it can be assessed that Cu is the element most of all detectable in the fraction of water soluble compounds. Among these elements, Pb can be assessed as the least bioavailable element, as it was found more bound in compounds with low solubility. In the fraction of acid soluble compounds dominant elements were Cu and Zn, but bound with organics they were less bioavailable. It suggests that in general Zn and Cu are elements which are more bioavailable for plants than Cd and Pb. This conclusion is well related with the existing knowledge of Zn and Cu physiological functions as much as these elements are essential micronutrients, while physiological functions of Cd and Pb are nearly insignificant and their abundance naturally is low.

Highest levels of elements in grown crops were detected mostly in sod-podzolic soil / sand S3. In comparison with other soils, sod-podzolic soil / sand S3 contained Cd in acid soluble forms which bioavailability is dependent on pH. As well in this soil type there was the highest concentration of Cu (51 %) that was bound in fraction of water soluble compounds. That can explain higher Cu uptake by plants from sod-podzolic soil / sand A3.

Obtained results reveal that organic matter content in soil can significantly influence element uptake by plants. The lowest element concentration in food crops almost in all cases was detected for plant samples grown in fen peat soil S1. For example, Cu content bound in fraction of water soluble compounds in fen peat soil S1, and also in sod-podzolic soil / loamy sand A4, where there was naturally higher content of organic substances, was much greater than in the same fraction of sod-podzolic soil / sand S3 with low content of organics.

In overall, it was detected that in soils elements were in the lowest content in fraction of water soluble compounds, but in highest content bound in low soluble compounds that suggests that majority of elements in soils would not be bioavailable for plants.

3.4.4. Assessment of element bioavailability in food chain segment **plant-human;** *the case study with lettuce*

Element bioavailability in food chain segment *plant-human* is complicated and affected by different factors including environmental conditions such as natural background of elements in soil and drinking water, chemical characteristics of substance and biochemical conversions within the individual organism. Tentative assessment of element bioavailability from plants was done by speciation analysis of lettuce samples with the aim to understand the fundamentals of element transfer from environment to food. Extraction of elements was done in three fractions: 1) fraction of water soluble compounds; 2) fraction of acid soluble compounds; 3) fraction of compounds in reduced forms. It was possible to detect 12 elements (As, Ba, Cd, Co, Cu, Mn, Ni, Pb, Rb, Se, Sr and Zn).

Distribution of elements into selected fractions revealed that greatest part of elements can be found in fraction of water soluble compounds (47 %), following by fraction of reduced forms of compounds (37 %) and fraction of acid soluble compounds (15 %) which quite differs of element distribution by fractions in soil. Also for individual elements, except As, distribution by fractions is similar. Arsenic was the element mostly found in fraction of reduced forms of compounds 93 % (Figure 3.42), thus suggesting its low bioavailability in food chain.

Analysis revealed that in the fraction of water soluble compounds in higher concentration (>50 %) were elements such as Co, Cu, Ni, Pb, Rb and Se and this tendency in favour of essential elements, but can lead to increased toxicity of potentially toxic elements. Such elements as As, Ba, Cd, Sr were found in higher concentration in the fraction of

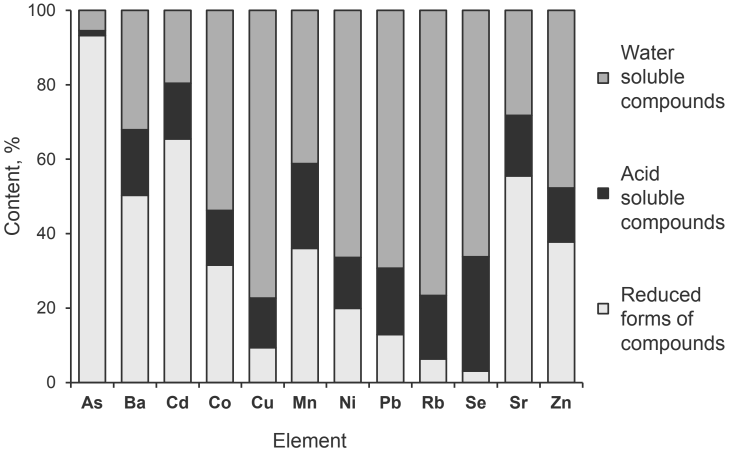

Figure 3.42. **Element distribution by fractions in lettuce samples**

reduced forms of compounds. Taking into account these findings after the study with lettuce it can be estimated that for largest part of elements transfer from soil to food plants is fairly low; however, other food contamination sources have to be evaluated.

It is assumed that generally the assessment of environmental pollution is based on the total concentration of elements assessed as potential pollutants, not taking into account their speciation forms which in a great extent may affect element fate in environment as well as in biochemical processes in living organisms. Depending on the chemical character, the intensity of impact of metals and non-metals on biota can be changed, in worst case inducing toxic effects on plants as well as on animal and human organs and tissues. Therefore, detection only of total metal concentration in a matrix (e.g., soil, water, biomass) is not effective method for assessment of element fate and pollution risks in environment (Harmsen and Naidu, 2013; Remon et al., 2013; Wang et al., 2004).

CONCLUSIONS

- Obtained results revealed recognizable influence of several factors (impact of seasonal, site-specific, botanical origin, 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.
- Site-specific 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

in 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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REFERENCES

1. Abebe, Y., Bogale, A., Hambidge, K.M., Stoecker, B.J., Bailey, K., Gibson, R.S. (2007) Phytate, zinc, iron and calcium content of selected raw and prepared foods consumed in rural Sidama, Southern Ethiopia, and implications for bioavailability. *Journal of Food Composition & Analysis* 20: 161-168.
2. Aberoumand, A., Deokule, S.S. (2010) Elements evaluation of some edible vegetables and fruits of Iran and India. *Asian Journal of Agricultural Sciences* 2(1): 35-37.
3. Abrahams, P.W. (2002) Soils: Their implications to human health. *The Science of the Total Environment* 291(1-3): 1-32.
4. ACS (2011) *Known and probable human carcinogens*. American Cancer Society (ACS). Accessed at *http://www.cancer.org/cancer/cancercauses/othercarcinogens/generalinformation-aboutcarcinogens/known-and-probable-carcinogens* on 15.12.2012.
5. Ajtony, Z., Bencs, L., Haraszi, R., Szigeti, J., Szoboszlai, N. (2007) Study on the simultaneous determination of some essential and toxic trace elements in honey by multi-element graphite furnace atomic absorption spectrometry. *Talanta* 71: 683-690.
6. Alam, M.G.M., Snow, E.T., Tanaka, A. (2003) Arsenic and heavy metal contamination of vegetables grown in Samta village, Bangladesh. *The Science of the Total Environment* 308: 83-96.
7. Aldahan, A., Kekli, A., Possnert, G. (2006) Distribution and sources of ^{129}I in rivers of the Baltic region. *Journal of Environmental Radioactivity* 88(1): 49-73.
8. Alexander, P.D., Alloway, B.J., Dourado, A.M. (2006) Genotypic variations in the accumulation of Cd, Cu, Pb and Zn exhibited by six commonly grown vegetables. *Environmental Pollution* 144(3): 736-745.
9. Allen, A.G., Nemitz, E., Shi, J.P., Harrison, R.M., Greenwood, J.C. (2001) Size distributions of trace metals in atmospheric aerosols in the United Kingdom. *Atmospheric Environment* 35: 4581-4591.
10. Alloway, J., Centeno, A., Finkelman, B., Fuge, R. (2004) *Essentials of Medical Geology. Impact of the Natural Environment on Public Health.* Elsevier Academic Press: Amsterdam, 832 p.
11. Alsina, I., Dubova, L., Smiltina, Z., Stroksa, L., Duma, M. (2012) The effect of selenium on yield quality of lettuce. *Acta Horticulturae* 939: 269-276.
12. Alvarez, J., Marco, L.M., Arroyo, J., Greaves, E.D., Rivas, R. (2003) Determination of calcium, potassium, manganese, iron, copper and zinc levels in representative samples of two onion cultivars using total reflection X-ray fluorescence and ultrasound extraction procedure. *Spectrochimica Acta, Part B: Atomic Spectroscopy* 58(12): 2183-2189.
13. Aras, N.K., Ataman, O.Y. (2006) *Trace Element Analysis of Food and Diet*. RSC Publishing: Cambridge, 344 p.
14. Arthur, J.D., Fischler, C., Dabous, A.A., Budd, D.A., Katz, B.G. (2007) Geochemical and mineralogical characterization of potential aquifer storage and recovery storage zones in the Floridan Aquifer System, comprehensive Everglades restoration plan. *Final report.* No page numbering.
15. ATSDR (s.a.) *Toxic substances portal*. Agency for Toxic Substances and Disease Registry (ATSDR), United States Department of Health and Human Services. Accessed at *http://www.atsdr.cdc.gov/toxprofiles/index.asp* on 16.09.2013.
16. Awuah, G.B., Ramaswamy, H.S., Economides, A. (2007) Thermal processing and quality: Principles and overview. *Chemical Engineering & Processing: Process Intensification* 46(6): 584-602.
17. Ayar, A., Sert, D., Akin, N. (2009) The trace metal levels in milk and dairy products consumed in middle Anatolia - Turkey. *Environmental Monitoring & Assessment* 152: 1-12.

18. Baltes, V. (1998) *Pārtikas ķīmija / Lebensmittelchemie*. (4th ed.) [In Latvian] Latvijas Universitāte: Rīga, 478 lpp.
19. Basu, M., Pande, M., Bhadoria, P.B.S., Mahapatra, S.C. (2009) Potential fly-ash utilization in agriculture: A global review. *Progress in Natural Science* 19: 1173-1186.
20. Berdanier, C.D., Dwyer, J.T., Feldman, E.B. (2007) *Handbook of Nutrition and Food*. (2nd ed.) CRC Press: Boca Raton, 1288 p.
21. Bibak, A., Sturup, S., Gundersen, V. (1998) *Levels of 44 Elements in Organically Grown Potatoes (Solanum tuberosum, Sava)*. Riso National Laboratory: Roskilde, 15 p.
22. Bowman, C.A., Bobrowsky, P.T., Selinus, O. (2003) Medical geology: New relevance in the earth sciences. *Episodes* 24(6): 270-278.
23. Braziewitzs, J., Kownacka, L., Majweska, U., Korman, A. (2004) Elemental concentrations in tropospheric and lower stratospheric air in a Northeastern region of Poland. *Atmospheric Environment* 38: 1989-1996.
24. Brekken, A., Steinnes, E., (2004) Seasonal concentrations of cadmium and zinc in native pasture plants: Consequences for grazing animals. *Science of the Total Environment* 326: 181-195.
25. Briggs, D., Wahlqvist, M. (1998) *Food Facts*. Penguin Books: Melbourne, 264 p.
26. Brumelis, G., Lapina, L., Nikodemus, O., Tabors, G. (2002) Use of the O horizon of forest soils in monitoring metal deposition in Latvia. *Water, Air & Soil Pollution* 135(1-4): 291-309.
27. Buldini, P.L., Cavalli, S., Mevoli, A., Sharma, J.L. (2001) Ion chromatographic and voltammetric determination of heavy and transition metals in honey. *Food Chemistry* 73: 487-495.
28. Callanan, A. (ed.) (2000) *Food and Nutrition Handbook*. World Food Programme: Rome, 124 p.
29. Carbonell-Barrachina, A.A., Wu, X., Ramirez-Gandolfo, A., Norton, G. J., Burlo, F., Deacon, C., Meharg, A.A. (2012) Inorganic arsenic contents in rice-based infant foods from Spain, UK, China and USA. *Environmental Pollution* 163: 77-83.
30. Cashman, K.D. (2006) Milk minerals (including trace elements) and bone health. *International Dairy Journal* 16: 1389-1398.
31. Čekstere, G. (2011) *Vides faktoru ietekme uz Holandes liepu (Tilia x vulgaris) vitalitāti Rīgas ielu apstādījumos / Impact of Environmental Factors on Vitality of Common Lime (Tilia x vulgaris) in the Street Greenery of Riga*. Doctoral thesis. [In Latvian] LU Akadēmiskais apgāds: Rīga, 225 lpp.
32. Cekstere, G., Nikodemus, O., Osvalde, A. (2008) Toxic impact of the de-icing material to street greenery in Riga, Latvia. *Urban Forestry & Urban Greening* 7(3):207-217.
33. Cekstere, G., Osvalde, A. (2013) A study of chemical characteristics of soil in relation to street trees status in Riga (Latvia). *Urban Forestry & Urban Greening* 12(1): 69-78.
34. Cekstere, G., Osvalde, A. (2010a) Macronutrient status in the different-aged lime trees (*Tilia x vulgaris* H.) in Riga streets. *Baltic Forestry* 16(1): 16-22.
35. Cekstere, G., Osvalde, A. (2010b) Young street greenery supply with nutrients in Riga, Latvia. *Acta Horticulturae* 881: 573-576.
36. Cheli, F., Campagnoli, A., Ventura, V., Brera, C., Berdini, C., Palmaccio, E., Dell'Orto, V. (2010) Effects of industrial processing on the distributions of deoxynivalenol, cadmium and lead in durum wheat milling fractions. *LWT - Food Science & Technology* 43: 1050-1057.
37. Chojancka, K., Chojancki, A., Gorecka, H., Gorecki, H. (2005) Bioavailability of heavy metals from polluted soils to plants. *Science of the Total Environment* 337: 175-182.
38. Chope, G.A., Terry, L.A. (2009) Use of canonical variate analysis to differentiate onion cultivars by mineral content as measured by ICPAES. *Food Chemistry* 115(3): 1108-1113.
39. Chudzinska, M., Baralkiewicz, D. (2010) Estimation of honey authenticity by multielements characteristics using inductively coupled plasma-mass spectrometry (ICP-MS) combined with chemometrics. *Food & Chemical Toxicology* 48(1): 284-290.

40. Cindric, I.J., Krizman, I., Zeiner, M., Kampic, S., Medunic, G., Stingeder, G. (2012) ICP-AES determination of minor- and major elements in apples after microwave assisted digestion. *Food Chemistry* 135(4): 2675-2680.
41. Combs, G.F. (2005) Geological impacts of nutrition. In: Selinus, O. (ed.-in-chief) *Essentials of Medical Geology*. Elsevier Academic Press: Amsterdam, 812 p., 161-177.
42. Conti, M.E. (1997) The content of heavy metals in food packaging paper boards: An atomic absorption spectroscopy investigation. *Food Research International* 30(5): 343-348.
43. Conti, M.E. (2007) Heavy metals in food packagings. In: Szefer, P., Nriagu, J.O. (eds.) *Mineral Components in Food*. CRC Press: Boca Raton, 446 p., 339-362.
44. Dabeka, R.W., McKenzie, A.D., Lacroix, G.M., Cleroux, C., Bowe, S., Graham, R.A., Conacher, H.B., Verdier, P. (1993) Survey of arsenic in total diet food composites and estimation of the dietary intake of arsenic by Canadian adults and children. *Journal of AOAC International* 76(1): 14-25.
45. Dewettinck, K., Van Bockstaele, F., Kuhne, B., Van de Walle, D., Courtens, T.M., Gellynck, X. (2008) Nutritional value of bread: Influence of processing, food interaction and consumer perception. *Journal of Cereal Science* 48: 243-257.
46. Diez, M., Simon, M., Martin, F., Dorronsoro, C., Garcia, I., Van Gestel, C.A.M. (2009) Ambient trace element background concentrations in soils and their use in risk assessment. *Science of the Total Environment* 407(16): 4622-4632.
47. Dimiņš, F. (2006) *Medus kvalitātes novērtēšanas rādītāji / Assessment Parameters of Honey Quality.* Doctoral thesis. [In Latvian] LLU: Jelgava, 85 lpp.
48. DiSilvestro, R.A. (2005) *Handbook of Minerals as Nutritional Supplements*. CRC Press: Boca Raton, 272 p.
49. Dobrzanski, Z., Gorecki, H., Chojnacka, K., Gorecka, H., Synoviec, M. (2007) Effect of dietary humic preparations on the content of the trace elements in the hens' eggs. *American Journal of Agricultural & Biological Sciences* 2: 234-240.
50. Duffus, J.H., Nordberg, M., Templeton, D.M. (2007) IUPAC glossary of terms used in toxicology (2nd ed.). *Pure Applied Chemistry* 79(7):1153-1344.
51. Duma, M., Alsina, I., Dubova, L., Stroksa, L., Smiltina, Z. (2011) The effect of sodium selenite and selenate on the quality of lettuce. *FOODBALT* 2011: 39-44.
52. ECHA (2013) *Candidate list of substances of very high concern for authorisation*. European Chemicals Agency (ECHA). Accessed at *http://echa.europa.ei/candidate-list-table* on 03.08.2013.
53. EC Regulation 889 (2008) Commission Regulation (EC) No 889/2008 of 5 September 2008 laying down detailed rules for the implementation of Council Regulation (EC) No 834/2007 on organic production and labelling of organic products with regard to organic production, labelling and control. *Official Journal of the European Union* L250: 1-84.
54. EC Regulation 629 (2008) Commission Regulation (EC) No 629/2008 of 2 July 2008 amending Regulation (EC) No 1881/2006 setting maximum levels for certain contaminants in foodstuffs. *Official Journal of the European Union* L173: 6-9.
55. EC Regulation 1881 (2006) Commission Regulation (EC) No 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs. *Official Journal of the European Union* L364: 5-24.
56. Eggen, T., Moder, M., Arukwe, A. (2011) Emerging contaminants in consumer products: environmental fate and transfer to human foodchain. In: Popov, V., Brebbia, C.A. (eds.) *Food and Environment*. WIT Press: Southampton, 225 p., 89-94.
57. Ekholm, P., Reinivuo, H., Mattila, P., Pakkala, H., Koponen, J., Happonen, A., Hellistrom, J., Ovaskainen, M.-L. (2007) Changes in the mineral and trace element contents of cereals, fruits and vegetables in Finland. *Journal of Food Composition & Analysis* 20(6): 487-495.

58. EXTOXNET (s.a.) *Toxicology information briefs*. Extension Toxicology Network (EXTOXNET). Accessed at *http://pmep.cce.cornell.edu/profiles/extoxnet/TIB/index.html* on 19.04.2012.
59. Favas, P. (2013) Environmental risk associated with heavy metal pollution in soils based on geochemical fractionation. *SGEM 2013 GeoConference Proceedings on Ecology, Economics, Education & Legislation* 1, 417-422.
60. Fairbrother, A., Wenstel, R., Sappington, K., Wood, W. (2007) Framework for metals risk assessment. *Ecotoxicology & Environmental Safety* 68(2): 145-227.
61. Fan, J.-L., Ziadi, N., Belanger, G., Parent, L.E., Cambouris, A., Hu, Z.-L. (2009) Cadmium accumulation in potato tubers produced in Quebec. *Canadian Journal of Soil Science* 89(4): 435-443.
62. FAO (2006) *Guidelines for Soil Description*. (4th ed.) Food and Agriculture Organisation (FAO): Rome, 97 p.
63. FAO (2001) *Human Vitamin and Mineral Requirements*. Food and Agriculture Organisation (FAO): Rome, 303 p.
64. Farid, S.M., Enani, M.A. (2010) Levels of trace elements in commercial fruit juices in Jeddah, Saudi Arabia. *The Medicinal Journal of the Islamic World Academy of Sciences* 18(1): 31-38.
65. Fernandez-Torres, R., Perez-Bernal, J.L., Bello-Lopez, M.A., Callejon-Mochon, M., Jimenez-Sanchez, J.C., Guiraum-Perez, A. (2005) Mineral content and botanical origin of Spanish honeys. *Talanta* 65(3): 686-691.
66. Ferre-Huguet, N., Marti-Cid, R., Schuhmacher, M., Domingo, J.L. (2008) Risk assessment of metals from consuming vegetables, fruits and rice grown in soils irrigated with waters of the Ebro River in Catalonia, Spain. *Biological Trace Element Research* 123(1-3): 66-79.
67. FNIC (s.a.) *Dietary reference intakes*. Food and Nutrition Information Center (FNIC). Accessed at *http://fnic.nal.usda.gov/dietary-guidance/dietary-reference-intakes* on 17.09.2013.
68. Fodor, P., Molnar, E. (1993) Honey as an environmental indicator: Effect of sample preparation on trace element determination by ICP-AES. *Microchimica Acta* 112(1-4): 113-118.
69. Forrest, M.J. (2009) *Food Contact Materials: Rubbers, Silicones, Coatings and Inks*. iSmithers: Shawbury, 362 p.
70. Fraga, C.G. (2005) Relevance, essentiality and toxicity of trace elements in human health. *Molecular Aspects of Medicine* 26(4-5): 235-244.
71. FSA (2006) *FSA Nutrient and Food Based Guidelines for UK Institutions*. Food Standards Agency (FSA): London, 7 p.
72. Gardea-Torresdey, J.L., Peralta-Videa, J.R., de la Rosa, G., Parsons, J.G. (2005) Phytoremediation of heavy metals and study of the metal coordination by X-ray absorption spectroscopy. *Coordination Chemistry Reviews* 249(17-18): 1797-1810.
73. Garrett, R.G. (2005) Natural distribution and abundance of elements. In: Selinus, O. (ed.-in-chief) *Essentials of Medical Geology*. Elsevier Academic Press: Amsterdam, 812 p., 17-41.
74. Giannenas, I., Nisianakis, P., Gavriil, A., Kontopidis, G., Kyriazakis, I. (2009) Trace mineral content of conventional, organic and courtyard eggs analysed by inductively coupled plasma mass spectrometry (ICP-MS). *Food Chemistry* 114(2): 706-711.
75. Gilucis, A. (2007) *Mikro- un makroelementu satura un izplatības likumsakarības Latvijas augšņu virsējos horizontos / Relevancies of Content and Distribution of Trace and Major Elements in the Latvian Topsoils*. Doctoral thesis. [In Latvian] LU: Rīga, 88 lpp.
76. Goldhaber, S.B. (2003) Trace element risk assessment: Essentiality vs. toxicity. *Regulatory Toxicology & Pharmacology* 38(2): 232-242.
77. Golob, T., Dobersek, U., Kump, P., Necemer, M. (2005) Determination of trace and minor elements in Slovenian honey by total reflection X-ray fluorescence spectroscopy. *Food Chemistry* 91: 593-600.

78. Gonzalvez, A., Armenta, S., Cervera, M.L., de la Guardia, M. (2008) Elemental composition of seasoning products. *Talanta* 74(5): 1085-1095.
79. Grant, C., Buckley, W., Bailey, L., Selles, F. (1998) Cadmium accumulation in crops. *Canadian Journal of Plant Science* 78(1): 1-17.
80. Gruber, X., Kregsamer, P., Wobrauschek, P., Streli, C. (2006) Total-reflection X-ray fluorescence analysis of Austrian wine. *Spectrochimica Acta Part B: Atomic Spectroscopy* 61(10-11): 1214-1218.
81. Guala, S.D., Vega, F.A., Covelo, E.F. (2010) The dynamics of heavy metals in plant-soil interactions. *Ecological Modelling* 221: 1148-1152.
82. Hao, X.-Z., Zhou, D.-M., Huang, D.-Q., Cang, L., Zhang, H.-L., Wang, H. (2009) Heavy metal transfer from soil to vegetable in Southern Jiangsu province, China. *Pedosphere* 19(3): 305-311.
83. Harju, L., Hulden, S.-G. (1990) Birch sap as a tool for biogeochemical prospecting. *Journal of Geochemical Exploration* 37(3), 351-365.
84. Harmsen, J., Naidu, R. (2013) Bioavailability as a tool in site management. *Journal of Hazardous Materials* 12: 1-7.
85. Hashmi, D.R., Ismail, S., Shaikh, G.H. (2007) Assessment of the level of trace metals in commonly edible vegetables locally available in the markets of Karachi city. *Pakistan Journal of Botany* 39(3): 747-751.
86. Hawkesford, M.J., Zhao, F.-J. (2007) Strategies for increasing the selenium content of wheat. *Journal of Cereal Science* 46: 282-292.
87. He, Z.L., Yang, X.E., Stoffella, P.J. (2005) Trace elements in agroecosystems and impacts on the environment. *Journal of Trace Elements in Medicine & Biology* 19: 125-140.
88. Heemsbergen, D.A., McLaughlin, M.J., Whatmuff, M., Warne, M.S., Broos, K., Bell, M., Nash, D., Barry, G., Pritchard, D., Penney, N. (2010) Bioavailability of zinc and copper in biosolids compared to their soluble salts. *Environmental Pollution* 158: 1907-1915.
89. Hernandez-Martinez, R., Navarro-Blasco, I. (2013) Survey of total mercury and arsenic content in infant cereals marketed in Spain and estimated dietary intake. *Food Control* 30(2): 423-432.
90. Hodges, S.C. (s.a.) *Soil Fertility Basics*. North Carolina State University (NCSU): Raleigh, 75 p.
91. Hoefler, H., Streli, C., Wobrauschek, P., Ovari, M., Zaray, G. (2006) Analysis of low Z elements in various environmental samples with total reflection X-ray fluorescence (TXRF) spectrometry. *Spectrochimica Acta Part B: Atomic Spectroscopy* 61(10-11): 1135-1140.
92. Holt, P.S., Davies, R.H., Dewulf, J., Gast, R.K., Huwe, J.K,. Jones, D.R., Waltman, D., Willian, K.R. (2011) The impact of different housing systems on egg safety and quality. *Poultry Science* 90: 251-262.
93. Inaba, S., Takenaka, C. (2005) Effects of dissolved organic matter on toxicity and bioavailability of copper for lettuce sprouts. *Environment International* 31(4): 603-608.
94. IOM (s.a.) *Dietary reference intake reports*. The Institute of Medicine (IOM) of the National Academies. Accessed at *http://www.iom.edu/Reports.aspx?Board1={32E1607 C-3E87-4E73-B9D4-7C96E29EB9A5}&page=1&Series={508F5CFF-EE88-4FF6-92BF-8D6CAB46F52E}* on 16.09.2013.
95. IRIS (s.a.) *Integrated Risk Information System (IRIS)*. United Stated Environmental Protection Agency. Accessed at *http://www.epa.gov/iris/search_human.htm* on 09.09.2013.
96. Jiao, W., Chen, W., Chang, A.C., Page, A.L. (2012) Environmental risks of trace elements associated with long-term phosphate fertilizers applications: A review. *Environmental Pollution* 168: 44-53.
97. Joshi, S.P., Toma, R.B., Medora, N., O'Connor, K. (2003) Detection of aluminium residue in sauces packaged in aluminium pouches. *Food Chemistry* 83: 383-386.

98. Joudisius, E., Simoneliene, A. (2009) Lietuvoje parduodamo medaus užterštumas sunkiaisiais metalais ir pesticidais / Trace metals and pesticide residues in honey on the Lithuanian market. [In Lithuanian] *Veterinarija & Zootechnika* 45(67): 27-32.
99. Juškevičs, V. (2000) *Kvartāra nogulumu karte / Map of Quaternary Sediments (1:200 000)*. Jāņa sēta: Rīga.
100. Kabata-Pendias, A. (2011) *Trace Elements in Soils and Plants*. (4th ed.) CRC Press: Boca Raton, 505 p.
101. Kabata-Pendias, A. (2004) Soil-plant transfer of trace elements – an environmental issue. *Geoderma* 122(2-4): 143-149.
102. Кабата-Пендиас, А. (2005) Проблемы современной биогеохимии микроелементов. *Российский Химический Журнал* XLIX(3): 15-19.
103. Kabata-Pendias, A., Mukherjee, A.B. (2007) *Trace Elements from Soil to Human*. Springer-Verlag: Berlin, 550 p.
104. Kārkliņš, A., Gemste, I., Mežals, H., Nikodemus, O., Skujāns, R. (2009) *Latvijas augšņu noteicējs / Soil Key-Book of Latvia*. [In Latvian] LLU: Jelgava, 235 lpp.
105. Karley, A.J., White, P.J. (2009) Moving cationic minerals to edible tissues: Potassium, magnesium, calcium. *Current Opinion in Plant Biology* 12: 291-298.
106. Карпова, Е.А. (2005) Роль удобрений в циклах микроэлементов в агроэкосистемах. *Российский Химический Журнал* XLIX(3): 20-25.
107. Kasparinskis, R., (2011) *Personal information.*
108. Kasparinskis, R., Nikodemus, O. (2012) Influence of environmental factors on the spatial distribution and diversity of forest soil in Latvia. *Estonian Journal of Earth Sciences* 61(1): 48-64.
109. Kazi, T.G., Jalbani, N., Baig, J.A., Kandhro, G.A., Afridi, H.I., Arain, M.B., Jamali, M.K., Shah, A.Q. (2009) Assessment of toxic metals in raw and processed milk samples using electrothermal atomic absorption spectrophotometer. *Food & Chemical Toxicology* 47: 2163-2169.
110. Kelly, D., Bateman, A.S. (2010) Comparison of mineral concentrations in commercially grown organic and conventional crops – tomatoes (*Lycopersicon esculentum*) and lettuces (*Lactuca sativa*). *Food Chemistry* 119: 738-745.
111. Khan, S., Cao, Q., Zheng, Y.M., Huang, Y.Z., Zhu, Y.G. (2008) Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China. *Environmental Pollution* 152(3): 686-692.
112. Kilic, Z., Acar, O., Ulasan, M., Ilim, M. (2002) Determination of lead, copper, zinc, magnesium, calcium and iron in fresh eggs by atomic absorption spectrometry. *Food Chemistry* 76(1): 107-116.
113. Klavins, M., Briede, A., Rodinov, V., Kokorite, I., Parele, E., Klavina, I. (2000) Heavy metals in rivers of Latvia. *Science of the Total Environment* 262(1-2): 175-184.
114. Klavins, M., Kokorite, I., Jankevica, M., Mazeika, J., Rodinov, V. (2011) Trace elements in sediments of lakes in Latvia. In: Mastorakis, N. (ed.-in-chief) *Recent Researches in Geography, Geology, Energy, Environment and Biomedicine.* WSEAS Press: Corfu, 518 p., 43-47.
115. Klavins, M., Potapovics, O., Rodinov, V. (2009a) Heavy metals in fish from lakes in Latvia: Concentrations and trends of changes. *Bulletin of Environmental Contamination & Toxicology* 82(1): 96-100.
116. Klavins, M., Rodinov, V., Druvietis, I. (2003) Aquatic chemistry and humic substances in bog lakes in Latvia. *Boreal Environment Research* 8(2): 113-123.
117. Klavins, M., Rodinov, V., Kokorite, I., Klavina, I., Apsite, E. (2001) Long-term and seasonal changes in chemical composition of surface waters in Latvia. *Environmental Monitoring & Assessment* 66(3): 233-254.

118. Klavins, M., Silamikele, I., Nikodemus, O., Kalnina, L., Kuske, E., Rodinov, V., Purmalis, O. (2009b) Peat properties, major and trace element accumulation in bog peat in Latvia. *Baltica* 22(1): 37-50.
119. Klavins, M., Vircavs, M. (2001) Metals in sediments of inland waters of Latvia. *Boreal Environment Research* 6(4): 297-306.
120. Klockenkamper, R. (1997) *Total-Reflection X-Ray Fluorescence Analysis*. John Wiley & Sons: New York, 245 p.
121. Kloke, A., Sauerbeck, D.R., Vetter, H. (1984) The contamination of plants and soils with heavy metals and the transport of metals in terrestrial food chain. In: Nriagu, J.O. (ed.) *Changing Metal Cycles and Human Health*. Springer-Verlag: Berlin, 446 p., 113-141.
122. Kokorite, I., Klavins, M., Rodinov, V. (2010) Impact of catchment properties on aquatic chemistry in the rivers of Latvia. *Hydrology Research* 41(3-4): 320-329.
123. Koplik, R., Kominkova, J., Borkova, M., Mestek, O., Kvasnicka, F., Suchanek, M. (2004) Effect of technological processing and maturity stage of seeds on the content and speciation of phosphorus and trace elements in peas. *Food Chemistry* 87(3): 423-432.
124. Kropf, U., Korosec, M., Bertoncelj, J., Ogrinc, N., Necemer, M., Kump, P., Golob, T. (2010) Determination of the geographical origin of Slovenian black locust, lime and chestnut honey. *Food Chemistry* 121(3): 839-846.
125. Kubala-Kukus, A., Braziewicz, J., Pajek, M. (2004) Total reflection X-ray fluorescence studies of trace elements in biomedical samples. *Spectrochimica Acta Part B: Atomic Spectroscopy* 59(8): 1283-1289.
126. Kucukyilmaz, K., Bozkurt, M., Yamaner, C., Cinar, M., Catli, A.U., Konak, R. (2012) Effect of an organic and conventional rearing system on the mineral content of hen eggs. *Food Chemistry* 132: 989-992.
127. Kuka, M., Cakste, I., Gersebeka, E. (2013) Determination of bioactive compounds and mineral substances in Latvian birch and maple saps. *Proceedings of the Latvian Academy of Sciences. Section B* 67(4/5): 437-441.
128. Kulikova, I., Seisuma, Z., Jansons, M. (2003) An assessment of metal pollution in the Liepaja harbour (Baltic Sea). *Fresenius Environmental Bulletin* 12(8): 906-913.
129. Kumar, N.J.I., Soni, H., Kumar, R.N. (2007) Characterization of heavy metals in vegetables using inductive coupled plasma analyzer (ICPA). *Journal of Applied Science & Environmental Management* 11(3): 75-79.
130. Lachman, J., Kolihova, D., Miholova, D., Kosata, J., Titera, D., Kult, K. (2007) Analysis of minority honey components: Possible use for the evaluation of honey quality. *Food Chemistry* 101: 973-979.
131. Lante, A., Lomolino, G., Cagnin, M., Spettoli, P. (2006) Content and characterisation of minerals in milk and in Crescenza and Squacquerone Italian fresh cheeses by ICP-OES. *Food Control* 17: 229-233.
132. Lawgali, Y.F. (2010) *Trace Element Levels in Mediterranean Grains*. Doctoral thesis. University of Aberdeen: Aberdeen, 204 p.
133. Liguts, V. (2001) *Toksikoloģijas rokasgrāmata / Handbook of Toxicology*. [In Latvian] Nacionālais Medicīnas Apgāds: Rīga, 1070 lpp.
134. Lin, J., Jiang, W., Liu, D. (2003) Accumulation of copper by roots, hypocotyls, cotyledons and leaves of sunflower (*Helianthus annuus* L.). *Bioresource Technology* 86: 151-155.
135. Ljung, K., Palm, B., Grander, M., Vahter, M. (2011) High concentrations of essential and toxic elements in infant formula and infant foods - A matter of concern. *Food Chemistry* 127(3): 943-951.
136. Luse, I., Bake, M.-A., Bergmanis, G., Podniece, Z. (2000) Risk assessment of manganese. *Central European Journal of Public Health* 8(suppl.): 51.

137. Luykx, D.M.A.M., van Ruth, S.M. (2008) An overview of analytical methods for determining the geographical origin of food products. *Food Chemistry* 107(2): 897-911.
138. Magdas, D.A., Dehelean, A., Puscas., R. (2012) Isotopic and elemental determination in some Romanian apple fruit juices. *The Scientific World Journal* 2012: 1-7.
139. Malandrino, M., Aballino, O., Buoso, S., Giacomino, A., La Gioia, C., Mentasti, E. (2011) Accumulation of heavy metals from contaminated soil to plants and evaluation of soil remediation by vermiculite. *Chemosphere* 82: 169-178.
140. Matos-Reyes, M.N., Cervera, M.L., Campos, R.C., de la Guardia, M. (2010) Total content of As, Sb, Se, Te and Bi in Spanish vegetables, cereals and pulses and estimation of the contribution of these foods to the Mediterranean daily intake of trace elements. *Food Chemistry* 122(1): 188-194.
141. Melece, L. (2009) Issues of food consumption in Latvia. *Economic Science for Rural Development* 20: 103-111.
142. Melece, L., Romanova, D., Golovcenko, A. (2008) Food consumption trends and its influencing factors in Latvia. *Economic Science for Rural Development* 16: 115-122.
143. Mendil, D. (2006) Mineral and trace metal levels in some cheese collected from Turkey. *Food Chemistry* 96: 532-537.
144. Melo, R., Gellein, K., Evje, L., Syversen, T. (2008) Minerals and trace elements in commercial infant food. *Food & Chemical Toxicology* 46(10): 3339-3342.
145. Meresova, J., Florek, M., Holy, K., Jeskovsky, M., Sykora, I., Frontasyeva, M.V., Pavlov, S.S., Bujdos, M. (2008) Evaluation of elemental content in air-borne particulate matter in low-level atmosphere of Bratislava. *Atmospheric Environment* 42: 8079-8085.
146. Mohamed, A.E., Rashed, M.N., Mofty, A. (2003) Assessment of essential and toxic elements in some kinds of vegetables. *Ecotoxicology & Environmental Safety* 55(3): 251-260.
147. Muceniece, M., Muszynska, M., Otto, G., Rozentale, Z., Rudkowski, B., Skerliene, K., Slotova, L., Suurorg, I., Tur, K.E., von Muhlendahl, K.E. (2007) Pediatric environmental medicine in Eastern Central Europe. *International Journal of Hygiene & Environmental Health* 210(5): 509-513S.
148. Muller-Karulis, B., Poikane, R., Seglins, V. (2003) Heavy metals in the Ventspils Harbour: Normalization based on a multi-parameter dataset. *Environmental Geology* 43(4): 445-456.
149. Murniece, I., Karklina, D., Galoburda, R., Santare, D., Skrabule, I., Costa, H. S. (2011) Nutritional composition of freshly harvested and stored Latvian potato (*Solanum tuberosum* L.) varieties depending on traditional cooking methods. *Journal of Food Composition & Analysis*, 24(4-5): 699-710.
150. Nabrzyski, M. (2007) Functional role of some minerals in foods. In: Szefer, P., Nriagu, J.O. (eds.) *Mineral Components in Food*. CRC Press: Boca Raton, 446 p., 123-162.
151. Navarro-Alarcon, M., Cabrera-Vique, C. (2008) Selenium in food and the human body: A review. *Science of the Total Environment* 400: 115-141.
152. Nikodemus, O., (2011) *Personal information*.
153. Nikodemus, O. (2004) *Latvijas augšņu karte / Map of Soils in Latvia* (1:2 250 000). Jāņa sēta: Rīga.
154. Nikodemus, O. (red.) (2008) *Augsnes ilgtspējīga izmantošana un aizsardzība / Soil Protection and Sustainable Use*. [In Latvian] LU Akadēmiskais apgāds: Rīga, 256 lpp.
155. Nikodemus, O., Brumelis, G., Tabors, G., Lapina, L., Pope S. (2004) Monitoring of air pollution in Latvia between 1990 and 2000 using moss. *Journal of Atmospheric Chemistry* 49: 521-531.
156. Nisianakis, P., Giannenas, I., Gavriil, A., Kontopidis, G., Kyriazakis, I. (2009) Variation in trace element contents among chickens, turkey, duck, goose and pigeon eggs, analyzed by inductively coupled plazma mass spectrometry (ICP-MS). *Biological Trace Element Research* 128: 62-71.

157. NTP (2011) *Report on Carcinogens*. (12th ed.) National Toxicology Program (NTP): North Carolina, 499 p.
158. Odriozola-Serrano, I., Aguilo-Aguayo, I., Soliva-Fortuny, R., Martin-Belloso, O. (2013) Pulsed electric fields processing effects on quality and health-related constituents of plant-based foods. *Trends in Food Science & Technology* 29(2): 98-107.
159. Okoro, H.K., Fatoki, O.S., Adekola, F.A., Ximba, B.J., Snyman, R.G. (2012) A review of sequential extraction procedures for heavy metals speciation in soils and sediments. *Open Access Scientific Reports* 1(3): 181, DOI:10.4172/scientificreports.181.
160. Onianwa, P.C., Adeltola, I.G., Iwegbue, C.M.A., Ojo, M.F., Tella, O.O. (1999) Trace heavy metal composition of some Nigerian beverages and food drinks. *Food Chemistry* 66(3): 275-279.
161. Osvalde, A., Karlsons, A. (2010) Evaluation of the nutrient status of American cranberry in Latvia during 2001-2007. *Acta Horticulturae* 868: 213-218.
162. Pansu, M., Gautheyrou, J. (2006) *Handbook of Soil Analysis: Mineralogical, Organic and Inorganic methods*. Springer Verlag: Berlin, 993 p.
163. Peralta-Videa, J.R., Lopez, M.L., Narayan, M., Saupe, G., Gardea-Torresdey, J. (2009) The biochemistry of environmental heavy metal uptake by plants: Implications for the food chain. *The International Journal of Biochemistry & Cell Biology* 41(8-9): 1665-1677.
164. Pingret, D., Fabiano-Tixier, A.-S., Chemat, F. (2013) Degradation during application of ultrasound in food processing: A review. *Food Control* 31(2): 593-606.
165. Pisani, A., Protano, G., Riccobono, F. (2008) Minor and trace elements in different honey types produced in Siena County (Italy). *Food Chemistry* 107: 1553-1560.
166. Pohl, C., Loffler, A., Schmidt, M., Seifert, T. (2006) A trace metal (Pb, Cd, Zn, Cu) balance for surface waters in the eastern Gotland Basin, Baltic Sea. *Journal of Marine Systems* 60(3-4): 381-395.
167. Pohl, P. (2009) Determination of metal content in honey by atomic absorption and emission spectrometries. *Trends in Analytical Chemistry* 28(1): 117-128.
168. Poikane, R., Carstensen, J., Dahllof, I., Aigars, J. (2005) Distribution patterns of particulate trace metals in the water column and nepheloid layer of the Gulf of Riga. *Chemosphere* 60(2): 216-225.
169. Pomerleau, J., McKee, M., Robertson, A., Kadziauskiene, K., Abaravicius, A., Bartkeviciute, R., Vaask, S., Pudule, I., Grinberga, D. (2001a) Dietary beliefs in the Baltic republics. *Public Health Nutrition* 4(2): 217-225.
170. Pomerleau, J., McKee, M., Robertson, A., Kadziauskiene, K., Abaravicius, A., Vaask, S., Pudule, I., Grinberga, D. (2001b) Macronutrient and food intake in the Baltic republics. *European Journal of Clinical Nutrition* 55(3): 200-207.
171. QI Macros (2013) *QI Macros for Excel*. KnowWare International Inc. Accessed at *http://www.qimacros.com/* on 12.05.2013.
172. Radwan, M.A., Salama, A.K. (2006) Market basket surveys for some heavy metals in Egyptian fruits and vegetables. *Food & Chemical Toxicology* 44(8): 1273-1278.
173. Regulation 804 (2005) Ministru Kabineta noteikumi Nr. 804 (25.10.2005.) *Noteikumi par augsnes un grunts kvalitātes normatīviem / Requirements for quality normative of top and bottom soils.* [In Latvian] *Latvijas Vēstnesis*, 172(3330).
174. Reilly, C. (2007) Pollutants in food – metals and metalloids. In: Szefer, P., Nriagu, J.O. (eds.) *Mineral Components in Food*. CRC Press: Boca Raton, 446 p., 363-388.
175. Remon, E., Bouchardon, J.L., Le Guedard, M., Bessoule, J.J., Conord, C., Faure, O. (2013) Are plants useful as accumulation indicators of metal bioavailability? *Environmental Pollution* 175: 1-7.
176. Rial-Otero, R., Gonzalez-Barreiro, E., Martinez-Carballo, E., Perez-Guerra, N., Pastrana-Castro, L., Simal-Gandara, J. (2009) Suitability of packaging for food based on interaction

studies. In: Bellinghouse, V.C. (ed.) *Food Processing: Methods, Techniques and Trends*. Nova Science Publisher: New York, 640 p., 439-462.

177. Richardson, E.A., Pearce, J., Tunstall, H., Mitchell, R., Shortt, N.K. (2013) Particulate air pollution and health inequalities: A Europe-wide ecological analysis. *International Journal of Health Geographics* 12: 34, DOI:10.1186/1476-072X-12-34.
178. Rivero, R.C., Hernandez, P.S., Rodriguez, E.M.R., Martin, J.D., Romero, C.D. (2003) Mineral concentrations in cultivars of potatoes. *Food Chemistry* 83(2): 247-253.
179. Rudoviča, V. (2012) *Analītisko metožu izveide arheoloģisko izrakumu antropoloģiskā materiāla izpētē / Establishment of Analytical Methods for the Investigation of Anthropological Material in Archaeological Excavations*. Doctoral thesis. [In Latvian] LU Akadēmiskais apgāds: Rīga, 104 lpp.
180. Salazar, M.J., Rodriguez, J.H., Nieto, G.L., Pignata, M.L. (2012) Effects of heavy metal concentrations (Cd, Zn and Pb) in agricultural soils near different emission sources on quality, accumulation and food safety in soybean. *Journal of Hazardous Materials* 233-234: 244-253.
181. Salminen, R., Chekushin, V., Gilucis, A., Gregorauskiene, V., Petersell, V., Tomilina, O. (2011) Distribution of elements in terrestrial mosses and the organic soil layer in the eastern Baltic region. *Special Paper of the Geological Survey of Finland* 50: 1-116.
182. Samsoe-Petersen, L., Larsen, E.H., Larsen, P.B., Bruun, P. (2002) Uptake of trace elements and PAHs by fruit and vegetables from contaminated soils. *Environmental Science & Technology* 36(14): 3057-3063.
183. Schrauzer, G.N. (2002) Lithium: Occurrence, dietary intakes, nutritional essentiality. *Journal of the American College of Nutrition* 21(1): 14-21.
184. Sharma, R.K., Agrawal, M., Marshall, F.M. (2008) Heavy metal (Cu, Zn, Cd and Pb) contamination of vegetables in urban India: A case study in Varanasi. *Environmental Pollution* 154(2): 254-263.
185. Silamikele, I., Klavins, M., Nikodemus, O. (2011) Major and trace element distribution in the peat from ombrotrophic bogs in Latvia. *Journal of Environmental Science & Health – Part A Toxic/Hazardous Substances & Environmental Engineering* 46(7): 805-812.
186. Silva, L.R., Videira, R., Monteiro, A.P., Valentao, P., Andrade, P.B. (2009) Honey from Luso region (Portugal): Physicochemical characteristics and mineral contents. *Microchemical Journal* 93: 73-77.
187. Simon, E., Braun, M., Vidic, A., Bogyo, D., Fabian, I., Tothmeresz, B. (2011) Air pollution assessment based on elemental concentration of leaves tissue and foliage dust along an urbanization gradient in Vienna. *Environmental Pollution* 159: 1229-1233.
188. Soceanu, A., Dobrinas, S., Popescu, V., Birghila, S., Magearu, V. (2007) Comparative study of some essential elements in different types of vegetables and fruits. *Environmental Engineering & Management Journal* 6(6): 593-596.
189. Stalikas, C.D., Mantalovas, A.C., Pilidis, G.A. (1997) Multielement concentrations in vegetable species grown in two typical agricultural areas of Greece. *The Science of the Total Environment* 206(1): 17-24.
190. Stalnacke, P., Grimvall, A., Libiseller, C., Laznik, M., Kokorite, I. (2003) Trends in nutrient concentrations in Latvian rivers and the response to the dramatic change in agriculture. *Journal of Hydrology* 283(1-4): 184-205.
191. Staniskiene, B., Matusevicius, P., Budreckiene, R. (2006) Medus – aplinkos taršos indikatorius / Honey as an indicator of environmental pollution. [In Lithuanian] *Environmental Research, Engineering & Management (LT)* 2(36): 53-58.
192. Stankovska, E., Stafilov, T., Sajn, R. (2008) Monitoring of trace elements in honey from the Republic of Macedonia by atomic absorption spectrometry. *Environmental Monitoring & Assessment* 142: 117-126.

193. Steinnes, E. (2009) Soils and geomedicine. *Environmental Geochemistry & Health* 31: 523-535.
194. Stibilj, V., Tercic, D., Holcman, A., (2002) Content of some mineral elements in eggs from farms and free range. *Acta Agraria Kaposvariensis* 6: 139-145.
195. Stosnach, H., Gross, A. (s.a.) Analysis of mercury in tap water and orange juice by TXRF spectrometry. *Lab Report XRF 430, S2 PICOFOX*. Bruker Nano GmbH: Berlin, Accessed at *www.brucker.com* on 16.09.2013.
196. Sudmalis, P. (2013) *Noturīgo organisko piesārņotāju noteikšanas iespējas biovidēs un vides paraugos / Possibilities of Persistent Organic Pollutants Detection and Determination in Environment and Biological Samples*. Doctoral thesis. [In Latvian] RSU: Rīga, 89 lpp.
197. Szefer, P., Grembecka, M. (2007) Mineral components in food crops, beverages, luxury food, spices, and dietary food. In: Szefer, P., Nriagu, J.O. (eds.) *Mineral Components in Food*. CRC Press: Boca Raton, 446 p., 231-322.
198. Szoboszlai, N., Polgari, Z., Mihucz, V.G., Zaray, G. (2009) Recent trends in total reflection X-ray fluorescence spectrometry for biological applications. *Analytica Chimica Acta* 633(1): 1-18.
199. Tabors, G., Brumelis, G., Lapina, L., Pospelova, G., Nikodemus, O. (2004) Changes in element concentrations in moss segments after cross-transplanting between a polluted and non-polluted site. *Journal of Atmospheric Chemistry* 49: 191-197.
200. Tao, S., Chen, Y.J., Xu, F.L., Cao, J., Li, B.G. (2003) Changes of copper speciation in maize rhizosphere soil. *Environmental Pollution* 122: 447-454.
201. Tessier, A., Campbell, P.G.C., Bisson, M. (1979) Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry* 51(7): 1-8.
202. Tuzen, M., Silici, S., Mendil, D., Soylak, M. (2007) Trace element levels in honeys from different regions of Turkey. *Food Chemistry* 103: 325-330.
203. Uluozlu, O.D., Tuzen, M., Mendil, D., Soylak, M. (2009) Assessment of trace element contents of chicken products from Turkey. *Journal of Hazardous Materials* 163: 982-987.
204. USDA (s.a.) *National nutrient database for standard reference*. Agricultural Research Service, United States Department of Agriculture (USDA). Accessed at *http://ndb.nal.usda.gov/ndb/nutrients/index* on 16.09.2013.
205. Van Reeuwijk, L.P. (ed.) (1995) *Procedures for Soil Analysis*. (5th ed.) International Soil Reference and Information Centre (ISRIC): Wageningen, 92 p.
206. Viadel, B., Barbera, R., Farre, R. (2006) Effect of cooking and legume species upon calcium, iron and zinc uptake by Caco-2 cells. *Journal of Trace Elements in Medicine & Biology* 20: 115-120.
207. Viksna, A., Lindgren, E.S., Standzenieks, P., Jacobsson, J. (2004) EDXRF and TXRF analysis of elemental size distributions and environmental mobility of airborne particles in the city of Riga, Latvia. *X-Ray Spectrometry* 33(6): 414-420.
208. Viksna, A., Lindgren, E.S., Standzenieks, P. (2001) Analysis of pine needles by XRF scanning techniques. *X-Ray Spectrometry* 30(4): 260-266.
209. Villalobos, M., Merino-Sanchez, C., Hall, C., Grieshop, J., Gutierrez-Ruiz, M.E., Handley, M.A. (2009) Lead (II) detection and contamination routes in environmental sources, cookware and home-prepared foods from Zimatlan, Oaxaca, Mexico. *Science of the Total Environment* 407(8): 2836-2844.
210. 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.
211. Viskelis, P., Rubinskiene, M. (2011) Beržų sulos cheminė sudėtis / Chemical composition of birch sap. [In Lithuanian] *Lietuvos Agrarinių & Miškų Mokslų Centro Filialo Sodininkystės & Daržininkystės Instituto & Lietuvos Žemės Ūkio Universiteto Mokslo Darbai. Sodininkystė & Daržininkystė* 30(3-4): 75-81.

212. Voutsa, D., Grimanis, A., Samara, C. (1996) Trace elements in vegetables grown in an industrial area in relation to soil and air particulate matter. *Environmental Pollution* 94(3): 325-335.
213. Voutsa, D., Samara, C. (1998) Dietary intake of trace elements and polycyclic aromatic hydrocarbons via vegetables grown in an industrial Greek area. *The Science of the Total Environment* 218: 203-216.
214. Waegeneers, N., De Steur, H., De Temmerman, L., Van Steenwinkel, S., Gellynck, X., Viaene, J. (2009a) Transfer of soil contaminants to home-produced eggs and preventive measures to reduce contamination. *Science of the Total Environment* 407(15): 4438-4446.
215. Waegeneers, N., Hoenig, M., Goeyens, L., De Temmerman, L. (2009b) Trace elements in home-produced eggs in Belgium: levels and spatiotemporal distribution. *Science of the Total Environment* 407: 4397-4402.
216. Waheed, S., Fatima, I., Mannan, A., Chaudhary, M.S., Qureshi, I.H. (1985) Trace element concentration in egg-yolk and egg-white of farm and domestic chicken eggs. *International Journal of Environmental Analytical Chemistry* 21: 333-344.
217. Walker, D.J., Clemente, R., Roig, A., Bernal, M.P. (2003) The effects of soil amendments on heavy metal bioavailability in two contaminated Mediterranean soils. *Environmental Pollution* 122: 303-312.
218. Wang, X., Shan, X., Zhang, S., Wen, B. (2004) A model for evaluation of the phytoavailability of trace elements to vegetables under the field conditions. *Chemosphere* 55(6): 811-822.
219. Wang, G., Su, M.-Y., Chen, Y.-H., Lin, F.-F., Luo, D., Gao, S.-F. (2006) Transfer characteristics of cadmium and lead from soil to the edible parts of six vegetable species in southeastern China. *Environmental Pollution* 144: 127-135.
220. Welch, R.M., Graham, R.D. (2005) Agriculture: The real nexus for enhancing bioavailable micronutrients in food crops. *Journal of Trace Elements in Medicine & Biology* 18: 299-307.
221. Welna, M., Szymczycha-Madeja, A., Pohl, P. (2011) Quality of the trace element analysis: Sample preparation steps. In: Akyar, I. (ed.) *Wide Spectra of Quality Control*. (4th ed.) InTech: Rijeka, 532 p., 54-70.
222. White, P.J., Broadley, M.R. (2005) Biofortifying crops with essential mineral elements. *Trends in Plant Science* 10(12): 586-593.
223. WHO (1996) *Trace Elements in Human Nutrition and Health*. World Health Organisation (WHO): Geneva, 343 p.
224. WHO (s.a.) *Concise international chemical assessment documents*. International Programme on Chemical Safety, World Health Organisation (WHO). Accessed at *http://www.who.int/ipcs/publications/cicad/cicads_alphabetical/en/index.html* on 25.07.2013.
225. Wuana, R.A., Okieimen, F.E. (2011) Heavy metals in contaminated soils: A review of sources, chemistry, risks and best available strategies for remediation. *ISRN Ecology* 2011: 1-20.
226. Wunderlich, S., Feldman, C., Latif, K., Punamiya, P. (2011) Soil composition of community gardens: Are there quality concerns? In: Popov, V., Brebbia, C.A. (eds.) *Food and Environment*. WIT Press: Southampton, 225 p., 95-101.
227. Xu, D., Zhou, P., Zhan, J., Gao, Y., Dou, C., Sun, Q. (2013) Assessment of trace metal bioavailability in garden soils and health risks via consumption of vegetables in the vicinity of Tongling mining area, China. *Ecotoxicology & Environmental Safety* 90: 103-11.
228. Yang, X.-E., Chen W.-R., Feng, Y. (2007) Improving human micronutrient nutrition through biofortification in the soil–plant system: China as a case study. *Environmental Geochemistry & Health*, 29(5): 413-428.
229. Yurkovskis, A. (2004) Dynamics of particulate major and trace elements in the lower reaches of the Daugava River and adjacent area of the Gulf of Riga (Baltic Sea). *Marine Pollution Bulletin* 49(3): 249-263.

230. Yurkovskis, A., Poikane, R. (2008) Biogeochemical, physical and anthropogenic transformations in the Daugava River estuary and plume, and the open Gulf of Riga (Baltic Sea) indicated by major and trace elements. *Journal of Marine Systems* 70(1-2): 77-96.
231. Zariņš, Z., Neimane, L. (2009) *Uztura mācība / Nutrition Studies*. (5th ed.) [In Latvian] LU Akadēmiskais apgāds: Rīga, 464 lpp.
232. Zegnere, L., Alsina, I. (2008) The effect of selenite on growth and storage of onions. *Latvian Journal of Agronomy* 10: 235-240.
233. Zhang, F.-S., Yamasaki, S., Kimura, K. (2001) Rare earth element content in various waste ashes and the potential risk to Japanese soils. *Environment International* 27(5): 393-398.
234. Zheljazkov, V.D., Craker, L.E., Xing, B. (2006) Effects of Cd, Pb, and Cu on growth and essential oil contents in dill, peppermint, and basil. *Environmental & Experimental Botany* 58: 9-16.
235. Zheng, N., Wang, Q., Zheng, D. (2007) Health risk of Hg, Pb, Cd, Zn, and Cu to the inhabitants around Huludao Zinc Plant in China via consumption of vegetables. *Science of the Total Environment* 383: 81-89.
236. Zimmermann, M.B. (2001) *Burgerstein's Handbook of Nutrition: Micronutrients in the Prevention and Therapy of Disease*. Georg Thieme Verlag: Stuttgart, 288 p.

APPENDICES

Appendix I

The main food sources of essential and possibly essential elements and their functions in human organism

(after Aras and Ataman, 2006; ATSDR, s.a.; Berdanier et al., 2007; Briggs and Wahlqvist, 1998; Comb, 2005; DiSilvestro, 2005; Kabata-Pendias and Mukherjee, 2007; Schrauzer, 2002; White and Broadley, 2005; WHO, s.a.; WHO, 1996)

Element	The main food sources	Functions in human organism
Al	Food packed, stored or stored cooked in Al containing dishes and vessels, tea, pharmaceuticals	*Unclear biological function in humans*; although animal studies suggest that Al may stimulate certain enzymes, may stimulate growth
As	Dairy products, meat, poultry, fish, grains and cereals	*Unclear biological function in humans*; although animal data indicate a requirement; involved in metabolism of methyl-compounds
B	Fruit-based products and beverages, potatoes, legumes, milk, avocado, peanuts	*Unclear biological function in humans*; although animal data indicate a functional role: B is involved in the control of membrane function, biosynthesis of nucleic acid and lignin
Ca	Dairy products (milk, cheese), fortified juices, kale, collards, mustard greens, broccoli, Chinese cabbage, sardines, oysters, clams, canned salmon	Basic constituent of bones and teeth, essential role in blood clotting and regulation of blood pressure, muscle contraction and relaxation, nervous system functioning
Cl	Table salt, sea salt, vegetables (rye, tomatoes, lettuce, celery, olives), seaweeds, seafood, dairy products, meat, eggs	Constituent of stomach acid and tissue fluids, essential for proper digestion as HCl
Co	Fish, nuts, green leafy vegetables (broccoli and spinach), cereals (oats)	Constituent of vitamin B_{12} which is involved in nerve function and blood formation
Cr^{3+}	Some cereals, meats, poultry, fish, beer	Associated with insulin, required for energy release from glucose cleavage
Cu	Organ meat, seafood oysters, crabs, nuts, seeds, wheat bran, cereals, whole grain products, beans, peas, lentils, cocoa products, mushrooms	Component of enzymes in iron metabolism
F	Fluoridated water, tea, marine fish; non-food source: fluoridated dental products	Important for formation, strengtheness and resistancy of bones and teeth, prevents bones of mineral loss, inhibits the initiation and progression of dental caries and stimulates new bone formation

Element	The main food sources	Functions in human organism
Fe	Fruits, vegetables, fortified bread and grain products such as cereal (non-haeme iron sources), meat and poultry (haeme iron sources)	Involved in haemoglobin formation, cell energy utilization, component of myoglobin and numerous enzymes, prevents of microcytic hypochromic anaemia
I	Marine origin food, kelp, processed food, iodized salt	Component of thyroid hormones, involved in metabolism processes
K	Fruits (bananas), vegetables, pulses, nuts, seeds, cereals, milk, fish, shellfish, meat (beef, chicken, turkey), bread	Supports many reactions, such as protein synthesis, nerve transmission and contraction of muscles
Li	Grains, vegetables, some natural mineral waters, sugarcane, seaweeds, tobacco	*Unclear biological function in humans*; may stabilize serotonin transmission in nervous system, influence sodium transport, may increase lymphocytic proliferation and depress the suppressor cell activity
Mg	Green leafy and dark green vegetables, beans, peas, unpolished grains, nuts, seeds, meat, starches, milk	Cofactor for enzyme system, involved in bone mineralization, protein synthesis, enzyme activation, contraction of muscles, nerve transmission
Mn	Nuts, legumes, tea, whole grains	Involved in many cell processes and enzyme functions; involved in formation of bones as well as in enzymes involved in amino acid, cholesterol, and carbohydrate metabolism
Mo	Legumes, dark green leafy vegetables, organ meat, grain products, nuts	Involved in many cell processes and enzyme functions, cofactor for enzymes involved in catabolism of sulphur amino acids, purines and pyridines
Na	Table salt, seafood, dairy products, ready meals, meat products (beacon), eggs, cheese, tinned vegetables, savoury snacks	Involved in the upkeep of ionic strength of body fluids
Ni	Nuts, legumes, cereals, sweeteners, chocolate	*Unclear biological function in humans*; may serve as a cofactor of metalloenzymes and facilitate iron absorption or metabolism in microorganisms, constituent of urease, reduce haemopoiesis
P	Dairy products (yogurt, ice-cream, cheese), meat, eggs, fish, peas, beans. lentils, nuts, some cereals and bread	Constituent of every cell; maintenance of pH, storage and transfer of energy and nucleotide synthesis
S	In all food in many different forms	Constituent of certain aminoacids, biotin, thiamin and insulin; involved in many processes, e.g., essential in cartilage formation

Element	The main food sources	Functions in human organism
Se	Organ meat, seafood, nuts, plants (depending on soil selenium content), e.g., garlic, broccoli grown on high-Se soils	Defence against oxidative stress and regulation of thyroid hormone action, and the reduction and oxidation status of vitamin C and other molecules, antioxidant, prevents cells from untimely ageing
Si	Plant-based food	Relevant for structural connective in tissues and osteogenic cells
Sn	Canned food, Sn(II) chloride used as food additive	Involved in interactions with riboflavin
V	Mushrooms, shellfish, black pepper, parsley, dill seeds	*Unclear biological function in humans*; may be involved in the control of sodium pump, inhibition of ATPase, p-transferases
Zn	Fortified cereals, whole grains, red meat, organ meat, certain seafood (shellfish), nuts, beans, peas, lentils	Component of multiple enzymes and proteins, present in insulin, involved in genetic material and protein formation, essential for immunity function, transport of vitamin A, taste, wound healing, development of spermatozoids and normal fetal development

Appendix II

The main adverse effects of element deficiency or excessive intake

(after Aras and Ataman, 2006; ATSDR, s.a.; Comb, 2005; DiSilvestro, 2005; FAO, 2001; IRIS, s.a.; Kabata-Pendias and Mukherjee, 2007; Schrauzer, 2002; White and Broadley, 2005; WHO, s.a.; WHO, 1996)

Element	Adverse effects at	
	Excessive intake	Deficiency
Al	Osteomalacia, neurotoxicity, dementia, possible accelerator of Alzheimer's disease	No data
As	No data about organic As compounds; inorganic As is a known toxic substance, induces variable disorders: failure of nervous system, liver and kidney functions, intestine tract distress, anaemia, skin cancer	No data
B	Reproductive and developmental effects as observed in animal studies	No data
Ca	Kidney stones, hypercalcemia, milk alkali syndrome, renal insufficiency	Childhood rickets, osteoporosis, hyperparathyroidism, hypertension, blood lipids alterations, possible connection with colon cancer
Cl	Increased body pressure, build-up of fluid in people with congestive heart failure or kidney diseases	No data
Co	Heart diseases, cardiomiopathy, marrow defects, excess of red blood cells, decrease of fertility in men	Anaemia, anorexia
Cr^{3+}	Chronic renal failure, lesions in skin, intestinal mucosa, pulmonary oedema, lung cancer	Defective glucose metabolism, hyperlipidemia
Cu	Gastrointestinal distress, liver damage, necrotic hepatitis, haemolysis, hyperglycemia	Anaemia and tissue defects
F	Enamel and skeletal fluorosis (variable effects, mottling of teeth enamel)	Teeth decay, growth retardation
Fe	Gastrointestinal distress, siderosis, haemachromamtosis, cardiac failure	Anaemia, premature or low birth weight infants
I	Elevated thyroid stimulating hormone (THS) concentration, hyperthyroidism	Goiter, impaired neurological function
K	Stomach pain, nausea, diarrhoea	Hypertension, athletic/exercise performance enhancement, kidney stones, muscle cramps, risk of strokes, osteoporosis
Li	Impaired central nervous system, cardiovascular and renal effete	Deficiency is not known, but low intakes of Li are associated with depression and increased rates of suicide

Element	Adverse effects at	
	Excessive intake	Deficiency
Mg	No data of adverse effects from the consumption of naturally occurring Mg in food; Mg containing dietary supplements may induce osmotic diarrhoea	Anorexia, nausea, vomiting, lethargy, weakness, personality change, tetany, tremor, muscle fasciculations
Mn	Elevated blood concentration and neurotoxicity, manganism, neurological disorders, liver cirrhosis	Skeletal and cartilage deformitis
Mo	Reproductive effects as observed in animal studies, molybdenosis, defects in copper metabolism, diarrhoea	Defects in keratosis, growth retardation
Na	Hypertension, risk of stroke and heart attack	No data
Ni	Decreased body weight as observed in animal studies, gastritic, liver and kidney defects, neurological effects, emphysema and lung cancer	No data
P	Metastatic calcification, skeletal porosity, interference with calcium absorption	No data
S	No data	No data
Se	Hair and nail brittleness and loss, selenosis, liver and kidney damage, fetal toxicity, cancer	Cardiomyopathy, osteoarthropathy, membrane malfunction
Si	No data of adverse effects from consumption of naturally occurred Si in food and water	No data
V	Renal lesions as observed in animal studies, nervous disturbances	Teeth defects
Zn	Reduced copper status, anaemia, tissue lesions	Anorexia, anaemia, impaired keratosis, teratogenic effects

Appendix III

Estimated daily oral intake of elements (for adult human with body mass of 70 kg) and values of oral minimal risk level (after ATSDR, s.a.)

Element	Predominant source of oral intake	Estimated average daily oral intake	Oral minimal risk level (MRL)
Ag	Drinking water and food	▪ 70-88 μg/day ▪ With food: ~4.5 μg/day ▪ With drinking water: 20-100 μg/day	No oral MRLs
Al	Food, pharmaceuticals, used as food additive	▪ 0.10-0.12 mg/kg/day ▪ With pharmaceuticals at recommended dosages: 12-71 mg/kg/day (with antacid/anti-ulcer products); 2-10 mg/kg/day (with buffered analgestics)	Aluminium: ▪ 1 mg/kg/day (intermediate) ▪ 1 mg/kg/day (chronic)
As	Food, drinking water, some pharmaceuticals	▪ 50.6 μg/day ♀ ▪ 58.5 μg/day ♂ ▪ With grains: 20 μg/day	Inorganic arsenic: ▪ 0.005 mg/kg/day (acute) ▪ 0.0003 mg/kg/day (chronic) Organic arsenic compounds: ▪ 0.1 mg MMA/kg/day (intermediate) ▪ 0.01 mg MMA/kg/day (chronic) ▪ 0.02 mg DMA/kg/day (chronic)
B	Food, beverages, drinking water, pharmaceuticals	▪ 1.0 mg/day ♀ ▪ 1.28 mg/day ♂	Boron and its compounds: ▪ 0.2 mg/kg/day (acute) ▪ 0.2 mg/kg/day (intermediate)
Ba	Food and drinking water	▪ With drinking water: 0.86 μg/kg/day ▪ With food: 9.30-25.30 μg/kg/day	Barium and its soluble salts: ▪ 0.2 mg/kg/day (intermediate) ▪ 0.2 mg/kg/day (chronic)
Cd	Food	▪ 0.30 mg/kg/day ♀ ▪ 0.35 mg/kg/day ♂	Cadmium: ▪ 0.0005 mg/kg/day (intermediate) ▪ 0.0001 mg/kg/day (chronic)
Cr	Food and drinking water	▪ 52-943 μg/day ▪ With selected diets (25 and 43 % of fat): 25-224 (mean 76) μg/day	Chromium (VI): ▪ 0.005 mg/kg/day (intermediate) ▪ 0.0009 mg/kg/day (chronic)
Co	Food and drinking water	▪ 12-15 μg/day ♀ ▪ 9-10 μg/day ♂	Cobalt: ▪ 0.01 mg/kg/day (intermediate)
Cu	Food and drinking water	▪ 1.0-1.3 mg/day (0.014-0.019 mg/kg/day)	Copper: ▪ 0.01 mg/kg/day (acute) ▪ 0.01 mg/kg/day (intermediate)
F	Food, drinking water, beverages, dental products	▪ 0.35-3.03 (mean 1.76) mg/day	Fluoride: ▪ 0.05 mg/kg/day (chronic)

Element	Predominant source of oral intake	Estimated average daily oral intake	Oral minimal risk level (MRL)
Hg	Food (fish and fish products), dental amalgams	▪ For methylmercury compounds with food 2.3-2.4 µg/day with fish, 0 µg/day with non-fish and 0 µg/day with water ▪ Elemental Hg vapour daily intake (only from dental amalgams): 3-21 µg/day	Mercury (II) chloride: ▪ 0.007 mg/kg/day (acute) ▪ 0.002 mg/kg/day (intermediate) ▪ Methylmercury: ▪ 0.0003 mg/kg/day (chronic)
I	Food and drinking water	▪ 0.064-0.379 mg/day	Iodide: ▪ 0.01 mg/kg/day (acute) ▪ 0.01 mg/kg/day (chronic)
Li	Food, certain pharmaceuticals	▪ 0.65-3.10 mg/day	No oral MRLs
Mn	Food	▪ 0.7-10.9 mg/day (higher for vegetarians)	No oral MRLs
Ni	Food and drinking water, cigarette smoke	▪ With food: 69-162 µg/day ▪ With water: 8 µg/day	No oral MRLs
Pb	Food and drinking water	▪ 24-56.5 µg/day	No oral MRLs
Se	Food and drinking water	▪ 1-2 µg/kg/day	Selenium: ▪ 0.005 mg/kg/day (chronic)
Sn	Food, dental products	▪ 1-38 mg/day (higher from canned food)	Tin, dibutyl-, dichloride: ▪ 0.005 mg/kg/day (intermediate) Inorganic tin: ▪ 0.3 mg/kg/day (intermediate) Tin, tributyl-, oxide: ▪ 0.0003 mg/kg/day (intermediate) ▪ 0.0003 mg/kg/day (chronic)
Sr	Food, drinking water, cigarette smoke	▪ 3.3 mg/day (46 µg/kg/day)	Strontium: ▪ 2 mg/kg/day (intermediate)
Tl	Food (especially, green vegetables)	▪ With food: 5 µg/day ▪ With water: 2 µg/day	No oral MRLs
U	Food (especially, root vegetables) and drinking water	▪ With food: 0.9-1.5 µg/day ▪ With water: 0.9-1.5 µg/day	Uranium soluble salts: ▪ 0.002 mg/kg/day (acute) ▪ 0.0002 mg/kg/day (intermediate)
V	Food, dietary supplements	▪ 10-20 µg/day ▪ With dietary supplements: 9 µg/day	Vanadium: ▪ 0.01 mg/kg/day (intermediate)
Zn	Food and drinking water, cigarette smoke, polluted air	▪ With food: 5.2-16.2 mg/day ▪ With water: <0.14 mg/kg/day	Zinc: ▪ 0.3 mg/kg/day (intermediate) ▪ 0.3 mg/kg/day (chronic)

Appendix IV

Estimated element bioavailability from oral intake associated with gastrointestinal (GIT) absorption in human body (after ATSDR, s.a.; WHO, s.a.)

Element	Bioavailability (BA), %	Remarks
Ag	▪ 21 % (Ag acetate)	▪ Apart from GIT absorption, Ag compounds, including Ag salts and Ag-protein colloids, are absorbed across mouth and nasal mucous membranes ▪ High intake of Se may lead to increased deposition of insoluble Ag salts in body tissues in the form of Ag selenide
Al	▪ 0.1-0.4 % ▪ 0.5-5 % (BA forms, e.g., Al citrate) ▪ ≤0.01 % (Al hydroxide which is widely used as antacide)	▪ Absorption of Al varies depending mainly on type of anion and the concurrent exposure to dietary chelators such as citric acid, ascorbic acid, lactic acid ▪ Al lactate has higher BA than other Al compounds found in water and food
Am	▪ <0.1 % ▪ Up to 0.5 % (in infants)	▪ Absorption increases with duration of exposure ▪ Absorption, distribution and excretion from organism is dependent on age
As	▪ >95 % (inorganic As) ▪ 75-85 % (organic As compounds such as MMA and DMA)	▪ Inorganic As(V) compounds are readily reduced to inorganic As(III) compounds which are taken up by the cell ▪ If highly insoluble forms are ingested, BA and absorption will be much lower ▪ Studies of BA suggest that absorptions of inorganic As in ingested dust or soil is likely to be considerably less than absorption of As from ingested salts ▪ Absorption of inorganic As from soil is reduced by low solubility and inaccessibility due to the presence of secondary reaction products or insoluble matrix components
B	▪ 81-92 % ▪ 93.9 % (boric acid)	▪ Apart from high BA, essentiality of B is established for plants and some animals, but not for humans
Ba	▪ <5-30 % ▪ With food: 1-15 % (mean 6 %) ▪ 20 % (in adults) ▪ 30 % (in children) ▪ 60 % (in infants)	▪ BA of Ba is significantly compound dependent ▪ Absorption of Ba sulphate is very low, higher BA has acid-soluble Ba compounds (Ba chloride, Ba carbonate) ▪ Absorption of Ba compounds is influenced by age

Element	Bioavailability (BA), %	Remarks
Cd	▪ 1.1-10.6 % ▪ 3-5 % (in healthy non-smokers)	▪ Absorption may be significantly affected by protein complexes ▪ Cd is more readily found in free ionic form in water, while in food Cd ion generally exists in a complex with variety of ligands, including proteins such as metallothionein ▪ Cd in cigarette smoke has higher absorption efficiency due to its small particle size ▪ Female organisms generally absorb greater amounts of Cd than male ▪ BA of Cd is increased in individuals with low Fe status in organism
Cr	▪ <10 %	▪ BA depends on the valence state and nature of ligands ▪ In general, BA is higher for soluble Cr(VI) compounds (e.g., $K_2Cr_2O_7$) than for soluble Cr(III) compounds (e.g., $CrCl_3$) ▪ Cr(VI) in stomach is reduced to Cr(III), which lowers the absorbed dose of Cr(VI), via intermediate forms Cr(V) and Cr(IV) ▪ Absorption is higher when dietary intakes of Cr are lower ▪ Can cross placenta
Co	▪ 18-97 %	▪ Absorption of Co is dependent on type and dose of compound ▪ More Co can be absorbed for humans with deficiency of Fe ▪ Co chloride can be significantly higher eliminated from female bodies that male
Cu	▪ 24-60 %	▪ Several mechanisms prevent Cu overload in organism ▪ BA dependent on Cu competition with other metals (e.g., Zn, Cd) ▪ Absorption is dependent on age
F	▪ 80-100 % (soluble F compounds such as Na fluoride, hydrogen fluoride, fluorosilic acid) ▪ <10 % (insoluble F compounds)	▪ Absorption dependent on intake with food or when fasted (e.g., Ca fluoride ingestion with food increases up to 33.5 % if compared ingestion without food (2.8 %)) ▪ Diet high in Ca, Mg or Al decreases F absorption ▪ Not metabolized in organism
Hg	▪ 2-38 % (inorganic Hg salts) ▪ Up to 90 % (organic Hg compounds) ▪ 7-15 % (metallic Hg)	▪ Highly lipophile metallic Hg can be transferred readily through the placenta and blood-brain barrier ▪ Organic Hg compounds in organism are transformed into inorganic Hg compounds
I	▪ >97-100 % (water soluble I salts)	▪ BA is not influenced by age, but for infants may be lower than in children and adults
Li	▪ 70-90 %	▪ Gender differences are revealed in Li absorption levels

Element	Bioavailability (BA), %	Remarks
Mn	▪ 3-5 %	▪ Absorption dependent on age and dietary Fe and Mn intake levels
Ni	▪ With drinking water: 27 % ▪ With food: 1 %	▪ More soluble Ni compounds have higher absorption efficiencies ▪ Not metabolized
Pb	▪ 40-50 % (in children) ▪ 3-15 % (in adults) ▪ 26 % (if ingested when fasted) ▪ 2.5 % (if ingested with meals)	▪ Extent and rate of BA of inorganic Pb compounds are influenced by the physiological state of the exposed individual and species of Pb compound ▪ Presence of food in GIT decreases Pb absorption ▪ Coadministration of Ca with Pb decreases Pb absorption ▪ Absorption from soil, if ingested, is less than of dissolved Pb, but similarly is depressed by meals
Pu	▪ <0.1 % (Pu citrate and Pu nitrate)	▪ Pu citrate is better absorbed than Pu nitrate, but PuO_2 has the lowest absorption levels ▪ Fasting tends to increase Pu absorption ▪ Absorption in infants is 10-1000 times greater than in adults ▪ Not metabolized in organism
Se	▪ >80 %	▪ BA is independent of the exposure concentration; however, absorption efficiency can increase when there is Se deficiency
Sn	▪ 3 % (Sn (II) compounds) ▪ 1 % (Sn (IV) compounds)	▪ BA is lower for inorganic Sn compounds, while organotin compounds are more readily absorbed ▪ Absorption of Sn compounds is dose dependent ▪ High amounts of Sn in diet may reduce Zn and Cu absorption
Sr	▪ 11-28 % (mean 20 %)	▪ Because Sr is similar to Ca, it is taken up by vegetables and fruits
Th	▪ 0.1-1 %	▪ Studies on rats show that in neonatal rats absorption of Th is 40-fold higher than for adult rats, thus suggesting that infants may be a susceptible population for exposure ▪ Th-EDTA absorption from GI tract is 60 times higher, Th nitrate 4 times, Th chloride 10-20 times (depending on dose) greater than Th dioxide, that is attributed to different solubility
Tl	▪ 85 %	▪ Acute oral exposure results in death
V	▪ 3-17 %	▪ BA significantly dependent on compound
W	▪ 55-93 % (mean 60 %)	▪ Not metabolized in organism
Zn	▪ 8-81 % (mean 20-30 %)	▪ Zn deficiency increase its absorption rates ▪ Dietary phytate reduces Zn absorption ▪ Presence of other metals (e.g., Hg, Cd, Cu) may diminish Zn absorption

LATVIJAS UNIVERSITĀTE
ĢEOGRĀFIJAS UN ZEMES ZINĀTŅU FAKULTĀTE
VIDES ZINĀTNES NODAĻA

Zane Vincēviča-Gaile

VIDES APSTĀKĻU IETEKME UZ MIKRO- UN MAKROELEMENTU SATURU PĀRTIKAS PRODUKTOS LATVIJĀ

PROMOCIJAS DARBA KOPSAVILKUMS

Doktora grāda iegūšanai ķīmijā, vides zinātnes nozarē
Apakšnozare: Vides ķīmija un ekotoksikoloģija

Rīga, 2014

Promocijas darbs izstrādāts Latvijas Universitātes Ģeogrāfijas un Zemes zinātņu fakultātes Vides zinātnes nodaļā laika posmā no 2009. gada līdz 2013. gadam.

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Šis darbs izstrādāts ar Eiropas Sociālā fonda atbalstu projektā "Atbalsts doktora studijām Latvijas Universitātē", Nr.2009/0138/ 1DP/1.1.2.1.2./ 09/IPIA/ VIAA/004.

Darbs sastāv no ievada, 3 nodaļām, secinājumiem, literatūras saraksta, 4 pielikumiem.

Darba forma: ķīmijas doktora disertācija vides zinātnes nozarē, vides ķīmijas un ekotoksikoloģijas apakšnozarē.

Darba zinātniskais vadītājs: profesors, *Dr. habil. chem.* **Māris Kļaviņš**

Darba recenzenti:
profesors, *Dr. habil. chem.* **Andris Zicmanis**, Latvijas Universitāte;
profesors, *Dr.* **Stanley Lutts**, Lēvenes Katoļu universitāte, Beļģija;
Dr. chem. **Vadims Bartkevičs**, Pārtikas drošības, dzīvnieku veselības un vides zinātniskais institūts BIOR.

Promocijas darba aizstāvēšana notiks Latvijas Universitātes Vides zinātnes nozares promocijas padomes atklātā sēdē 2014. gada 24. aprīlī plkst. 10:00 Latvijas Universitātes Ģeogrāfijas un Zemes zinātņu fakultātē (Alberta ielā 10, Rīgā).

Ar promocijas darbu un tā kopsavilkumu var iepazīties Latvijas Universitātes Bibliotēkā Rīgā, Raiņa bulvārī 19.

LU Vides zinātņu nozares promocijas padomes priekšsēdētājs:
prof., *Dr. biol.* **Viesturs Melecis**

Promocijas padomes sekretāre
asoc. prof., *Dr. biol.* **Gunta Spriņģe**

ANOTĀCIJA

Bez vitāli svarīgo mikro- un makroelementu ieneses pārtikā no vides (augsnes, ūdens un gaisa) ir iespējams arī barības ķēdes, t. sk., pārtikas piesārņojums ar toksiskiem vai potenciāli toksiskiem elementiem, piemēram, As, Cd, Hg, Pb. Promocijas darba mērķa ietvaros tika veikta Latvijā iegūtu pārtikas produktu paraugu mikro- un makroelementu sastāva kvantitatīvā analīze, lai noskaidrotu vides apstākļu ietekmi uz elementu koncentrāciju un ieneses ceļiem pārtikā. Papildus, lai vērtētu elementu biopieejamību barības ķēdē, tika veikta eksperimentāla pārtikas kultūraugu audzēšana mākslīgi piesārņotā augsnē. Iegūtie dati liecina par vairāku dabiskas un antropogēnas izcelsmes vides apstākļu, piemēram, sezonalitātes, botāniskās izcelsmes, vietas specifisku apstākļu, lauksaimniecības prakses, pārtikas pārstrādes ietekmi uz elementu koncentrāciju pārtikā.

Atslēgvārdi: mikro- un makroelementi, kvantitatīvā analīze, elementu pārnese, pārtikas sastāvs, vide, Latvija.

SATURS

VISPĀRĪGS DARBA RAKSTUROJUMS

Ievads

Pārtika un dzeramais ūdens ir galvenie avoti, lai nodrošinātu cilvēka organismu ar barības vielām. Bez pamata uzturvielām, taukiem, ogļhidrātiem un olbaltumvielām, normālai funkcionēšanai cilvēka organismam nepieciešami vitamīni, aminoskābes, fermenti, šķiedrvielas, kā arī mikro- un makroelementi. Makroelementi (Ca, K, Mg, Na) un mikroelementi (piemēram, Co, Cr, Cu, Fe, Mn, Mo, Se, V, Zn) ir vitāli nepieciešami normālai cilvēka organisma attīstībai un funkcionēšanai, nodrošinot organisma audos neitrālu reakciju un noteiktu osmotisko spiedienu, piedaloties šūnu kairinājuma-uzbudinājuma procesos, veicinot vai kavējot fermentu darbību un tādējādi ietekmējot organisma vielmaiņas procesus (Aras and Ataman, 2006; Fraga, 2005). Tomēr dažādu dabīgu vai antropogēnu vides apstākļu ietekmē uzturā var nonākt arī potenciāli kaitīgi elementi, piemēram, As, Cd, Hg, Pb, tāpēc svarīgi novērtēt iespējamos elementu ieneses ceļus pārtikā un potenciālos riskus patērētājam.

Lai gan ir plaši pieejama informācija par pārtikas ķīmisko sastāvu un uzturvērtību, kas apkopota rokasgrāmatās, piemēram, *Burgerstein's handbook of nutrition* (Zimmermann, 2001), *Handbook of nutrition and food* (Berdanier et al., 2007), *Uztura mācība* (Zariņš un Neimane, 2009) vai datu bāzes (piemēram, USDA, s.a.), ko veidojušas lauksaimniecības un uztura pētniecības un uzraudzības iestādes, mikro- un makroelementu saturs reģionāli iegūtos pārtikas produktos ir mainīgs, par ko liecina daudzi zinātniskie pētījumi (Aberoumand and Deokule, 2010; Ekholm et al., 2007; Ferre-Huguet et al., 2008; Hashmi et al., 2007). Specifiski vides apstākļi mijiedarbībā ar antropogēnām ietekmēm var ietekmēt elementu ienesi un koncentrāciju pārtikā. Piemēram, elementu saturs augsnē var ietekmēt veģetācijas sastāvu, ko patērē dzīvnieki vai kas tiek izmantota cilvēka uzturā, tādējādi elementi no vides nonāk barības ķēdē. Pārtikas piesārņojums ar toksiskiem un potenciāli toksiskiem elementiem var ietekmēt cilvēka veselību, ilgmūžību un dzīves kvalitāti kopumā (Combs, 2005; Fraga, 2005; Nabrzyski, 2007). Tādējādi reģionāla vai izcelsmes vietas specifiska pārtikas analīze ir svarīgs faktors tās vērtības un drošības novērtēšanā.

Informācija par mikro- un makroelementu koncentrāciju reģionāli ražotā pārtikā var būt kā rādītājs reģionālai elementu fona koncentrācijai vidē. Kvantitatīvie dati par mikro- un makroelementu saturu pārtikā ir nozīmīgs rādītājs, izmantojams riska novērtējuma analīzē, lai noskaidrotu elementu deficītu vai pretēji, pārmērīgu saturu uzturā (Goldhaber, 2003). Tādējādi mikro- un makroelementu satura pārtikā analīze var būt kā objekts starpdisciplināriem pētījumiem, kas ietver vides, ķīmijas, uztura un veselības zinātnes.

Promocijas darba mērķis

Izpētīt mikro- un makroelementu kvantitatīvo sastāvu izvēlētos pārtikas produktos Latvijā, lai raksturotu vides un antropogēno apstākļu ietekmi uz elementu saturu un koncentrāciju, kā arī ieneses intensitāti pārtikā no vides un iespējamo biopieejamību barības ķēdē *augsne-augs-cilvēks*.

Promocijas darba uzdevumi

- Metodikas pielāgošana un pilnveidošana pārtikas paraugu ievākšanai, sagatavošanai, priekšapstrādei un kvantitatīvai analīzei, ņemot vērā kvalitātes nodrošinājuma prasības.
- Izvēlēties pārtikas paraugu veidus un ievākt paraugus Latvijas teritorijā; veikt paraugu sagatavošanu, priekšapstrādi un kvantitatīvo analīzi mikro- un makroelementu satura noteikšanai; izstrādāt shematisku pārskatu iespējamo vides apstākļu un antropogēno ietekmju novērtējumu uz elementu koncentrāciju analizētajos pārtikas paraugos.
- Izpētīt mikro- un makroelementu iespējamos ieneses ceļus pārtikā no vides (augsnes, ūdens, gaisa) un antropogēniem avotiem, kā arī novērtēt elementu biopieejamību barības ķēdes segmentos *augsne-augs* un *augs-cilvēks*.
- Novērtēt potenciālos riskus patērētājam attiecībā uz elementu ienesi uzturā, kā arī veikt iegūto datu salīdzinājumu starptautiskā mērogā.

Pētījuma galvenais ietvars – izvēlēto pārtikas produktu Latvijā skrīninga analīze, lai novērtētu mikro- un makroelementu koncentrācijas maiņu tendences iespējamo vides apstākļu ietekmē.

Hipotēze

Mikro- un makroelementu kvantitatīvā analīze Latvijā pieejamos pārtikas produktos ir viens no pārtikas kvalitātes, drošības un uzturvērtības rādītājiem, kas var mainīties dabīgu un antropogēnu vides apstākļu ietekmē.

Izvirzītās tēzes

1. Mikro- un makroelementu kvantitatīvā sastāva noteikšana pārtikas produktu paraugos izmantojot analītiskās ķīmijas analīzes metodes – izaicinājums pārtikas analīzes metodoloģijas pilnveidošanai un skrīninga metožu attīstības izstrādei.
2. Mikro- un makroelementu kvantitatīvā sastāva analīze pārtikā ir būtisks pārtikas drošības un kvalitātes novērtējuma rādītājs, ko var pētīt apzinot specifisku pārtikas ieguves apstākļu kopumu.
3. Sezonalitāte, vietas specifiskie, botāniskie faktori, lauksaimniecības prakse, pārtikas pārstrādes procesi – apstākļi, kas ietekmē pārtikas sastāvu attiecībā uz mikro- un makroelementu saturu un koncentrāciju.
4. Elementu biopieejamības izpēte barības ķēdes posmos – nozīmīgs iespējamā piesārņojuma apjoma ieneses ar pārtiku uzturā novērtējuma aspekts.
5. Pārtikas kvantitatīva analīze ir perspektīvs pētījumu virziens vides, ķīmijas un veselības zinātņu nozarēs, kas potenciāli jāattīsta plašākā mērogā.

Promocijas darba novitāte

- Analītiskās metodoloģijas pielietojums pārtikas un vides paraugu analīzē ar iespējamu virzību uz racionālāku metožu izvēli, ekspresmetožu attīstīšanu pārtikas kvalitātes novērtēšanā, ko var ieviest pārtikas kvalitātes uzraudzības procedūrā.
- Starpnozaru pētnieciskās pieejas attīstība vides apstākļu un antropogēno ietekmju uz pārtikas sastāvu novērtēšanai ar mērķi saistīt tādas nozares kā vides zinātne, pārtikas zinātne un veselības zinātnes.
- Salīdzinošs ietekmējošo faktoru izvērtējums uz elementu akumulāciju barības ķēdē un atsevišķos tās posmos, kā arī dažādu apstākļu ietekmes izpēte uz elementu koncentrāciju pārtikā, piemēram, pārtikas ieguves intensīvā lauksaimniecībā salīdzinājums ar bioloģisko lauksaimniecību u.tml.
- Mikro- un makroelementu analīzes *pirkstu nospieduma* koncepcijas attīstīšana kā līdzeklis reģionāli iegūtas pārtikas un vides saiknes identificēšanai, kas piemērojama pārtikas izcelsmes un autentiskuma noteikšanā.

Promocijas darba praktiskā nozīme

Pirmo reizi veikta plaša mēroga pārtikas produktu mikro- un makroelementu satura kvantitatīva analīze Latvijā, kas izvērtēta starpdisciplināri, lai izpētītu vides apstākļu un antropogēnās ietekmes uz elementu koncentrāciju. Iegūti nozīmīgi dati, kas izmantojami turpmākos elementu biopieejamības pētījumos, kā arī ilgtspējīgas lauksaimniecības stratēģiju izstrādē.

Iegūtie dati izmantojami pārtikas drošības un riska analīzē, kā arī sabiedrības veselības un vides faktoru ietekmju integrētā analīzē. Iegūtos datus iespējams salīdzināt ar citu valstu pētījumiem, tādējādi iegūstot Latvijas izcelsmes pārtikas produktu kvalitātes vērtējumu starptautiskā mērogā.

Promocijas darba rezultātu aprobācija

Promocijas darba rezultāti ir apspriesti un atspoguļoti 12 zinātniskās publikācijās, 15 ziņojumos starptautiskās zinātniskās konferencēs un 10 referātos vietēja mēroga konferencēs Latvijā.

Promocijas darba izstrādes ietvaros autore vadījusi 4 bakalaura darbus un sniegusi konsultācijas 3 maģistra darbu izstrādē.

Zinātniskās publikācijas:

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. *Latvijas Lauksaimniecības Universitātes Raksti* 25(320): 54-66.

Ziņojumi starptautiskajās konferencēs:

1. Rīgas Tehniskās universitātes 54. starptautiskā zinātniskā konference. Latvija, Rīga, 2013. gada 14.-16. oktobrī. Referāts "Quantitative content of elements in food: How can it reflect impact of environmental and other influencing factors?" (**Vincēviča-Gaile, Z.**, Kļaviņš, M.)
2. IUPAC (*International Union of Pure and Applied Chemistry*) 44. Pasaules ķīmijas kongress. Turcija, Stambula, 2013. gada 8.-16. augustā. Referāts "Metal uptake and bioavailability: From soil to food through crops" (**Vincēviča-Gaile, Z.**, Stapkēviča, M., Dūdare, D., Kļaviņš, M.)
3. 13. starptautiskā multidisciplinārā ģeokonference *SGEM 2013*. Bulgārija, Albena, 2013. gada 16.-22. jūnijā. Referāts "Analysis of major and trace elements in food: Aspects of methodological applications" (**Vincēviča-Gaile**, Z., Rudoviča, V., Burlakovs, J., Kļaviņš, M.)
4. 19. ikgadējā starptautiskā zinātniskā konference *Research for Rural Development 2013*. Latvija, Jelgava, 2013. gada 15.-17. maijā. Referāts "Metal uptake from contaminated soils by some plant species (radish, lettuce, dill)" (Stapkēviča, M., **Vincēviča-Gaile, Z.**, Kļaviņš, M.)

5. Starptautiskā zinātniskā konference *Environmental Health 2013, Science and Policy to Protect Future Generations*. ASV, Bostona, 2013. gada 3.-6. martā. Referāts "Presence of arsenic in baby food: Is it the issue of concern?" (**Vincēviča-Gaile, Z.**, Lawgali, Y.F., Meharg, A.A., Kļaviņš, M.)
6. 14. starptautiska zinātniskā konference *Environmental Science and Development*. AAE, Dubaija, 2013. gada 19.-20. janvārī. Referāts "Food and environment: Trace element content of hen eggs from different housing types" (**Vincēviča-Gaile, Z.**, Gāga, K., Kļaviņš, M.)
7. Rīgas Tehniskās universitātes 53. starptautiskā zinātniskā konference. Latvija, Rīga, 2012. gada 11.-12. oktobrī. Referāts "Transfer of metals in food chain: An example with copper and lettuce" (**Vincēviča-Gaile, Z.**, Kļaviņš, M.)
8. Ķīnas-Eiropas simpozijs *Environment and Health, SESEH 2012*. Īrija, Golveja, 2012. gada 20.-25. augustā. Referāts "Research of food from Latvia: Analysis of essential elements and possible contaminants" (**Vincēviča-Gaile, Z.**, Kļaviņš, M., Rudoviča, V., Vīksna, A.)
9. 18. ikgadējā starptautiskā zinātniskā konference *Research for Rural Development 2012*. Latvija, Jelgava, 2012. gada 16.-18. maijā. Referāts "Root vegetables from Latvia: Background levels and risks of contamination with toxic elements" (**Vincēviča-Gaile, Z.**, Kļaviņš, M.)
10. 8. IASME/WSEAS (*International Association of Mechanical Engineering / World Scientific and Engineering Academy and Society*) starptautiskā zinātniskā konference *Energy, Environment, Ecosystems and Sustainable Development, EEESD 2012*. Portugāle, Faro, 2012. gada 2.-4. maijā. Referāts "Potentially toxic metals in honey from Latvia: Is there connection with botanical origin?" (**Vincēviča-Gaile, Z.**, Kļaviņš, M., Rudoviča, V., Vīksna, A.)
11. 12. Eirāzijas ķīmijas zinātņu konference *EuAsC$_2$S 2012*. Grieķija, Korfu, Dāsija, 2012. gada 16.-21. aprīlī. Referāts "Trace and major elements in root vegetables: A study in Latvia" (**Vincēviča-Gaile, Z.**, Kļaviņš, M., Rudoviča, V., Vīksna, A.)
12. Apvienotais pasaules latviešu zinātnieku 3. kongress un Letonikas 4. kongress (PLZK), sekcija *Vides kvalitāte Latvijā: esošais stāvoklis, izaicinājumi, risinājumi*. Latvija, Rīga, 2011. gada 24.-27. oktobrī. Referāts "Mikro- un makroelementu analīze dārzeņos vides zinātnes kontekstā" (**Vincēviča-Gaile, Z.**, Kļaviņš, M., Rudoviča, V., Vīksna, A.)
13. 4. starptautiskā zinātniskā konference *Medical Geology, GEOMED 2011*. Itālija, Bari, 2011. gada 20.-25. septembrī. Referāts "Risk and benefit assessment of trace and major elements detected in honey of different origins" (**Vincēviča-Gaile, Z.**, Kļaviņš, M., Rudoviča, V., Vīksna, A.)
14. 1. starptautiskā zinātniskā konference *Food and Environment, FENV 2011*. Apvienotā Karaliste, Ņūforesta, Lindhērsta, 2011. gada 21.-23. jūnijā. Referāts "Geographical dissemination of trace and major elements in honey" (**Vincēviča-Gaile, Z.**, Kļaviņš, M., Rudoviča, V., Vīksna, A.)
15. 2. WSEAS (*World Scientific and Engineering Academy and Society*) starptautiskā zinātniskā konference *Environment, Medicine and Health Sciences, EMEH 2011*. Spānija, Grankanārija, Meloneras, 2011. gada 24.-26. martā. Referāts "Trace and major element concentration in cottage cheese from Latvia" (**Vincēviča-Gaile, Z.**, Zilgalve, L., Kļaviņš, M.)

Ziņojumi vietēja mēroga konferencēs:

1. LU 72. zinātniskā konference. Rīga, 2014. gada 27. janvārī. Referāts "Vides ietekme uz mikroelementu sastāvu pārtikā: graudaugu produktu analīze" (**Vincēviča-Gaile, Z.,** Gāga, K., Rudoviča, V., Kļaviņš, M.) Kopsavilkums publicēts: *Ģeogrāfija. Ģeoloģija. Vides zinātne: Referātu tēzes*, 67-69.
2. LU 71. zinātniskā konference. Rīga, 2013. gada 29. janvārī. Referāts "Smago metālu ienese barības ķēdē augsne-augs" (Stapkēviča, M., **Vincēviča-Gaile, Z.,** Kļaviņš, M.) Kopsavilkums publicēts: *Ģeogrāfija. Ģeoloģija. Vides zinātne: Referātu tēzes*, 215-216.
3. LU 70. zinātniskā konference. Rīga, 2012. gada 31. janvārī. Referāts "Mikro- un makroelementu saturs sakņu dārzeņos Latvijā" (**Vincēviča-Gaile, Z.,** Kļaviņš, M., Rudoviča, V., Vīksna, A.) Kopsavilkums publicēts: *Ģeogrāfija. Ģeoloģija. Vides zinātne: Referātu tēzes*, 398-399.
4. LU 70. zinātniskā konference. Rīga, 2012. gada 31. janvārī. Referāts "Metālu (Cu^{2+} piemērā) pārnese barības ķēdē: augsne-augs" (**Vincēviča-Gaile, Z.,** Kļaviņš, M.) Kopsavilkums publicēts: *Ģeogrāfija. Ģeoloģija. Vides zinātne: Referātu tēzes*, 397-398.
5. LU 70. zinātniskā konference. Rīga, 2012. gada 31. janvārī. Referāts "Pilnīgas atstarošanas rentgenfluorescences spektrometrijas pielietojums šķidru paraugu tiešai analīzei" (**Vincēviča-Gaile, Z.,** Purmalis, O., Kļaviņš, M.) Kopsavilkums publicēts: *Ģeogrāfija. Ģeoloģija. Vides zinātne: Referātu tēzes*, 400-401.
6. LU 70. zinātniskā konference. Rīga, 2012. gada 31. janvārī. Referāts "Sezonālā ietekme uz mikro- un makroelementu saturu vistu olās" (Gāga, K., **Vincēviča-Gaile, Z.,** Kļaviņš, M.) Kopsavilkums publicēts: *Ģeogrāfija. Ģeoloģija. Vides zinātne: Referātu tēzes*, 291-292.
7. LU 70. zinātniskā konference. Rīga, 2012. gada 31. janvārī. Referāts "Botāniskās izcelsmes ietekme uz elementu saturu medū Latvijā" (Priedīte, E., **Vincēviča-Gaile, Z.,** Kļaviņš, M., Rudoviča, V., Vīksna, A.) Kopsavilkums publicēts: *Ģeogrāfija. Ģeoloģija. Vides zinātne: Referātu tēzes*, 356-357.
8. LU 69. zinātniskā konference. Rīga, 2011. gada februārī. Referāts "Ķīmisko elementu satura biezpienā mainību ietekmējošie vides faktori" (**Vincēviča-Gaile, Z.,** Zilgalve, L., Kļaviņš, M.) Kopsavilkums publicēts: *Ģeogrāfija. Ģeoloģija. Vides zinātne: Referātu tēzes*, 501-504.
9. LU 69. zinātniskā konference. Rīga, 2011. gada februārī. Referāts "Mikro- un makroelementu satura medū nozīme vides zinātnes skatījumā" (**Vincēviča-Gaile, Z.,** Bula, R., Kļaviņš, M.) Kopsavilkums publicēts: *Ģeogrāfija. Ģeoloģija. Vides zinātne: Referātu tēzes*, 499-501.
10. LU 68. zinātniskā konference. Rīga, 2010. gada februārī. Referāts "Selēna bioģeoķīmiskā nozīmība" (**Vincēviča-Gaile, Z.**) Kopsavilkums publicēts: *Ģeogrāfija. Ģeoloģija. Vides zinātne: Referātu tēzes*, 440-442.

1. TEORĒTISKAIS PAMATOJUMS

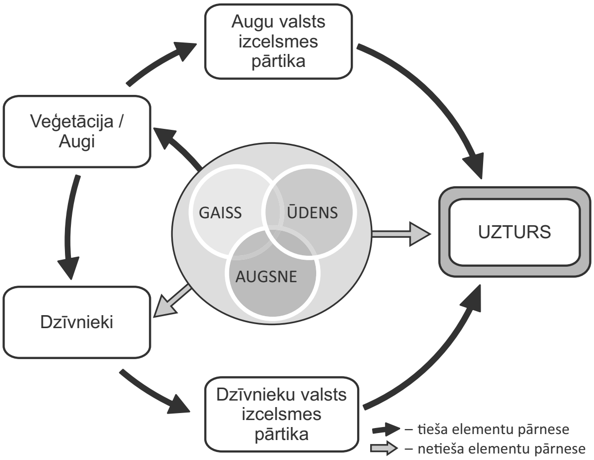
1.1. Mikro- un makroelementu nozīme un ieneses ceļi pārtikā

Bez pamatelementiem (C, H, N un O), kas veido līdz pat 97 % no dzīvās matērijas, ķīmiskie elementi tiek iedalīti makroelementos un mikroelementos, atkarībā no to vidējās koncentrācijas organismā, kā arī ņemot vērā nepieciešamo ikdienas nodrošinājumu. Makroelementi (Ca, Cl, K, Mg Na, P, S) organisma normālai attīstībai un funkcionēšanai nepieciešami salīdzinoši lielā daudzumā; katrs no tiem veido aptuveni 0,03-1,4 % no cilvēka ķermeņa masas. Savukārt, mikroelementu grupa ietver tādus elementus kā piemēram Ag, Al, As, Au, B, Ba, Co, Cr, Cu, F, Fe, I, Mn, Mo, Ni, Rb, Se, Sn, Sr, V, Zn un to koncentrācija organismā ir mainīga – no mazāk par 0,1 mg/kg līdz vairāk nekā 100 mg/kg. Nepieciešamā mikroelementu dienas deva parasti nepārsniedz 100 mg/dienā, bet makroelemenus parasti jāuzņem no 100 līdz >1000 mg/dienā (Abrahams, 2002; Aras and Ataman, 2006; Fraga, 2005). No visiem zināmajiem ķīmiskajiem elementiem aptuveni 50 elementus var atrast dzīvo organismu, tostarp augu, dzīvnieku un cilvēku audos un šūnās, bet tikai 23 elementiem ir pierādīta fizioloģiskā nozīmība cilvēka organismā (Combs, 2005; Fraga, 2005; Goldhaber, 2003). A. Kabata-Pendias un A.B. Mukherjē (2007) ķīmiskos elementos pēc to nepieciešamības dzīviem organismiem sarindo šādi: a) vitāli nepieciešamie elementi – As, B, Br, Cl, Co, Cr, Cu, F, Fe, I, Li, Mn, Mo, P, S, Se, Si, V un Zn; b) iespējams nepieciešamie elementi – Al, Ba, Ge, Ni, Rb, Sn, Sr un Ti; c) elementi, kas nav nepieciešami – Ag, Au, Cs, Hf, In, Ir, Sb, Ta, Te, U, Y, Zr un retzemju elementi; d) elementi, kas nav nepieciešami un toksiski – Be, Bi, Cd, Hg, Pb un Tl. Tomēr šis iedalījums var mainīties balstoties uz jaunākajiem atklājumiem zinātnē.

Pārtika ir nozīmīgākais elementu avots cilvēka organismam, tāpēc svarīgi ir apzināt elementu ieneses ceļus pārtikas produktos no vides – augsnes, ūdens un gaisa – jo iespējama ne tikai vitāli nepieciešamo elementu pārnese, bet arī pārtikas piesārņojums ar toksiskiem un potenciāli toksiskiem elementiem. Mūsdienās rūpnieciska pārtikas ražošana ir strauji attīstījusies, un ir stingri ierobežota ar likumiem un noteikumiem, kas nosaka gan pārtikas enerģētisko vērtību, gan pieļaujamo potenciāli toksisko elementu klātbūtni, tomēr augu un dzīvnieku izcelsmes pārtika, ko ražo zemnieku saimniecības, kā arī mājsaimniecības joprojām ir pakļauta reģionālai vides faktoru ietekmei. Taču šīs ietekmes vietējā mērogā ir maz pētītas.

Elementu aprite vidē notiek nemitīgi, un to ienese barības ķēdē un cilvēka uzturā var notikt tiešā un netiešā veidā (1.1. attēls).

Ņemot vērā spēju uzņemt elementus tieši no augsnes, ūdens un gaisa, augus var vērtēt kā galvenos ekosistēmas komponentus, kas iesaistīti elementu pārnesē no vides pārtikā. Barības ķēdē notiek ne tikai elementu biokoncentrēšanās, bet arī augsnē un ūdenī esošo savienojumu resintezēšana, lai tie kļūtu biopieejami ķēdes augstākos posmos. Tā kā augsne ir galvenais minerālvielu avots, tad elementu pārnese no vides pārtikā var tikt apskatīta arī ģeoloģiskās izpētes aspektā (Bowman et al., 2003; Combs, 2005). Tādējādi elementu saturs pārtikā ar zināmu izcelsmes vietu var būt atkarīgs no elementu satura augsnē un ūdenī. Elementu ienese pārtikā no atmosfēras parasti notiek mazākā mērā un vairāk atkarīga no gaisā esošo daļiņu daudzuma, izmēra un ķīmiskā sastāva – jo mazāks ir daļiņu



1.1. attēls. **Elementu ienese uzturā no vides**

izmērs, jo vieglāk tās var absorbēt augi un ieelpot dzīvnieki vai uzņemt ar barību, tādējādi paaugstinot barības ķēdes kontaminācijas risku (Allen et al., 2001).

Pārtikas piesārņojuma risks ir nozīmīgs jautājums, kas Latvijā maz pētīts. Reģionālas elementu satura īpatnības augsnē, ģeoķīmiskās anomālijas ir dabīgs faktors, kas var ietekmēt elementu saturu pārtikā. Savukārt, lauksaimnieciskās darbības veids, vides piesārņojums var būt saistāms ar antropogēno ietekmi elementu pārnesē no vides pārtikā. Šo apstākļu ietekmes būtiskums ir pētīts promocijas darba ietvaros.

1.2. Elementu biopieejamība barības ķēdē

Biopieejamība ir elementa daudzums noteiktā matricā, piemēram, augiem augsnē vai cilvēkiem pārtikā, kas potenciāli pieejams organismam un absorbējot izmantojams metaboliskos procesos (Welch and Graham, 2005). Biopieejamības noteikšana ir sarežģīts process, ko ietekmē dažādi faktori tādi kā ķīmisko savienojumu forma, vides apstākļi, individuālas organisma īpatnības.

Elementu biopieejamība barības ķēdes segmentā *augsne-augs* ciešā mērā saistīta ar savienojumu šķīdību. Augi spēj uzņemt elementus, kas augsnē atrodas šķīstošu jonu veidā organisku vai neorganisku kompleksu struktūrā. Elementu biopieejamība no augsnes lielā mērā atkarīga ne tikai no savienojuma ķīmiskām īpašībām, bet arī no augsnes īpašībām, starp kurām kā nozīmīgākās var minēt organisko vielu saturu un pH (Gardea-Torresdey et al., 2005; Inaba and Takenaka, 2005; Peralta-Videa et al., 2009).

Elementu biopieejamība augstākā barības ķēdes segmentā *pārtika-cilvēks* ir īpaši nozīmīga attiecībā uz vitāli nepieciešamajiem elementiem, kā arī potenciālajiem piesārņotājiem. Elementu biopieejamība no pārtikas atkarīga ne tikai no savienojuma ķīmiskās formas, bet arī no uztura sastāva īpatnībām un indivīda veselības stāvokļa. Tomēr, lai arī kopējais elementu saturs pārtikā neatspoguļo elementu biopieejamību, pētījumos *in vivo* un *in vitro* daudziem elementiem ir aprēķināta biopieejamības pakāpe (parasti izteikta %) (ATSDR, s.a.), ko var izmantot pārtikas uzturvērtības, kā arī drošības izvērtēšanā, zinot elementu kvantitatīvo sastāvu.

1.3. Jaunākie mikro- un makroelementu satura pētījumi Latvijā

Ar elementu analīzi saistītie pētījumi Latvijā izvērtēti balstoties uz starptautiskajās zinātniskajās datu bāzēs (*Scopus*, *Science Direct*, *Springer Link* un *ISI Web of Knowledge*) pieejamajiem zinātniskajiem rakstiem, kas publicēti laikā no 2000. gada līdz 2013. gadam.

Ir pieejams plašs informācijas klāsts par elementu pētījumiem vides objektos. Piemēram, detalizētu pētījumu, lai noteiktu vides faktoru ietekmi uz elementu saturu Rīgas ielu apstādījumos, ir veikusi G. Čekstere ar kolēģiem (Čekstere, 2011; Cekstere and Osvalde, 2013; Cekstere and Osvalde, 2010a; Cekstere and Osvalde, 2010b; Cekstere et al., 2008). Savukārt, gaisa piesārņojuma un elementu satura sūnās mijiedarbība pētīta prof. O. Nikodemus vadībā (Nikodemus et al., 2004; Tabors et al., 2004). Arī Somijas zinātnieki R. Salminena (2011) vadībā pētījuši elementu sadalījumu sūnās un organiskajā augsnes slānī Austrumbaltijas reģionā. Elementu saturu Latvijas augsnēs sava promocijas darba ietvaros analizējis A. Gilucis (2007), kā arī pieejami dati par metālisko elementu izgulsnēšanos meža augsnēs (Brumelis et al., 2002; Kasparinskis and Nikodemus, 2012).

Plaši pētījumi veikti analizējot elementu un barības vielu saturu iekšzemes ūdeņos (Aldahan et al., 2006; Klavins et al., 2001; Klavins et al., 2000; Kokorite et al., 2010; Stalnacke et al., 2003) un ezeru nogulumos (Klavins et al., 2011; Klavins and Vircavs, 2001), kā arī daudz pētīti ir purvi (Klavins et al., 2009b; Klavins et al., 2003; Silamikele et al., 2011).

Ņemot vērā nelielo publikāciju skaitu, var secināt, ka vides faktoru ietekme uz elementu saturu pārtikā Latvijā ir maz pētīts jautājums. Kā piemēru var minēt smago metālu satura izpēti zivīs no ezeriem Latvijā (Klavins et al., 2009a), elementu satura noteikšanu medū Latvijā (Dimiņš, 2006) un dažus pētījumus, kas vairāk saistīti ar uzturvielu sastāva novērtēšanu (Murniece et al., 2011; Osvalde and Karlsons, 2010).

Kopumā var rezumēt, ka promocijas darba ietvaros veiktā mikro- un makroelementu kvantitatiīvā satura pārtikā izpēte ir nozīmīgs starpdisciplinārs pētījums vides, ķīmijas, uztura un veselības zinātņu ietvaros.

2. MATERIĀLI UN METODES

2.1. Pārtikas paraugu ievākšana un sagatavošana analīzei

2.1.1. Pārtikas paraugu ievākšana

Pārtikas paraugi tika ievākti laikā no 2009. līdz 2013. gadam Latvijas teritorijā. Ievāktie pārtikas paraugi pētījumam (metodoloģija pēc Aras and Ataman, 2006; Ekholm et al., 2007): (I) augu valsts produkti – neapstrādāti, piemēram, augļi un dārzeņi (āboli, burkāni, sīpoli, kartupeļi, salāti) un pēc pārstrādes (graudaugu produkti biezputrām un graudaugu maisījumi bērnu uzturam); (II) dzīvnieku valsts produkti – neapstrādāti, piemēram, bišu produkti (medus, ziedputekšņi, bišu maize), vistu olas, un pēc pārstrādes (biezpiens); (III) dzērieni - neapstrādāti (ābolu sula, bērzu sula) un pēc pārstrādes (ābolu vīns). Ievācot paraugus īpaša vērība tika attiecināta uz pārtikas izcelsmi un sezonalitāti. Kopumā analizēti 510 pārtikas paraugi.

Augu valsts izcelsmes pārtikas paraugi:

- sakņu dārzeņi – sīpoli *Allium cepa* (n_s[1]$=98$), burkāni *Daucus carota* ($n_s=81$), kartupeļi *Solanum tuberosum* ($n_s=55$) un kartupeļu miza ($n_s=6$) (2.1., 2.2., 2.3. attēls);
- lapu dārzeņi – lapu salāti *Lactuca sativa* (ievākti Latvijas teritorijā ($n_s=7$) un audzēti piesārņotā augsnē ($n_s=3$) (2.4. attēls);
- augļi – āboli *Malus domestica* ($n_s=21$) un ābolu miza ($n_s=3$) (2.4. attēls);
- graudaugu produkti biezputrām un graudaugu maisījumi bērnu uzturam – graudaugu produktu maisījumi ($n_s=10$), piemēram, trīsgraudu pārslas, rīsu produkti ($n_s=10$), kviešu produkti ($n_s=12$) un griķu produkti ($n_s=11$).

Augu valsts pārtikas paraugi iespēju robežās tika ievākti Latvijas teritorijā, un, ievācot paraugus, tika noteikta to izcelsme. Paraugi tikai ievākti svaigā veidā tirdzniecības vietās vai tieši no audzētāja. Izņemot graudaugu produktus, kuri tika ievākti pieejamos komerciepakojumos, viens paraugs ietvēra 3–5 dārzeņus vai augļus, kas tika nomazgāti, nomizoti, sasmalcināti ar keramikas nazi (*Kiocera*) un izžāvēti žāvskapī (*Labassco*) pie temperatūras 80-105 °C atkarībā no mitruma daudzuma paraugā. Pēc žāvēšanas paraugi tika saberzti piestā līdz pulvera konsistencei un uzglabāti hermētiski noslēdzamos polietilēna maisiņos tumšā un sausā vietā istabas temperatūrā (Aras and Ataman, 2006).

Dzīvnieku valsts izcelsmes pārtikas paraugi:

- bišu produkti – medus ($n_s=80$), ziedputekšņi ($n_s=5$) un bišu maize ($n_s=5$) (2.5. attēls);
- biezpiens ($n_s=27$) ar atšķirīgu izcelsmi (zemnieku saimniecības un piena pārstrādes uzņēmumi) ievākts vasaras un ziemas sezonās (2.6. attēls);
- vistu olas ($n_s=33$) ar atšķirīgu izcelsmi (no bioloģiskām saimniecībām, piemājas saimniecībām un putnu fermām), kā arī paraugi ($n_s=24$) sezonalitātes ietekmes novērtēšanai, kas ievākti gada garumā piemājas saimniecībā Aizkrauklē ar zināmiem mājputnu turēšanas apstākļiem (2.7. attēls).

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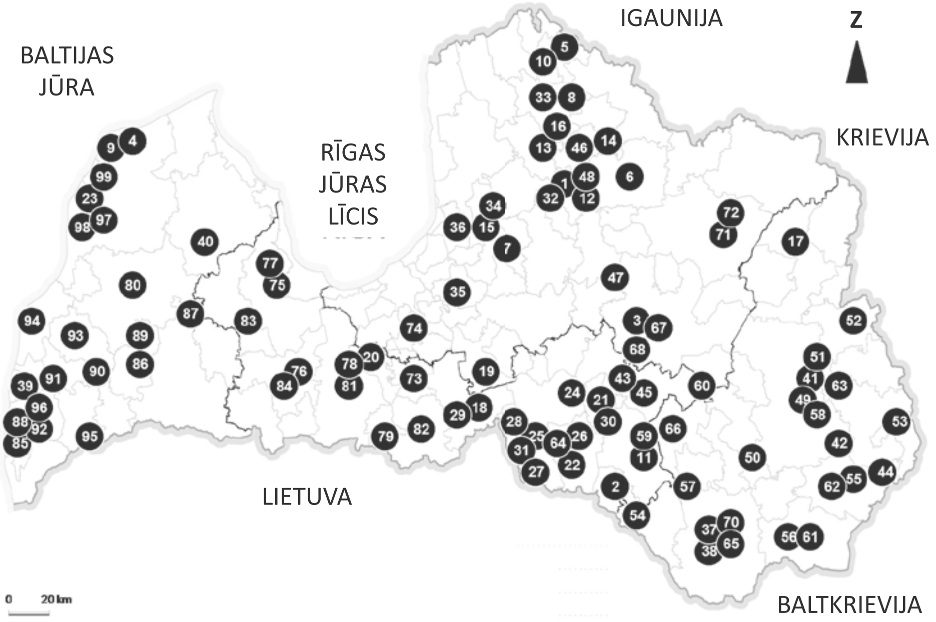
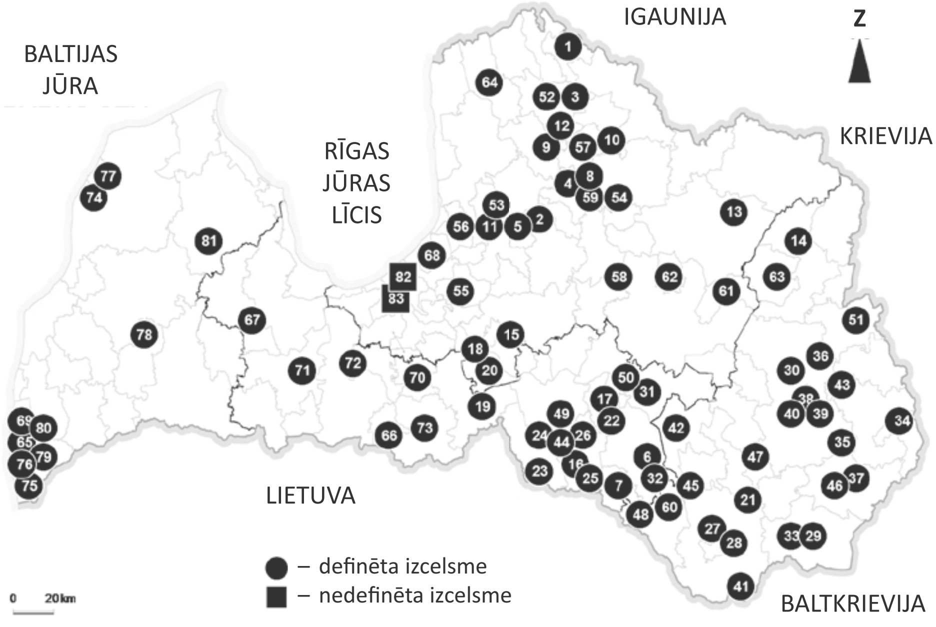
[1] Šeit un turpmāk n_s – paraugu skaits



2.1. attēls. **Sīpolu (*Allium cepa*) paraugu izcelsme**[1]



2.2. attēls. **Burkānu (*Daucus carota*) paraugu izcelsme**

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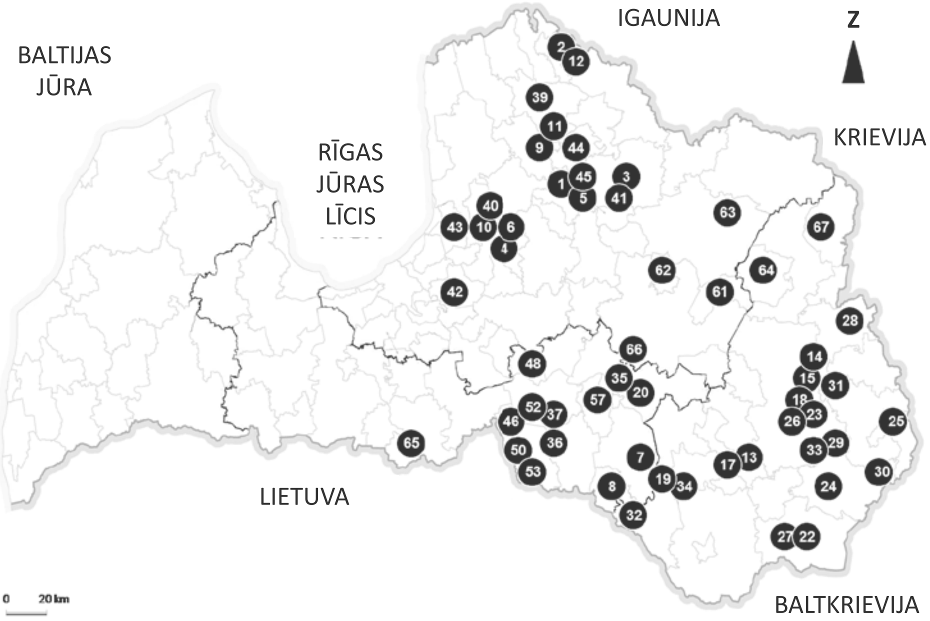
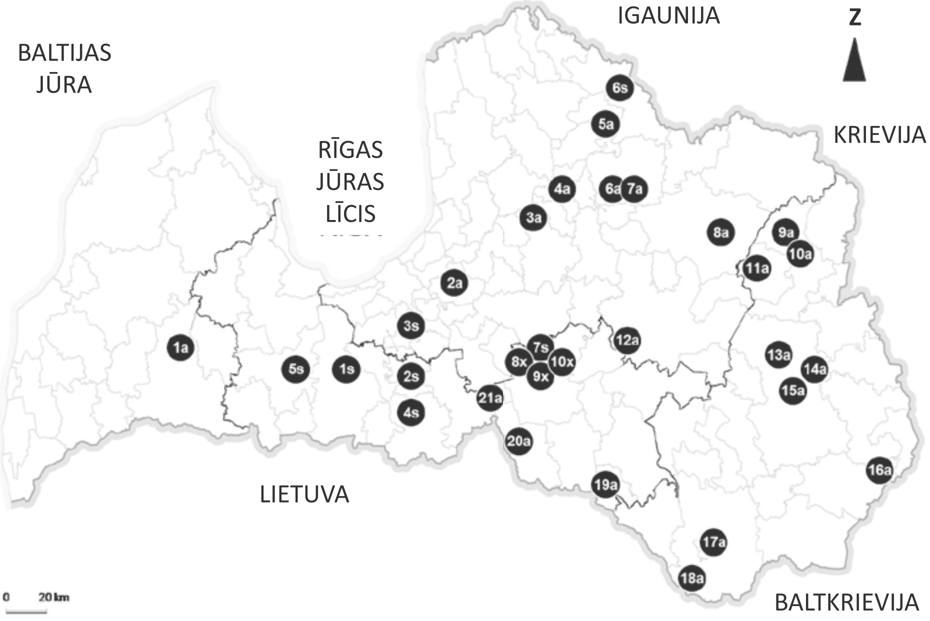
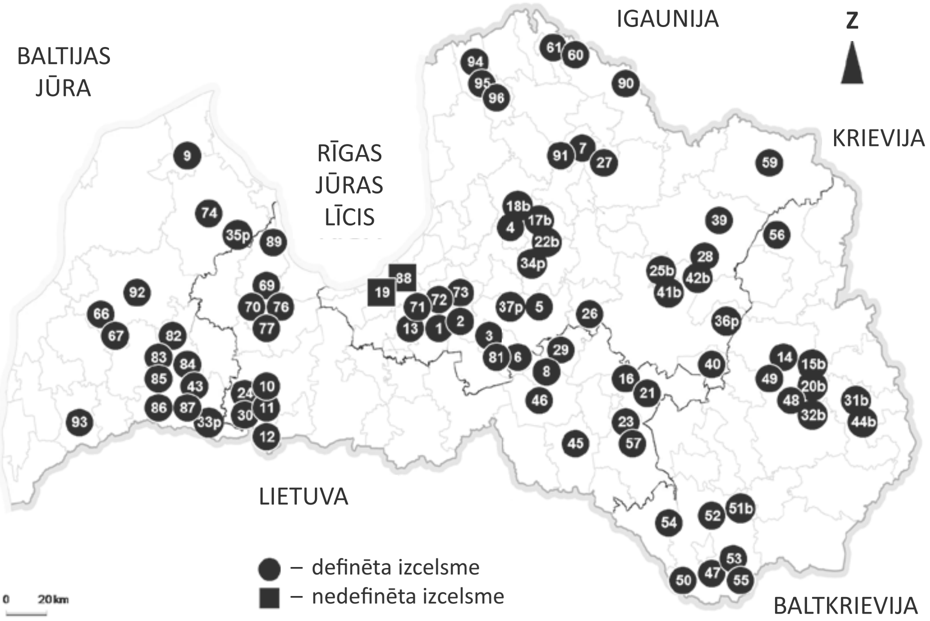
[1] Šeit un turpmāk shematiskajās kartēs ar cipariem apzīmēts parauga numurs



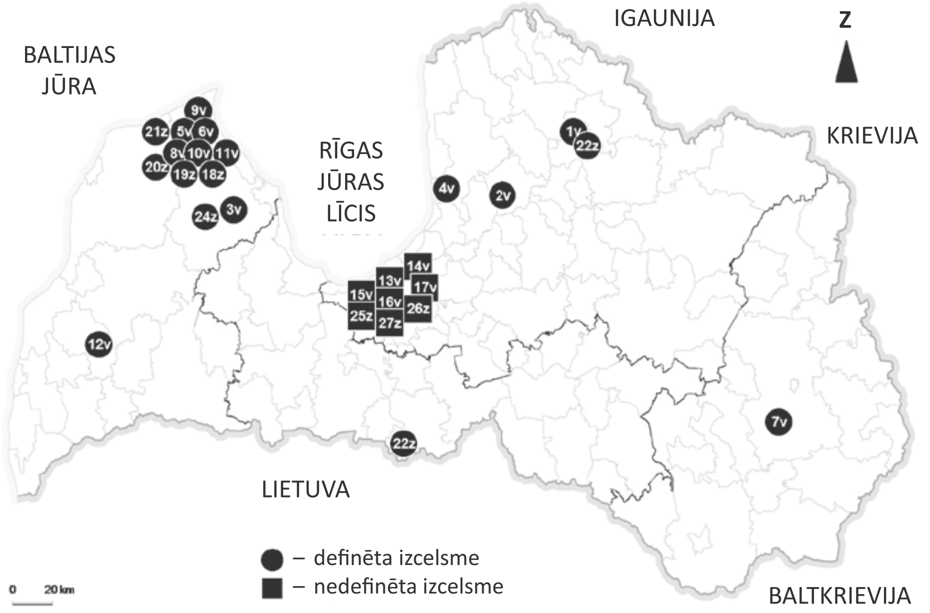
2.3. attēls. **Kartupeļu (*Solanum tuberosum*) paraugu izcelsme**



2.4. attēls. **Salātu (*Lactuca sativa*) paraugu izcelsme (s) un paraugi, kas audzēti piesārņotā augsnē (x); ābolu (*Malus domestica*) paraugu izcelsme (a)**

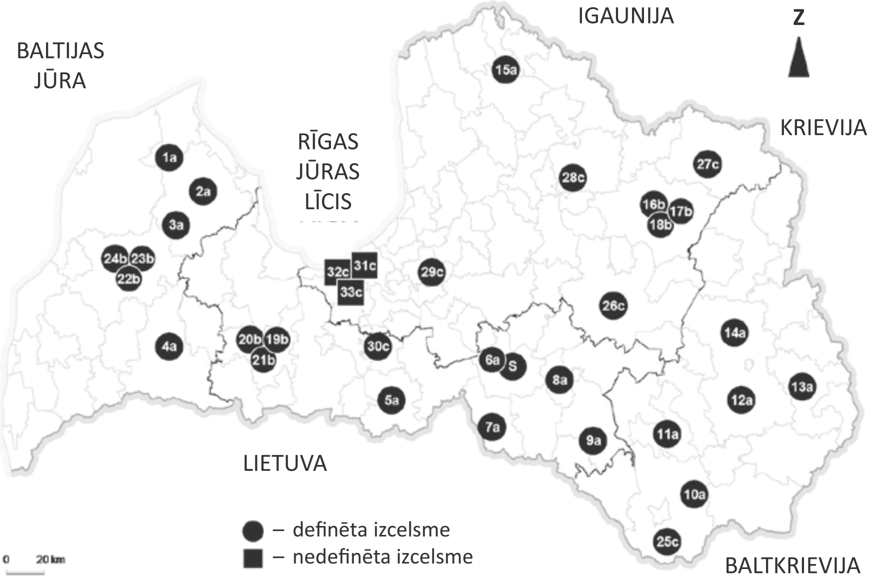


2.5. attēls. **Bišu produktu paraugu izcelsme: ziedputekšņi un bišu maize (p), medus; paraugi no bioloģiskam saimniecībām (b)**



2.6. attēls. **Biezpiena paraugu izcelsme; paraugi ievākti ziemas (z) un vasaras (v) sezonās**

Dzīvnieku valsts izcelsmes pārtikas paraugi tādi kā medus produkti tika uzglabāti polipropilēna trauciņos ar vāku tumšā un vēsā vietā. Biezpiena paraugi tika izžāvēti žāvskapī (*Labassco*) 60 °C temperatūrā un pēc tam uzglabāti saldētavā -20 °C. Olu paraugi tika atdalīti no čaumalām un uzglabāti saldētā veidā hermētiski noslēgtos polietilēna maisiņos (Aras and Ataman, 2006).

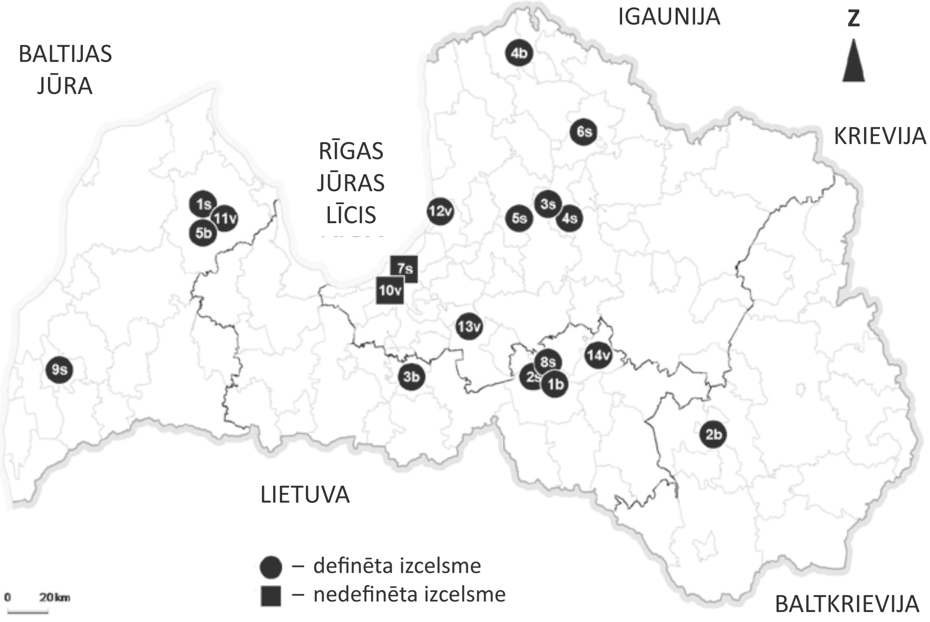


2.7. attēls. **Vistu olu paraugu izcelsme; paraugi ievākti no piemājas saimniecībām (a), bioloģiskām saimniecībām (b) un putnu fermām (c), paraugi sezonalitātes analīzei (s)**

Dzērienu paraugi (2.8. attēls) – ābolu sula (n_s=9), bērzu sula (n_s=5) un ābolu vīns (n_s=5) tika uzglabāti ledusskapī (+4 °C) polipropilēna mēģenēs ar vāku. Paraugu analīze tika veikta uzreiz pēc nogādāšanas laboratorijā.

2.1.2. Pārtikas paraugu sagatavošana pirms kvantitatīvās analīzes

Pirms kvantitatīvās analīzes pārtikas paraugi tika sagatavoti izmantojot slapjās mineralizācijas metodi, t.i., precīzs parauga iesvars tika šķīdināts koncentrētā analītiski tīrā HNO_3 (65 % w/v, *Scharlau*, *Penta* vai *Merck*) un koncentrētā analītiski tīrā H_2O_2 (30 % w/v, *Merck*). Diennakti pēc paraugu apliešanas ar reaģentiem, mineralizācijas process tika veicināts paraugus karsējot termoblokā (*Biosan*) līdz pilnīgai mineralizācijai vai šķeļot mikroviļņu šķelšanas iekārtā (*Milestone*). Pēc paraugu mineralizācijas, izmantojot dejonizētu ūdeni (<0.1 µS/cm, 18 MΩ/cm, *Millipore*), uzpildot līdz noteiktam tilpumam tika iegūti pārtikas paraugu šķīdumi kvantitatīvai analīzei. Daži paraugi, piemēram, dzērienu paraugi, olu un medus paraugi tika analizēti arī bez iepriekšējas apstrādes, ko pieļauj pilnīgās atstarošanas rentgenfluorescences spektrometrijas tehniskās iespējas (Klockenkamper, 1997).



2.8. attēls. **Dzērienu paraugu izcelsme: ābolu sula (s), bērzu sula (b), ābolu vīns (v)**

2.1.3. Kvantitatīvās analīzes metodes

Lai noteiktu mikro- un makroelementu koncentrāciju, pārtikas paraugu šķīdumi tika analizēti ar šādām kvantitatīvās analīzes metodēm: TXRF – pilnīgas atstarošanas rentgenfluorescence spektrometrija (Röntec PicoTAX, *Röntec GmbH*), AAS – atomabsorbcijas spektrometrija (AANALYST 200, *Perkin Elmer*) un ICP-MS – induktīvi saistītas plazmas masas spektrometrija (ELAN DRC-e, *Perkin Elmer*). Mērījumiem piemērotākā metode tika izvēlēta atkarībā no analizējamā parauga specifikas un nosakāmo elementu spektra. Analītisko mērījumu verifikācijai un rezultātu ticamības novērtēšanai tika veikti kontrolmērījumi izmantojot sertificētus references materiālu paraugus: burkānu sakņu pulveris *CS-CR-2 Carrot root powder* (*LGC Standards*), ābolu pulveris *NCS ZC73017 Apple powder* (*Promochem*), ķērpju pulveris *IAEA-336 Lichen* (*IAEA*), vājpiena pulveris *BCR-063R Skim milk powder* (*IRMM*) un sarkanā vīna standarta paraugs *PT Red wine Chilian* (*LGC Standards*), kas pirms analīzes tika sagatavoti līdzīgi kā analizējamie pārtikas paraugi, mineralizējot ar koncentrētu HNO_3.

Analītisko metožu mērījumu precizitātes novērtējuma rādītāji pēc references parauga *NCS ZC73017 Apple powder* analīzes apkopoti 2.1. tabulā.

2.1. tabula

Analītisko metožu (TXRF, AAS, ICP-MS) precizitātes novērtējums izmantojot references paraugu *NCS ZC73017 Apple powder*

Elements	Sertificētā koncentrācija, ($\bar{x}$±*s*), mg/kg	Koncentrācija ($\bar{x}$±*s*; n_m=5)[1], kas noteikta ar attiecīgo metodi, mg/kg (Precizitāte, %)		
		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)

2.2. Eksperimentāla pārtikas kultūraugu audzēšana

2.2.1. Augsnes paraugu analīze un sagatavošana

Augsnes paraugi kultūraugu eksperimentālai audzēšanai tika ievākti 2011. gada pavasarī Vidzemes augstienes DR Vecpiebalgas novada Taurenes pagastā, Lodes muižas apkārtnē, ņemot vērā Latvijai raksturīgākos augšņu tipus un tekstūru (Kārkliņš et al., 2009; Kasparinskis, 2011; Nikodemus, 2011). Paraugi tika ievākti no H vai Ap horizonta, 0-20 cm dziļumā. Augšņu paraugi tika identificēti šādi: S1 – zemā purva kūdraugsne; S2 – velēnu podzolaugsne / smilšmāls; S3 – velēnu podzolaugsne / smilts; S4 – velēnu podzolaugsne / mālsmilts; S5 – velēnu podzolaugsne / smilšains smilšmāls (FAO, 2006; Kārkliņš et al., 2009; Nikodemus, 2011; Noteikumi 804, 2005). Laboratorijā, izmantojot standartmetodiku, tika noteikti tādi augšņu raksturlielumi kā granulometriskais sastāvs, pH_{H2O} un pH_{KCl}, organisko vielu saturs, katjonu bāzu summa, elementu koncentrācija (FAO, 2006; Pansu and Gautheyrou, 2006).

Lai veiktu pārtikas kultūraugu audzēšanu un elementu biopieejamības pētījumu, augsnes paraugi tika mākslīgi piesārņoti sekojoši:

a) monokontaminācija, izmantojot vara sulfāta pentahidrāta $CuSO_4 \times 5H_2O$ šķīdumu pie noteiktām Cu mērķkoncentrācijām (40, 70, 100, 130 un 200 mg/kg);

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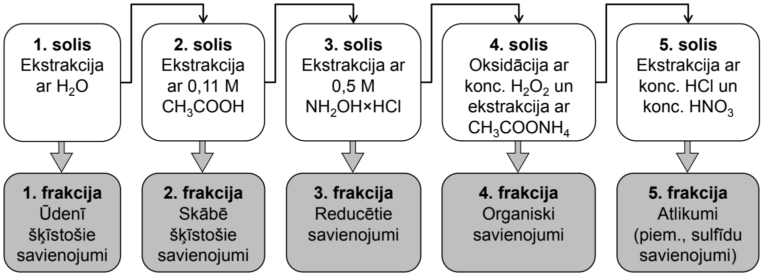
[1] Šeit un turpmāk $\bar{x}$ – vidējā vērtība, *s* – standartnovirze, n_m – mērījumu skaits

b) multielementu kontaminācija, izmantojot metālisko elementu (Cd, Cu, Pb un Zn) sāļu šķīduma maisījumu pie noteiktām elementu mērķkoncentrācijām (6 mg/kg Cd, 130 mg/kg Cu, 750 mg/kg Pb un 300 mg/kg Zn), pielietojot šādus reaģentus – kadmija acetāta dihidrāts $Cd(CH_3COO)_2 \times 2H_2O$, vara sulfāta pentahidrāts $CuSO_4 \times 5H_2O$, svina (II) nitrāts $Pb(NO_3)_2$ un cinka sulfāta heptahidrāts $ZnSO_4 \times 7H_2O$.

Augsnes paraugi tika piesātināti ar aprēķināto reaģenta šķīduma daudzumu, mehāniski maisot, kā tas aprakstīts literatūrā (Alexander et al., 2006; Inaba and Takenaka, 2005). Daļa augsnes paraugu tika atstāti nepiesārņoti kontrolei. Daļa piesārņoto paraugu tikai piesātināti ar humusvielu šķīdumu (3 g/kg; augstā tipa purva kūdra ar C 54,35 %, H 2,36 %, N 1,26 %, Mw 4 500 – 12 000 dal). Pēc 2 nedēļām tika veikta atkārtota augsnes paraugu mehāniska homogenizācija, kam sekoja augsnes iepildīšana stādu kastēs ar mērķi audzēt 3 kultūraugu sugas – redīsus *Raphanus sativus* L. 'Saxa 2', lapu salātus *Lactuca sativa* L. 'Grand Rapids' un dilles *Anethum graveolens* L. 'Mammut'. Kultūraugu audzēšana tika veikta 2011. gada vasarā lauku teritorijā Aizkraukles apkārtnē.

2.2.2. Augsnes un augu paraugu frakcionēšanas analīze

Lai noteiktu elementu biopieejamību no augsnes augiem, tika veikta augsnes frakcionēšanas analīze (attēls 2.9.), izdalot 5 frakcijas: 1) ūdenī šķīstošo savienojumu frakcija; 2) skābē šķīstošo savienojumu frakcija; 3) reducēto savienojumu frakcija; 4) organisko savienojumu frakcija; 5) ar sulfīdiem saistīto savienojumu frakcija (Arthur et al., 2007; Malandrino et al., 2011; Tessier et al., 1979).



2.9. attēls. **Frakcionēšanas analīzes shēma**

Lai vērtētu elementu biopieejamību barības ķēdes segmentā *augs-cilvēks*, tika veikta ievākto salātu paraugu frakcionēšanas analīze, izdalot 3 frakcijas: 1) ūdenī šķīstošo savienojumu frakcija; 2) skābē šķīstošo savienojumu frakcija; 3) reducēto savienojumu frakcija (Arthur et al., 2007; Malandrino et al., 2011; Tessier et al., 1979).

Iegūtajos paraugu frakciju šķīdumos tika noteikts kvantitatīvais elementu saturs izmantojot atomabsorbcijas spektrometrijas un induktīvi saistītas plazmas masas spektrometrijas metodes.

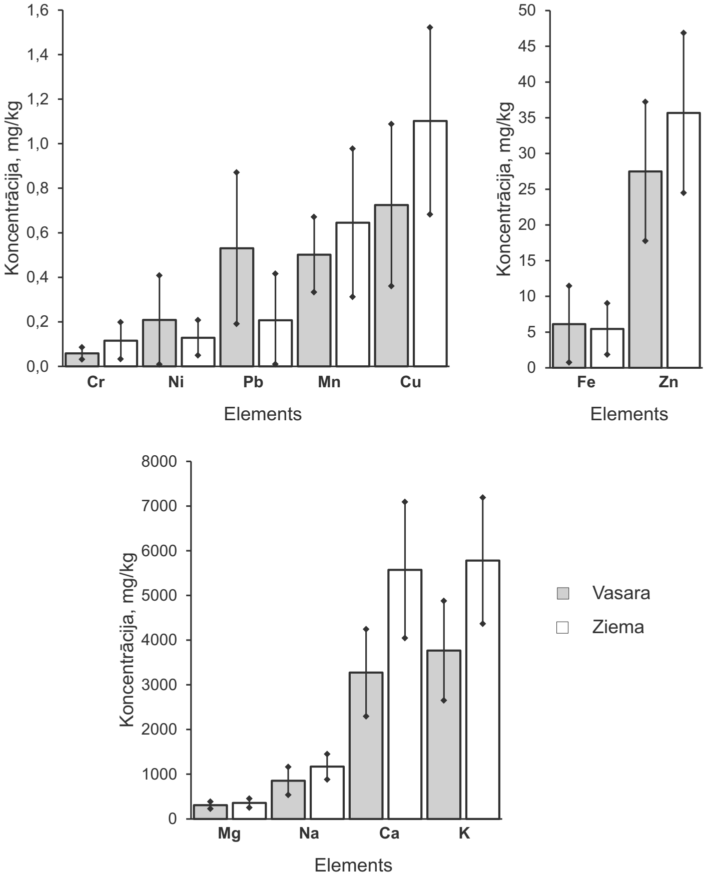
3. REZULTĀTI UN DISKUSIJA

3.1. Vides apstākļu ietekmju uz elementu saturu pārtikā izvērtējums

3.1.1. Sezonalitātes ietekme uz elementu koncentrāciju

Sezonalitātes ietekme tika izvērtēta ņemot vērā konstatēto elementu koncentrāciju biezpiena un vistu olu paraugos.

Biezpiens. Biezpiena paraugi tika ievākti divu sezonu (pavasaris/vasara un rudens/ziema) ietvaros. Attiecībā uz makroelementu saturu ziemas sezonas laikā ievāktajos paraugos tika konstatēts augstāka elementu koncentrācija, īpaši Ca un K (3.1. attēls), ko var saistīt ar dzīvnieku uzturēšanas atšķirībām sezonalitātes ietekmē.



3.1. attēls. **Vidējā elementu koncentrācija biezpienā atkarībā no sezonas**

Arī lielāka mikroelementu koncentrācija (Cr, Cu, Mn, Zn) konstatēta paraugos, kas ievākti ziemas periodā. Tomēr daži elementi, piemēram, Fe, Ni un it īpaši Pb augstākā koncentrācijā konstatēti paraugos, kas ievākti vasaras sezonā. To visticamāk var saistīt ar vides faktoru ietekmi, piemēram, liellopu ganībās autoceļu vai dzelzceļa tuvumā iespējama Pb un Ni nonākšana uz zāles putekļu veidā, kas var veicināt barības ķēdes piesārņojumu. Nozīmīgs ir lopu barošanas režīms, kas ziemas un vasaras sezonā ir atšķirīgs, t.i., ziemas periodā dzīvnieki saņem minerālvielām bagātāku barību (piemēram, kombinētu mikro-, makroelementiem un vitamīniem bagātinātu spēkbarību) nekā vasaras sezonā, kad lielākā mērā iespējama to barošana ar zāli vai sezonālu augu izcelsmes barību.

Vistu olas. Sezonalitātes noteikšanai vistu olu paraugi tika ievākti katru mēnesi viena gada garumā (2011. gada aprīlis – 2012. gada marts) no piemājas saimniecības Aizkrauklē ar zināmiem mājputnu uzturēšanas apstākļiem: pavasara sezonā un vasaras sezonā mājputni tika turēti āra apstākļos ar iespēju brīvi pārvietoties un meklēt barību noteiktā teritorijā, bet rudens un ziemas sezonā mājputni tika turēti no ārējās vides norobežotā telpā un saņēma kombinēto barību, kā arī graudus. Atsevišķi tika analizēts olu baltums un olu dzeltenums. Iegūtie dati liecināja, ka augstāka mikroelementu (Cu, Fe, Zn) koncentrācija kopumā konstatējama olu paraugos, kas ievākti vasaras vai pavasara sezonā (3.2. attēls). Izņēmums ir Se, kas vairāk ir konstatēts paraugos no ziemas sezonas, pie tam, olu baltumā Se varēja kvantificēt tikai ziemas sezonas paraugos, ko cieši var saistīt ar sezonalitātes ietekmi, jo augsnēs Latvijā ir konstatēts Se deficīts (Zegnere and Alsina, 2008). Tas izskaidro zemo Se saturu olu paraugos vasaras un pavasara sezonā, kad putniem barības uzņemšana vairāk iespējama no apkārtējās vides, t.sk., no augsnes, mezobiotas un augiem.

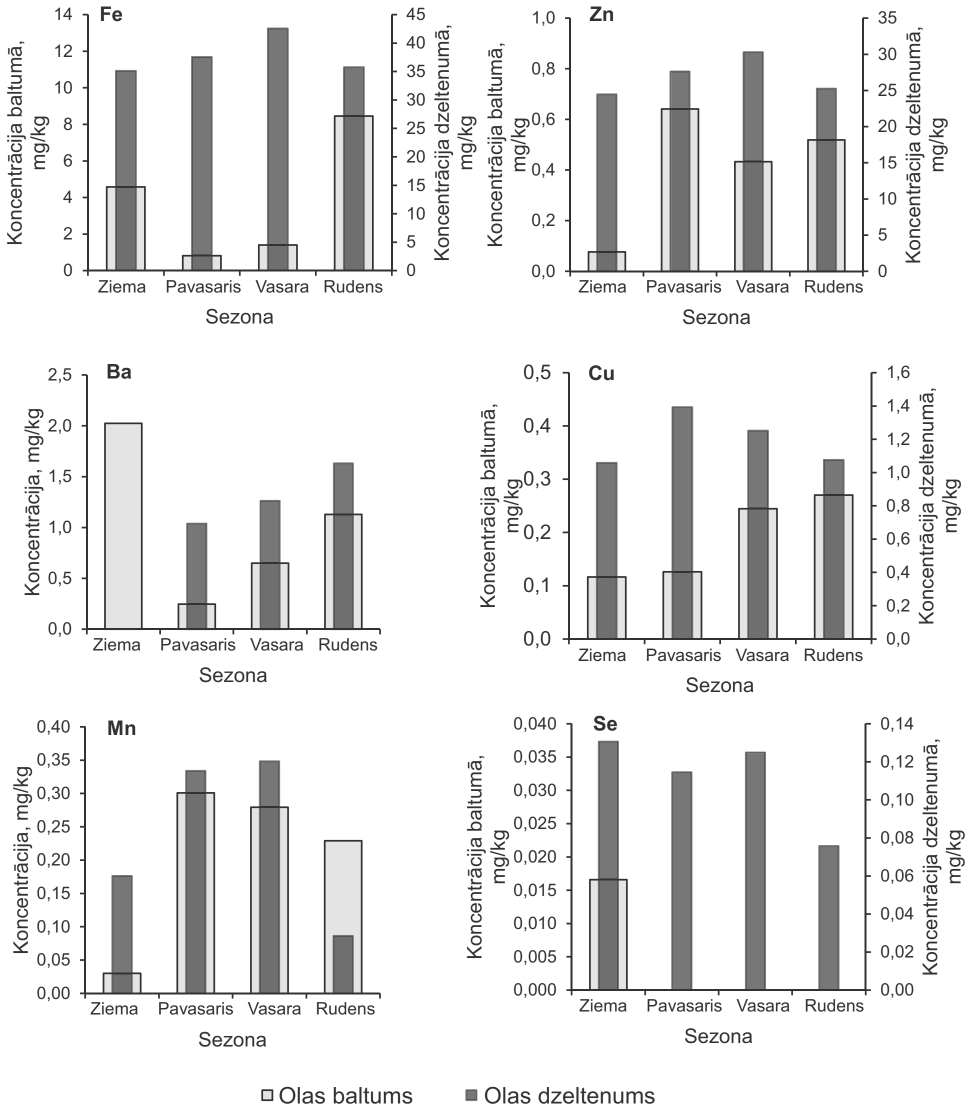
Līdzīgi kā konstatēts biezpiena izpētē, arī olu paraugos augstāka makroelementu koncentrācija attiecināma uz paraugiem, kas ievākti ziemas sezonā, ko var saistīt ar mājputnu turēšanas apstākļiem un barošanās iespēju sezonālo mainību.

3.1.2. Botāniskās izcelsmes ietekme uz elementu koncentrāciju pārtikā

Zinot ievākto paraugu botānisko izcelsmi bija iespējams noteikt šīs ietekmes nozīmi attiecībā uz elementu satura mainību medū. Medus paraugi tika iedalīti 7 botāniskās izcelsmes grupās: 1) dažādu ziedu medus ($n_s=33$); 2) viršu un meža ziedu medus ($n_s=16$); 3) rapša un pavasara ziedu medus ($n_s=5$); 4) griķu un āboliņa ziedu medus ($n_s=9$); 5) liepu ziedu medus ($n_s=6$); 6) pļavas ziedu medus ($n_s=8$); 7) rūpnieciski ražots medus maisījums ar nezināmu botānisko izcelsmi ($n_s=3$).

Lai novērtētu arī piesārņojuma ietekmi, medus paraugu analīzē lielāka vērība tikai pievērsta potenciāli toksisko elementu noteikšanai. Kopumā medus paraugu kvantitatīvā analīze atklāja, ka, ņemot vērā vidējo rezultātu, potenciāli toksiskie elementi medū kvantificējami šādā secībā: Zn >Al >Cu >Ni >Cr >Pb >Co >Cd >As. Iegūtie dati par samērā augsto Al, Cu, Ni un Zn koncentrāciju medū liecina par iespējamu medus piesārņojumu tā sagatavošanas vai uzglabāšanas laikā, jo šie metāli ir plaši sastopami mājsaimniecības lietu izejmateriālos (Joudisius ir Simoneliene, 2009).

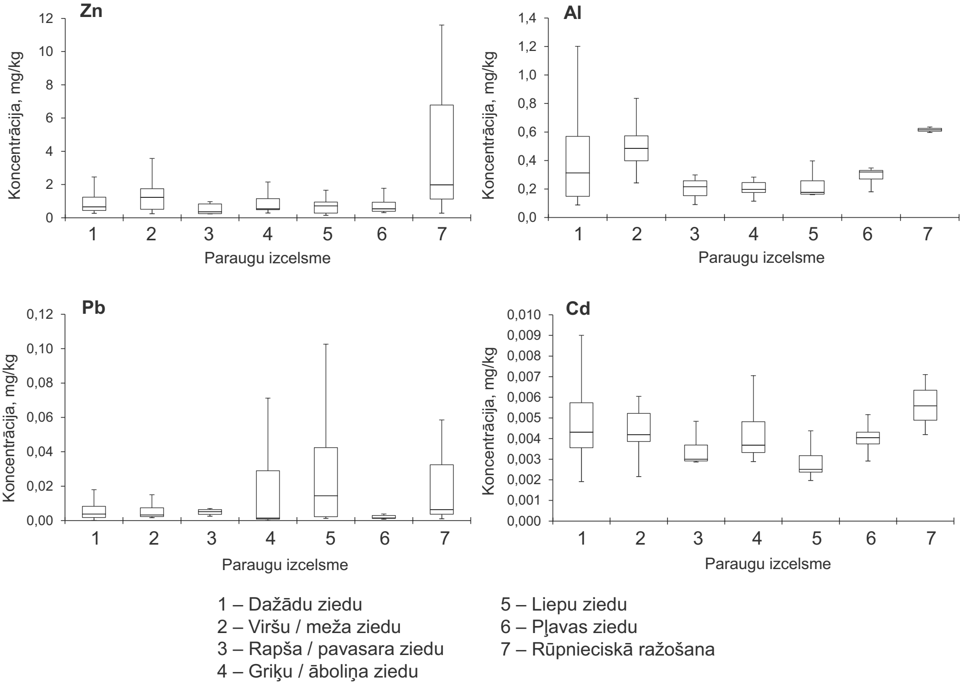
Atkarībā no botāniskās izcelsmes, ņemot vērā vidējās vērtības, kopumā medus paraugos potenciāli toksiskie elementi tika konstatēti šādā secībā (no augstākās koncentrācijas uz zemāko): rūpnieciski ražotie medus maisījumi >viršu un meža ziedu medus >dažādu



3.2. attēls. **Sezonālā ietekme uz Fe, Zn, Cu, Ba, Mn un Se koncentrāciju vistu olu paraugos**

ziedu medus >pļavas ziedu medus >liepu ziedu medus >griķu un āboliņa ziedu medus >rapšu un pavasara ziedu medus. Zn, Al, Pb un Cd koncentrācija analizētajos medus paraugos pēc botāniskās izcelsmes apkopota 3.3. attēlā.

Elementu satura botāniskās ietekmes īpatnības var saistīt arī ar vides faktoru ietekmēm. Piemēram, tādi elementi kā As un Pb augstākā koncentrācijā konstatēti liepu ziedu medū, kas liecina par iespējamu vides piesārņojuma ietekmi, jo liepas parasti aug apdzīvotās teritorijās, autoceļu tiešā tuvumā, kas var kalpot kā piesārņojuma avots. Savukārt lauksaimniecības veids, agroķīmijas un mēslošanas līdzekļu lietošana var ietekmēt rapšu vai griķu ziedu medus sastāvu. Bet augstāko konstatēto elementu koncentrāciju rūpnieciski ražotā medū visdrīzāk var saistīt ar nepiemērota aprīkojuma, piemēram, metālu sakausējumus saturošu materiālu pielietošanu ražošanas procesā.



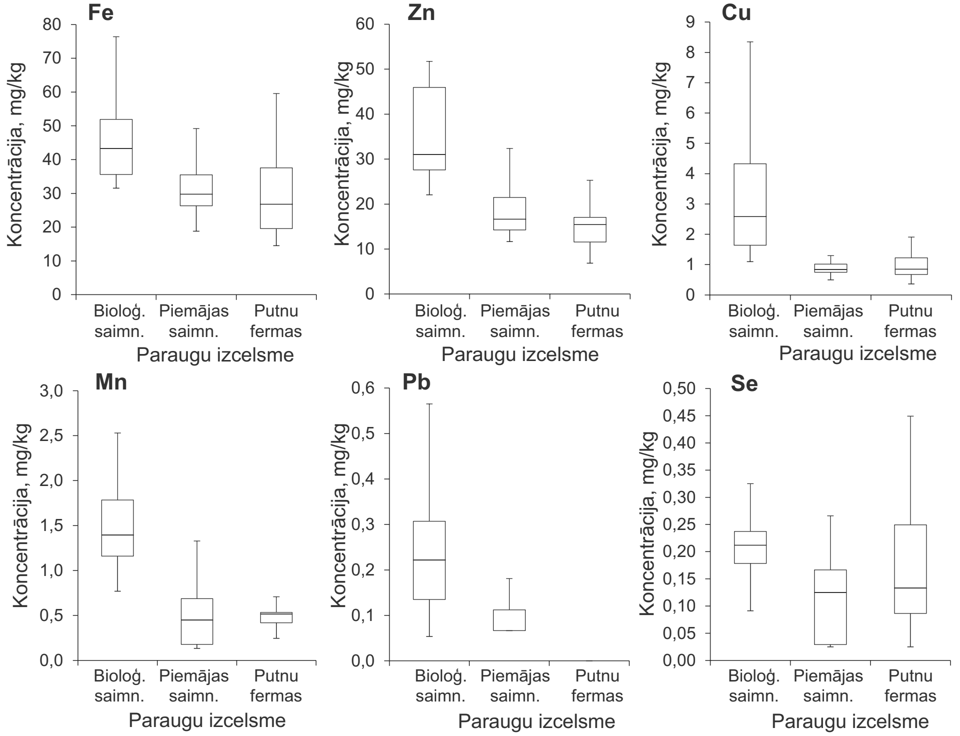
3.3. attēls. **Zn, Al, Pb un Cd koncentrācija medus paraugos ar dažādu botānisko izcelsmi**

3.1.3. Lauksaimniecības prakses ietekme uz elementu koncentrāciju pārtikā

Lauksaimniecības prakses, kā arī pārtikas ražošanas ietekme uz elementu koncentrāciju tika novērtēta tādiem produktiem kā sakņu dārzeņi, biezpiens un vistu olas.

Sakņu dārzeņi. Zinot ievākto sakņu dārzeņu paraugu izcelsmi un to ieguvē pielietoto lauksaimniecības praksi, bija iespējams salīdzināt elementu koncentrāciju starp sīpolu un burkānu paraugiem, kas audzēti intensīvas lauksaimniecības ietekmē un piemājas saimniecībās. Koncentrāciju atšķirību statistiskā nozīmība tika novērtēta izmantojot Fišera kritēriju un atbilstošu t-testu. Piemēram, sīpolu paraugu analīze atklāja būtiskas atšķirības starp minētajām apakšgrupām vairākiem elementiem (Sr, Ni, Cd, Se un Co), kuru koncentrācija bija būtiski augstāka sīpolu paraugos, kas auguši intensīvās lauksaimniecības ietekmē, tikmēr Rb koncentrācija bija daudz augstāka paraugos no piemājas saimniecībām. Savukārt burkāni, kas auguši piemājas saimniecībās, saturēja vairāk Zn, Mn un Rb nekā burkānu paraugi, kas iegūti intensīvā lauksaimniecībā. Konstatētās sakarības pamato lauksaimniecības prakses ietekmi uz elementu saturu pārtikas kultūraugos, liecinot, ka intensīvā lauksaimniecība var ietekmēt potenciāli toksisku elementu ienesi augos, bet piemājas saimniecībās audzētos augos uz elementu saturu, visticamāk, nozīmīgāka būs ģeoķīmiskā fona ietekme. Piemājas saimniecībās mazāka ietekme ir no pesticīdu vai mākslīgā mēslojuma izmantošanas, tomēr bieži vien mazdārziņi ģimenes vajadzībām tiek ierīkoti apdzīvotās vietās, intensīvas satiksmes piesārņojuma joslās, kā arī tuvu rūpniecības teritorijām vai rekultivētās teritorijās, kas var būt piesārņotas. Dotā pētījuma ietvaros paraugos no piemājas saimniecībām netika konstatēts paaugstināts piesārņojums ar potenciāli toksiskiem elementiem, ko var saistīt ar paraugu ievākšanu pārsvarā lauku teritorijās, kur piesārņojuma ietekme ir mazāk būtiska.

Vistu olas. Analizējot vistu olu paraugus no dažāda veida ražotājiem (bioloģiskām saimniecībām, piemājas saimniecībām un vistu fermām), tika konstatētas būtiskas atšķirības. Piemēram, paraugos no bioloģiskām saimniecībām tika konstatēta augstākā Cu, Fe, Mn, Pb un Zn koncentrācija (3.4. attēls). Savukārt Pb netika konstatēts nevienā no paraugiem, kas ievākti no putnu fermām.



3.4. attēls. **Fe, Zn, Cu, Mn, Pb un Se koncentrācija vistu olu paraugos atkarībā no izcelsmes**

Praktiski visiem elementiem augstākās vidējās koncentrāciju vērtības tika konstatētas olu paraugos, kas iegūti bioloģiskās saimniecībās, bet elementu koncentrācija piemājas saimniecību olās un vistu fermu olas bija zemāka un samērā līdzīga. Tā kā bioloģisko saimniecību darbība tiek stingri reglamentēta (EK Regula 889, 2008), tad būtībā var izslēgt iegūto datu interpretāciju saistībā ar piesārņojumu, kas varētu rasties no agroķīmijas, mākslīgā mēslojuma vai veterināro medikamentu izmantošanas mājputnu audzēšanā. Līdz ar to augstās elementu koncentrācijas saistāmas ar neatkarīgu vides faktoru ietekmi, ka vides piesārņojuma pārnese, uz ko norāda tādu elementu (piemēram, Cu, Pb, Zn) paaugstinātā koncentrācija, kas ir labi zināmi kā vidi piesārņojošie elementi.

3.2. Elementu biopieejamības novērtējums

3.2.1. Augsnes paraugu raksturojums

Lai veiktu elementu biopieejamības izpēti, tika veikta eksperimentāla pārtikas kultūraugu audzēšana, kam tika izmantoti 5 dažāda tipa un granulometriskā sastāva augsnes paraugi: S1 – zemā purva kūdraugsne; S2 – velēnu podzolaugsne / smilšmāls; S3 – velēnu podzolaugsne / smilts; S4 – velēnu podzolaugsne / mālsmilts; S5 – velēnu podzolaugsne / smilšains smilšmāls (FAO, 2006; Kārkliņš et al., 2009; Nikodemus, 2011; Noteikumi 804, 2005).

Augstākā pH vērtība tika konstatēta augsnei S1 (pH_{H2O} 5,31 / pH_{KCl} 5,06), bet zemākā augsnei S5 (pH_{H2O} 4,61 / pH_{KCl} 5,11). Organisko vielu saturs mainījās no 2,9 % līdz 4,2 % minerālaugsnēm (S2-S5), bet zemā purva kūdraugsnei (S1) – 29,3 %. Katjonu bāzu summa (CBS) lielā mērā ir atkarīga no organisko vielu satura augsnē un augsnes pH. CBS minerālaugsnēm (S2-S5) konstatēts 3,13-8,17 cmol/kg, bet 142,29 cmol/kg – zemā purva kūdraugsnei (S1). Ca^{2+} jonu saturs tika konstatēts 70,9 % no CBS velēnu podzolaugsnei / smilšains smilšmāls (S5), bet zemā purva kūdraugsnei (S1) 87,5 % no CBS, kas liecina, ka izvēlētie augsnes paraugi ir ar augstu auglības pakāpi un ir piemērojami kultūraugu audzēšanai (Hodges, s.a.).

Kopējais elementu saturs augšņu paraugos tika novērtēts pirms mākslīgas piesārņošanas (3.1. tabula).

Velēnu podzolaugsne / smilšains smilšmāls (S5) saturēja ievērojami augstāku Cr, Ni un Pb koncentrāciju nekā pārējās augsnes, kas varētu būt saistīts ar elementu adsorbciju uz māla daļiņām, jo šis augsnes paraugs vērtēts kā māliem bagāts. Nozīmīga pozitīva korelācija ($r>0,8$) tika konstatēta šādu elementu pāriem: Zn ar Ca, Co, Cr, Fe, K, Ni, Mg; K ar Cu, Pb; Ca ar Co, Mn.

Pēc augsnes piesārņošanas gan ar $CuSO_4 \times 5H_2O$ šķīdumu dažādās Cu mērķkoncentrācijās (40, 70, 100, 130 un 200 mg/kg), gan izmantojot Cd, Cu, Pb un Zn sāļu maisījumu, tika konstatēta elementu hiperakumulācija, it īpaši zemā purva kūdraugsnē (S1) (3.2. tabula).

3.1. tabula

Elementu koncentrācija augsnes paraugos pirms piesārņošanas procedūras

Elements	Augsnes paraugs				
	S1	S2	S3	S4	S5
	Elementa koncentrācija ($\bar{x}\pm s$; $n_m=3$), 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
	Elementa koncentrācija ($\bar{x}\pm s$; $n_m=3$), 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

3.2. tabula

Elementu koncentrācija augsnes paraugos pēc piesārņošanas ar Cd, Cu, Pb un Zn sāļu maisījumu

Elements	Elementa mērķkoncentrācija, mg/kg	Faktiskā elementa koncentrācija augsnē ($\bar{x}\pm s$; $n_m=3$), 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

Iegūtie dati liecina par ciešu saikni starp augsnes piesārņojuma līmeni un organisko vielu saturu augsnē, kā arī augsnes granulometriskā sastāva nozīmību.

3.2.2. Elementu akumulācija eksperimentāli audzētajos pārtikas kultūraugos

Kontaminētajos augsnes paraugos tika audzēti tādi pārtikas kultūraugi kā lapu salāti *Lactuca sativa*, dilles *Anethum graveolens* un redīsi *Raphanus sativus*. Lai noteiktu elementu ienesi no augsnes un akumulācijas intensitāti, tika aprēķināts pārneses koeficients (TF – *transfer factor*). Augstākās TF vērtības (>10) tika iegūtas attiecībā uz Zn pārnesi salātu paraugos minerālaugsnēs (S2-S4), bet zemākās TF vērtības attiecināmas uz paraugiem, kas iegūti augsnēs ar augstāku organisko vielu saturu, piemēram, zemā purva kūdraugsnē (S1). Tāpat arī humusvielu pievienošana augsnēm samazina elementu pārneses intensitāti un akumulāciju augos (3.3. tabula).

3.3. tabula

Pārneses koeficients (TF) salātu un redīsu paraugiem audzētiem ar Cd, Cu, Pb un Zn sāļu maisījumu piesārņotās augsnēs

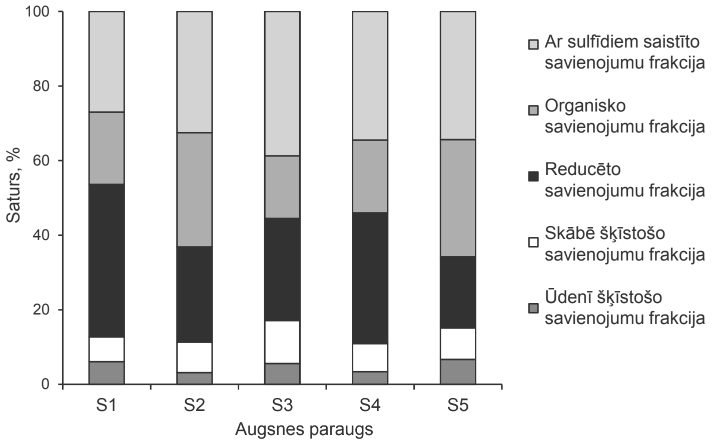
Elements	Paraugs	TF, attiecīgi bez (S) vai ar (S_H) humusvielu šķīduma pievienošanas augsnei									
		S1	S2	S3	S4	S5	$S1_H$	$S2_H$	$S3_H$	$S4_H$	$S5_H$
Cd	Salāti	0,11	1,84	1,52	1,06	0,63	0,09	0,41	0,53	0,35	0,50
	Redīsi	-	-	-	-	-	0,06	0,43	0,31	0,18	0,35
Cu	Salāti	0,02	0,49	1,55	0,82	0,04	0,02	0,11	0,07	0,07	0,08
	Redīsi	-	-	-	-	-	0,02	0,18	0,33	0,16	0,06
Pb	Salāti	0,005	0,28	0,64	0,59	0,03	0,003	0,09	0,07	0,02	0,04
	Redīsi	-	-	-	-	-	0,005	0,09	0,16	0,04	0,09
Zn	Salāti	0,48	10,47	11,95	11,43	1,51	0,38	1,29	1,90	1,67	1,21
	Redīsi	-	-	-	-	-	0,28	3,48	3,31	2,21	2,12

Starp pētāmajiem elementiem zemāki TF tika aprēķināti svinam. Kopumā augstākas TF vērtības konstatētas pārnesē uz augu saknēm nekā uz lakstiem. Dati liecināja, ka multielementu piesārņojums augsnē paaugstina elementu akumulācijas intensitāti augos, piemēram, mijiedarbībā ar citiem metāliskiem elementiem augstā koncentrācijā (Cd, Pb, Zn) augsnē Cu akumulācija salātos var pieaugt par 31 %, nekā ja augsnes kontaminētas ar vienu piesārņojošo elementu. Savukārt augsnēm pievienojot humusvielu šķīdumu, elementu akumulāciju var samazināt pat par 90 % lapu dārzeņos (salātos), un par apmēram 25 % sakņu dārzeņos (redīsos).

3.2.3. Elementu biopieejamība barības ķēdes segmentā augsne-augs

Elementu biopieejamības novērtējums tika veikts izmantojot frakcionēšanas analīzes rezultātus. Kopumā tika konstatēts, ka elementu koncentrācijas atšķirības starp frakcijām būtiskākas ir salīdzinot zemā purva kūdraugsni (S1) un minerālaugsnes (S2-S5). Lielākās daļas elementu saistība reducētu savienojumu frakcijā attiecināma uz augsnēm S1 un S4, respektīvi, 41 % un 35 %, kas satur salīdzinoši vairāk organisko vielu nekā pārējās augsnes (3.5. attēls).

Lielākā elementu daļa, kas saistīta ar sulfīdu savienojumiem konstatēta augsnei S3 (39 %). Vismazāk elementi saistīti ūdenī šķīstošo savienojumu frakcijā (3-7 %), kam seko skābē šķīstošo elementu frakcija (7-12 %). Tas liecina, ka tikai neliels daudzums no kopējā satura elementu augsnē ir biopieejams augiem, bet lielākā daļa elementu ir saistīti frakcijās ar zemu biopieejamības pakāpi. Kvantificējot 13 elementus (As, Cd, Ce, Co, Cs, Cu, La, Ni, Pb, Rb, Sr, V un Zn) katrā no frakcijām, tikai veikts salīdzinājums par individuālu elementu biopieejamību atkarībā no augsnes tipa un granulometriskā sastāva.



3.5. attēls. **Kopējais elementu sadalījums pa frakcijām analizētajos augsnes paraugos** (S1 – zemā purva kūdraugsne; S2 – velēnu podzolaugsne / smilšmāls; S3 – velēnu podzolaugsne / smilts; S4 – velēnu podzolaugsne / mālsmilts; S5 – velēnu podzolaugsne / smilšains smilšmāls)

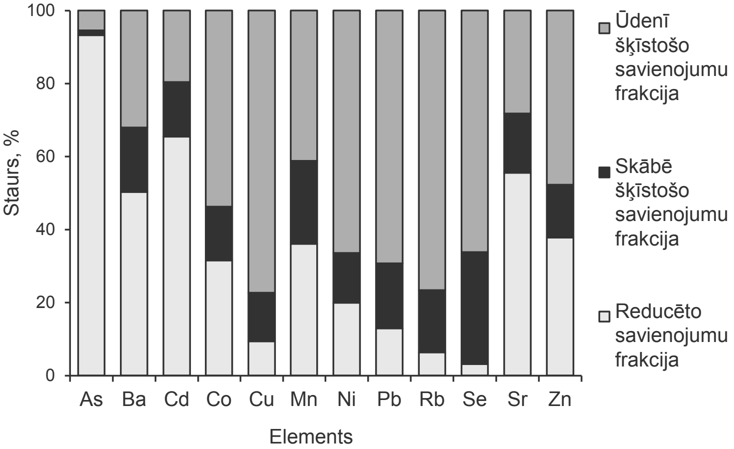
3.2.4. *Elementu biopieejamības aspekti barības ķēdes segmentā* **augs-cilvēks** – *pētījums ar lapu salātiem*

Elementu biopieejamības barības ķēdes segmentā *augs-cilvēks* ir komplicēts izpētes jautājums, ko var ietekmēt gan vides faktori, savienojumu ķīmiskās īpašības un bioķīmisko procesu reakcijas, gan indivīda organisma īpatnības. Tomēr provizorisku elementu biopieejamības vērtējumu var veikt, pielietojot frakcionēšanas analīzes principus un zinot, ka lielā mērā elementu biopieejamība ir atkarīga no ķīmisko savienojumu šķīdības.

Frakcionēšanas analīze tika veikta analizējot lapu salātu paraugu ekstraktus 3 frakcijās: 1) ūdenī šķīstošo savienojumu frakcija; 2) skābē šķīstošo savienojumu frakcija; 3) reducēto savienojumu frakcija. Katrā frakcijā tika kvantificēti 12 elementi (As, Ba, Cd, Co, Cu, Mn, Ni, Pb, Rb, Se, Sr un Zn). Kopumā elementu sadalījums pa frakcijām liecināja, ka lielākā mērā elementi saistīti ūdenī šķīstošo savienojumu frakcijā (47 %) un reducēto savienojumu frakcijā (37 %), bet skābē šķīstošo savienojumu frakcijā tikai 15 %, kas ir krasi atšķirīgi nekā konstatētais elementu sadalījums pa frakcijām augsnēs. Vērtējot individuālu elementu saistību frakcijās, var secināt, ka vismazāk biopieejamie elementi ir As, Cd un Sr, jo to saistība ūdenī šķīstošo savienojumu frakcijā konstatēta vismazākā (3.6. attēls).

Ūdenī šķīstošo savienojumu frakcijā vairāk saistīti (>50 %) tādi elementi kā Co, Cu, Ni, Pb, Rb un Se, kas var radīt iespējamu risku attiecībā un potenciāli toksiskiem elementiem.

Ņemot vērā konstatētās īpatnības elementu pārnesē, var secināt, ka elementu ienese cilvēka uzturā no augsnes salīdzinoši ir neliela, tomēr jāņem vērā, ka pieaugot elementu



3.6. attēls. **Elementu sadalījums pa frakcijām lapu salātos**

koncentrācijai augsnē, kur audzēti kultūraugi, arī augos elementu koncentrācija var pieaugt, un tas var radīt iespējamu risku patērētājam. Veiktie elementu biopieejamības analīžu dati un aprēķini ļauj vienkāršoti izvērtēt provizorisko elementu biopieejamības apjomu zinot kopējo elementu koncentrāciju matricā, kas ļauj veikt ātru riska būtiskuma novērtējumu.

SECINĀJUMI

- Iegūtie rezultāti atklāja vairāku apstākļu (sezonalitātes, vietas specifisko, botāniskās izcelsmes, lauksaimniecības prakses, pārstrādes procesu) ietekmi uz elementu koncentrāciju analizētajos pārtikas paraugos, tomēr elementu pārneses no vides pārtikā specifika nav vienota un ir atkarīga no individuālām katram pārtikas produktam vai līdzīgu pārtikas produktu grupai raksturīgam iezīmēm mijiedarbībā ar apkārtējās vides apstākļiem pārtikas ieguves un ražošanas procesā.
- Dabisko vides ietekmes apstākļu, tādu kā sezonalitāte, novērtējums atklāja elementu koncentrācijas atšķirības dzīvnieku izcelsmes pārtikas produktos ciešā saistībā ar pielietoto lauksaimniecības praksi. Sezonālo ietekmi uz elementu koncentrāciju pārtikā netieši var saistīt arī ar vides piesārņojuma ietekmi.
- Antropogēna rakstura ietekmes apstākļu, tādu kā lauksaimniecības veida ietekmes izpēte atklāja atšķirības starp elementu (piemēram, Cd, Co, Na, Ni, Se) sastāvu kultūraugos audzētos atšķirīgos apstākļos, ko var saistīt ar agroķīmijas un mēslojuma pielietošanas intensitāti. Liela nozīme elementu satura īpatnību noteikšanā ir auga sugai.
- Konstatētās atšķirības starp elementu koncentrāciju dzīvnieku izcelsmes pārtikas produktos, kas iegūti no bioloģiskās un intensīvās lauksaimniecības, liecina par elementu satura vidē ietekmēm, kas var būt gan dabīgas izcelsmes, kā ģeoķīmiskais fons, gan antropogēnas izcelsmes, kā vides piesārņojums. Bioloģiskās saimniecībās būtu jāpievērš lielāka nozīme vides faktoru iespējamo ietekmju uz pārtikas sastāvu identificēšanai un izpētei.
- Salīdzinot elementu koncentrāciju starp kultūraugu pārtikā lietojamām daļām un mizu, konstatēts, ka vairākiem mikroelementiem (piemēram, As, Co, Cr, Fe, Pb) ir tendence uzkrāties mizā, kamēr citi elementi (piemēram, Cd, Se, Zn) tiek viegli asimilēti augā un tādējādi vieglāk var kļūt par potenciāliem pārtikas piesārņotājiem.
- Vietas specifisko apstākļu ietekmi uz elementu koncentrāciju pārtikā nevar vērtēt viennozīmīgi, piemēram, medus paraugu analīze atklāja nelielas elementu koncentrāciju atšķirības, tomēr netika konstatēta nozīmīga korelācija ar reģionāliem apkārtējo vidi raksturojošiem faktoriem.
- Dati par elementu pārneses intensitāti barības ķēdē *augsne-augs* apstiprināja augsnes īpašību, piemēram, organisko vielu satura un augsnes granulometriskā sastāva nozīmību elementu pārnesē un akumulācijā augos. Organisko vielu spēju saistīt smagos metālus nešķīstošos kompleksos savienojumos ir iespējams attīstīt kā perspektīvu praktiskai izmantošanai, pielietojot humusvielu piedevas elementu pārneses samazināšanai piesārņotās augsnēs, piemēram, lauksaimniecības zemēs.
- Elementu biopieejamības izpēte atklāja, ka tikai neliela daļa no elementa kopējā satura augsnē, atkarībā no elementa specifikas, ir pieejama augšup pa barības ķēdi *augsne-augs-cilvēks*. Tomēr pārtikas piesārņojuma risks var kumulatīvi palielināties, ja elementu koncentrācija vidē ir augsta. Noteiktā elementu biopieejamības atkarība no augsnes īpašībām var tikt izmantota riska analīzē.

- Gan dabīgie, gan antropogēnie vides apstākļi var radīt pārtikas piesārņojuma risku ar potenciāli toksiskiem elementiem, kas ir svarīgs jautājums attiecībā uz patērētāju drošību, tāpēc būtu nepieciešams reģionāls pārtikas monitorings noteiktu ietekmes faktoru aspektā, it īpaši attiecībā uz mājražotāju produktiem. Kopumā var secināt, ka pārtikas paraugu kvantitatīva analīze ir nozīmīgs pētījumu virziens gan vides, gan ķīmijas un veselības zinātņu nozarēs, kas jāattīsta plašākā mērogā.

IZMANTOTĀ LITERATŪRA

1. Aberoumand, A., Deokule, S.S. (2010) Elements evaluation of some edible vegetables and fruits of Iran and India. *Asian Journal of Agricultural Sciences* 2(1): 35-37.
2. Abrahams, P.W. (2002) Soils: Their implications to human health. *The Science of the Total Environment* 291(1-3): 1-32.
3. Aldahan, A., Kekli, A., Possnert, G. (2006) Distribution and sources of ^{129}I in rivers of the Baltic region. *Journal of Environmental Radioactivity* 88(1): 49-73.
4. Allen, A.G., Nemitz, E., Shi, J.P., Harrison, R.M., Greenwood, J.C. (2001) Size distributions of trace metals in atmospheric aerosols in the United Kingdom. *Atmospheric Environment* 35: 4581-4591.
5. Alexander, P.D., Alloway, B.J., Dourado, A.M. (2006) Genotypic variations in the accumulation of Cd, Cu, Pb and Zn exhibited by six commonly grown vegetables. *Environmental Pollution* 144(3): 736-745.
6. Aras, N.K., Ataman, O.Y. (2006) *Trace Element Analysis of Food and Diet*. RSC Publishing: Cambridge, 344 p.
7. Arthur, J.D., Fischler, C., Dabous, A.A., Budd, D.A., Katz, B.G. (2007) Geochemical and mineralogical characterization of potential aquifer storage and recovery storage zones in the Floridan Aquifer System, comprehensive Everglades restoration plan. *Final report.* No page numbering.
8. ATSDR (s.a.) *Toxic substances portal*. Agency for Toxic Substances and Disease Registry (ATSDR), United States Department of Health and Human Services**.** Pieejams: *http://www.atsdr.cdc.gov/toxprofiles/index.asp* [16.09.2013.]
9. Berdanier, C.D., Dwyer, J.T., Feldman, E.B. (2007) *Handbook of Nutrition and Food.* (2nd ed.) CRC Press: Boca Raton, 1288 p.
10. Bowman, C.A., Bobrowsky, P.T., Selinus, O. (2003) Medical geology: New relevance in the Earth sciences. *Episodes* 24(6): 270-278.
11. Brumelis, G., Lapina, L., Nikodemus, O., Tabors, G. (2002) Use of the O horizon of forest soils in monitoring metal deposition in Latvia. *Water, Air & Soil Pollution* 135(1-4): 291-309.
12. Čekstere, G. (2011) *Vides faktoru ietekme uz Holandes liepu (Tilia x vulgaris) vitalitāti Rīgas ielu apstādījumos / Impact of Environmental Factors on Vitality of Common Lime (Tilia x vulgaris) in the Street Greenery of Riga*. Doctoral thesis. [In Latvian] LU Akadēmiskais apgāds: Rīga, 225 lpp.
13. Cekstere, G., Nikodemus, O., Osvalde, A. (2008) Toxic impact of the de-icing material to street greenery in Riga, Latvia. *Urban Forestry & Urban Greening* 7(3):207-217.
14. Cekstere, G., Osvalde, A. (2013) A study of chemical characteristics of soil in relation to street trees status in Riga (Latvia). *Urban Forestry & Urban Greening* 12(1): 69-78.
15. Cekstere, G., Osvalde, A. (2010a) Macronutrient status in the different-aged lime trees (*Tilia x vulgaris* H.) in Riga streets. *Baltic Forestry* 16(1): 16-22.
16. Cekstere, G., Osvalde, A. (2010b) Young street greenery supply with nutrients in Riga, Latvia. *Acta Horticulturae* 881: 573-576.
17. Combs, G.F. (2005) Geological impacts of nutrition. In: Selinus, O. (ed.-in-chief) *Essentials of Medical Geology*. Elsevier Academic Press: Amsterdam, 812 p., 161-177.
18. Ekholm, P., Reinivuo, H., Mattila, P., Pakkala, H., Koponen, J., Happonen, A., Hellistrom, J., Ovaskainen, M.-L. (2007) Changes in the mineral and trace element contents of cereals, fruits and vegetables in Finland. *Journal of Food Composition & Analysis* 20(6): 487-495.
19. EK Regula 889 (2008) Commission Regulation (EC) No 889/2008 of 5 September 2008 laying down detailed rules for the implementation of Council Regulation (EC) No 834/2007 on

organic production and labelling of organic products with regard to organic production, labelling and control. *Official Journal of the European Union* L250: 1-84.

20. FAO (2006) *Guidelines for soil description*. (4th ed.) Food and Agriculture Organisation (FAO): Rome, 97 p.
21. Ferre-Huguet, N., Marti-Cid, R., Schuhmacher, M., Domingo, J.L. (2008) Risk assessment of metals from consuming vegetables, fruits and rice grown in soils irrigated with waters of the Ebro River in Catalonia, Spain. *Biological Trace Element Research* 123(1-3): 66-79.
22. Fraga, C.G. (2005) Relevance, essentiality and toxicity of trace elements in human health. *Molecular Aspects of Medicine* 26(4-5): 235-244.
23. Gardea-Torresdey, J.L., Peralta-Videa, J.R., de la Rosa, G., Parsons, J.G. (2005) Phytoremediation of heavy metals and study of the metal coordination by X-ray absorption spectroscopy. *Coordination Chemistry Reviews* 249(17-18): 1797-1810.
24. Goldhaber, S.B. (2003) Trace element risk assessment: Essentiality vs. toxicity. *Regulatory Toxicology & Pharmacology* 38(2): 232-242.
25. Hashmi, D.R., Ismail, S., Shaikh, G.H. (2007) Assessment of the level of trace metals in commonly edible vegetables locally available in the markets of Karachi city. *Pakistan Journal of Botany* 39(3): 747-751.
26. Hodges, S.C. (s.a.) *Soil fertility basics*. Raleigh: North Carolina State University (NCSU), 75 p.
27. Inaba, S., Takenaka, C. (2005) Effects of dissolved organic matter on toxicity and bioavailability of copper for lettuce sprouts. *Environment International* 31(4): 603-608.
28. Joudisius, E., Simoneliene, A. (2009) Lietuvoje parduodamo medaus užterštumas sunkiaisiais metalais ir pesticidais / Trace metals and pesticide residues in honey on the Lithuanian market. [In Lithuanian] *Veterinarija & Zootechnika* 45(67): 27-32.
29. Juškevičs, V. (2000) *Kvartāra nogulumu karte / Map of Quaternary Sediments (1:200 000)*. Jāņa sēta: Rīga.
30. Kabata-Pendias, A., Mukherjee, A.B. (2007) *Trace Elements from Soil to Human*. Springer-Verlag: Berlin, 550 p.
31. Kārkliņš, A., Gemste, I., Mežals, H., Nikodemus, O., Skujāns, R. (2009) *Latvijas augšņu noteicējs / Soil Key-Book of Latvia*. [In Latvian] LLU: Jelgava, 235 lpp.
32. Kasparinskis, R., (2011) *Personīgā informācija.*
33. Kasparinskis, R., Nikodemus, O. (2012) Influence of environmental factors on the spatial distribution and diversity of forest soil in Latvia. *Estonian Journal of Earth Sciences* 61(1): 48-64.
34. Klavins, M., Briede, A., Rodinov, V., Kokorite, I., Parele, E., Klavina, I. (2000) Heavy metals in rivers of Latvia. *Science of the Total Environment* 262(1-2): 175-184.
35. Klavins, M., Kokorite, I., Jankevica, M., Mazeika, J., Rodinov, V. (2011) Trace elements in sediments of lakes in Latvia. In: Mastorakis, N. (ed.-in-chief) *Recent Researches in Geography, Geology, Energy, Environment and Biomedicine.* WSEAS Press: Corfu, 518 p., 43-47.
36. Klavins, M., Potapovics, O., Rodinov, V. (2009a) Heavy metals in fish from lakes in Latvia: Concentrations and trends of changes. *Bulletin of Environmental Contamination & Toxicology* 82(1): 96-100.
37. Klavins, M., Rodinov, V., Druvietis, I. (2003) Aquatic chemistry and humic substances in bog lakes in Latvia. *Boreal Environment Research* 8(2): 113-123.
38. Klavins, M., Rodinov, V., Kokorite, I., Klavina, I., Apsite, E. (2001) Long-term and seasonal changes in chemical composition of surface waters in Latvia. *Environmental Monitoring & Assessment* 66(3): 233-254.
39. Klavins, M., Silamikele, I., Nikodemus, O., Kalnina, L., Kuske, E., Rodinov, V., Purmalis, O. (2009b) Peat properties, major and trace element accumulation in bog peat in Latvia. *Baltica* 22(1): 37-50.

40. Klavins, M., Vircavs, M. (2001) Metals in sediments of inland waters of Latvia. *Boreal Environment Research* 6(4): 297-306.
41. Klockenkamper, R. (1997) *Total-Reflection X-Ray Fluorescence Analysis*. John Wiley & Sons: New York, 245 p.
42. Kokorite, I., Klavins, M., Rodinov, V. (2010) Impact of catchment properties on aquatic chemistry in the rivers of Latvia. *Hydrology Research* 41(3-4): 320-329.
43. Malandrino, M., Aballino, O., Buoso, S., Giacomino, A., La Gioia, C., Mentasti, E. (2011) Accumulation of heavy metals from contaminated soil to plants and evaluation of soil remediation by vermiculite. *Chemosphere* 82: 169-178.
44. Murniece, I., Karklina, D., Galoburda, R., Santare, D., Skrabule, I., Costa, H. S. (2011) Nutritional composition of freshly harvested and stored Latvian potato (*Solanum tuberosum* L.) varieties depending on traditional cooking methods. *Journal of Food Composition & Analysis*, 24(4-5): 699-710.
45. Nabrzyski, M. (2007) Functional role of some minerals in foods. In: Szefer, P., Nriagu, J.O. (eds.) *Mineral Components in Food*. CRC Press: Boca Raton, 446 p., 123-162.
46. Nikodemus, O. (2011) *Personīgā informācija.*
47. Nikodemus, O. (2004) *Latvijas augšņu karte / Map of Soils in Latvia* (1:2 250 000). Jāņa sēta: Rīga.
48. Nikodemus, O. (red.) (2008) *Augsnes ilgtspējīga izmantošana un aizsardzība / Soil Protection and Sustainable Use.* [In Latvian] LU Akadēmiskais apgāds: Rīga, 256 lpp.
49. Nikodemus, O., Brumelis, G., Tabors, G., Lapina, L., Pope S. (2004) Monitoring of air pollution in Latvia between 1990 and 2000 using moss. *Journal of Atmospheric Chemistry* 49: 521-531.
50. Noteikumi 804 (2005) Ministru Kabineta noteikumi Nr. 804 (25.10.2005.) Par augsnes un grunts kvalitātes normatīviem. *Latvijas Vēstnesis*, 172(3330).
51. Osvalde, A., Karlsons, A. (2010) Evaluation of the nutrient status of American cranberry in Latvia during 2001-2007. *Acta Horticulturae* 868: 213-218.
52. Pansu, M., Gautheyrou, J. (2006) *Handbook of Soil Analysis: Mineralogical, Organic and Inorganic Methods*. Springer Verlag: Berlin, 993 p.
53. Peralta-Videa, J.R., Lopez, M.L., Narayan, M., Saupe, G., Gardea-Torresdey, J. (2009) The biochemistry of environmental heavy metal uptake by plants: Implications for the food chain. *The International Journal of Biochemistry & Cell Biology* 41(8-9): 1665-1677.
54. Poikane, R., Carstensen, J., Dahllof, I., Aigars, J. (2005) Distribution patterns of particulate trace metals in the water column and nepheloid layer of the Gulf of Riga. *Chemosphere* 60(2): 216-225.
55. Salminen, R., Chekushin, V., Gilucis, A., Gregorauskiene, V., Petersell, V., Tomilina, O. (2011) Distribution of elements in Terrestrial Mosses and the Organic Soil Layer in the Eastern Baltic Region. *Special Paper of the Geological Survey of Finland* 50: 1-116.
56. Silamikele, I., Klavins, M., Nikodemus, O. (2011) Major and trace element distribution in the peat from ombrotrophic bogs in Latvia. *Journal of Environmental Science & Health – Part A Toxic/Hazardous Substances & Environmental Engineering* 46(7): 805-812.
57. Stalnacke, P., Grimvall, A., Libiseller, C., Laznik, M., Kokorite, I. (2003) Trends in nutrient concentrations in Latvian rivers and the response to the dramatic change in agriculture. *Journal of Hydrology* 283(1-4): 184-205.
58. Tabors, G., Brumelis, G., Lapina, L., Pospelova, G., Nikodemus, O. (2004) Changes in element concentrations in moss segments after cross-transplanting between a polluted and non-polluted site. *Journal of Atmospheric Chemistry* 49: 191-197.
59. Tessier, A., Campbell, P.G.C., Bisson, M. (1979) Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry* 51(7): 1-8.

60. USDA (s.a.) *National nutrient database for standard reference*. Agricultural Research Service, United States Department of Agriculture (USDA). Pieejams: *http://ndb.nal.usda.gov/ndb/nutrients/index* [16.09.2013.]
61. Welch, R.M., Graham, R.D. (2005) Agriculture: The real nexus for enhancing bioavailable micronutrients in food crops. *Journal of Trace Elements in Medicine & Biology* 18: 299-307.
62. Zariņš, Z., Neimane, L. (2009) *Uztura mācība / Nutrition Studies*. (5th ed.) [In Latvian] LU Akadēmiskais apgāds: Rīga, 464 lpp.
63. Zegnere, L., Alsina, I. (2008) The effect of selenite on growth and storage of onions. *Latvian Journal of Agronomy* 10: 235-240.
64. Zimmermann, M.B. (2001) *Burgerstein's Handbook of Nutrition: Micronutrients in the Prevention and Therapy of Disease*. Georg Thieme Verlag: Stuttgart, 288 p.

Latvijas Universitātes Akadēmiskais apgāds
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