

Trace and Major Elements in Food Articles in Latvia: Root Vegetables

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Abstract – It is known that the content of trace and major elements in plants is dependent on several factors, such as type of species, soil properties, climate conditions, agricultural and agrichemical factors, pollution. The aim of the study was to quantify element content of root vegetables grown in farmlands and allotment gardens in Latvia. Samples of onion bulbs and carrot roots were analyzed by atomic absorption spectrometry and inductively coupled plasma mass spectrometry. Quantitative amounts of 17 trace elements (Ag, As, Ba, Cd, Ce, Co, Cr, Cu, La, Mn, Ni, Pb, Rb, Se, Sr, V, Zn) and 5 major elements (Ca, Fe, K, Mg, Na) were determined. It was detected that carrot roots contained higher amounts of several elements than onion bulbs. Differences in element content of vegetables were also detected between the subgroups of samples grown in farmlands versus samples grown in allotment gardens. Data revealed that onions grown in farmlands were more affected by contaminants.

Keywords – Environmental impacts, food analysis, major and trace elements, root vegetables, spectrometry

I. INTRODUCTION

Analysis of the chemical composition of food is a complicated process which, as a research method, is used mainly within the scope of food chemistry. It is known that the content of trace and major elements in plants is affected by various factors, such as a type of plant species, soil properties, weather conditions, a way of agricultural practice, use of fertilizers and pesticides, as well as a plant development stage [1]. Therefore, investigation of food plants – chemical composition of plants versus their growing conditions – may be an issue of interest within the context of other sciences, particularly with regard to environmental science. 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 lead, cadmium, copper, 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 [2-4].

From about fifty elements that can be quantitatively detected in biological systems, the role and physiological activity has been discovered only for 23 elements. Essential

components of organic substances are carbon, hydrogen, oxygen, nitrogen and sulphur. Other elements can be split in two subdivisions of trace elements or micronutrients (Cr, Co, Cu, F, I, Mn, Mo, Se, V, Zn) and major elements or macronutrients (Ca, Cl, Fe, K, Mg, Na, P) [5, 6]. The human body is supplied by nutrient elements mainly via food and drinking water, as well as by consuming natural or artificial food supplements, while vegetables and fruits are a natural source of essential elements. It is important to estimate not only the contribution of vitally essential elements from vegetable consumption, but also possible presence of a potentially harmful trace element (e.g. As, Ni, Sr, Pb) and contamination sources in food should be assessed.

The aim of the study was to analyze root vegetables, onions *Allium cepa* and carrots *Daucus carota*, grown in farmlands and allotment gardens of Latvia. It was hypothesized that quantitative detection of trace and major elements in edible parts of vegetables can give useful information not only for the description of regional peculiarities of elemental composition of vegetables but also can be used as a tool for assessment of environmental impact on locally grown plants, as well as compared with data from other countries.

II. MATERIALS AND METHODS

A. Sample collecting and preparation

Fresh samples of root vegetables, carrot roots and onion bulbs were collected over the territory of Latvia in the 2010 harvesting season. All of the samples were confirmed as locally grown products and were obtained at markets or directly from farmers and individual households, as well as it was clarified whereas the vegetables were grown in farmlands or allotment gardens. Sampling was carried out by selecting 5 pieces of vegetables within every single sample.

Only the edible parts of vegetables were prepared for the analyses. Carrot roots and onion bulbs were cleaned, washed, peeled and crushed. Crushed samples were dried in drying oven "Gallenkamp Plus II Oven" at the temperature of 80 °C for 20 hours and at the temperature of 105 °C for extra 5-6 hours. The amount of dry matter was also calculated. After the drying, every sample was triturated until the consistence of powder. Until the analyses, the samples were stored in closed disposable plastic bags in a dry and dark place.

For trace element analysis, it is very important to avoid any contact of samples with any contaminants, particularly metals. Therefore, cutting, peeling and crushing of samples was done

by using a ceramic knife and a ceramic mill made by “Kyocera”, and sample solutions were kept in polypropylene tubes. Heating was performed in chemically persistent glass beakers.

The mineralization process, or sample pretreatment, is an important step for sample preparation before analytical determination can be performed. The process should be applied not only for cleavage of organic matrix of biological samples, but it also helps to prevent analytical techniques from unwanted residues that can settle on the burner head and in the spray chamber, and can affect spectral interferences that can result in inaccuracy of measurements [e.g. 7]. Sample pretreatment can be conducted by several methods, e.g. dry ashing, wet ashing, wet digestion that may be forced by heat, microwave or ultrasound influence [8]. The selected method, wet digestion of organic matter, is widely applied for samples of a biological origin [e.g. 1, 7]. The sample pretreatment procedure was implemented as follows: a) 0.5000 ± 0.0020 g of dry sample was weighted on analytical balances; b) 10 ml of analytically pure concentrated HNO₃ and 5 ml of ultra pure concentrated H₂O₂ was added; c) after hold overnight, the sample solutions were digested by heating at temperature 160 °C; d) after the digestion, sample solutions were filled up to 50 ml with ultra pure deionised water.

For the accuracy of the data, every sample was prepared in triplicate, and the mean values were used for statistical analysis which was performed using MS Excel data analysis tools.

B. Applied analytical methods

There are several kinds of analytical methodologies that can be used for trace and major element detection in biological samples. Applied analytical methods have to meet several criteria, such as trustable precision and accuracy, certain simplicity and moderate consumption of time and resources. Therefore, some analytical methods have been used more frequently, for example, atomic absorption spectrometry (AAS) methods, such as atomic absorption spectrometry on graphite furnace [4] or flame atomic absorption spectrometry [7, 9], that can be useful also for the analysis of vegetables and also fruits. Inductively coupled plasma mass spectrometry (ICP-MS) or inductively coupled plasma atomic emission spectroscopy (ICP-AES) are more sensitive techniques and can be used for trace and ultra trace analysis of element content [1, 4, 10]. Total reflection X-ray spectroscopy (TRXS) can also be applied [8].

In total, 30 samples of onion bulbs and 30 samples of carrot roots have been analyzed in this study. Major elements (Ca, Fe, K, Mg, Na) and some trace elements (Cu, Mn, Zn) were quantitatively analyzed by AAS apparatus “Perkin Elmer AAnalyst 200”, but other trace elements (Ag, As, Ba, Cd, Ce, Co, Cr, La, Ni, Pb, Rb, Se, Sr, V) were detected by ICP-MS techniques.

The precision of the applied analytical method was verified by a comparative analysis of certified reference samples CS-CR-2 Carrot Root Powder and NCS ZC73017 (GSB-10)-Apple. The analysis of the carrot root reference sample helped

to determine the accuracy of analytical methods for just five trace elements, while the apple reference sample enclosed a wider range of certified values of trace and major elements; the results obtained for some elements are summarized in Table I.

TABLE I

ACCURACY AND PRECISION OF APPLIED ANALYTICAL METHODS FOR SOME ELEMENTS; CERTIFIED AND MEASURED VALUES, MG/KG DRY MATTER

Element	Certified value (95% confidence interval)	Performance of AAS: mean ± standard deviation	Performance of ICP-MS:
Ba	2.5 (2.2 – 2.8)	n.a.*	2.42 ± 0.08
Ca	490 (480 – 500)	497 ± 22	n.a.
Cd	0.0058 (0.0046 – 0.0070)	0.008 ± 0.004	0.0051 ± 0.0002
Cu	2.5 (2.3 – 2.7)	2.36 ± 0.13	2.33 ± 0.04
Mn	2.7 (2.5 – 2.9)	2.70 ± 0.54	2.65 ± 0.04
Pb	0.084 (0.052 – 0.116)	<0.1	0.077 ± 0.007
Rb	5.0 (4.4 – 5.6)	n.a.	5.28 ± 0.09
Zn	2.1 (1.7 – 2.5)	2.58 ± 0.34	1.63 ± 0.17

*n.a. – not analyzed

III. RESULTS AND DISCUSSION

A. Content of trace elements in root vegetables

Current research of onion bulbs and carrot roots revealed that the dissemination of trace elements in both kinds of samples is quite comparable with some exceptions. In general, it was possible to quantify 17 trace elements (Ag, As, Ba, Cd, Ce, Co, Cr, Cu, La, Mn, Ni, Pb, Rb, Se, Sr, V, Zn). Hereinafter, the content of elements is expressed as units of dry matter (DM). The determined mean moisture content for onion samples was 88 % and 90 % for carrot samples. Trace elements detected in the highest concentrations – above 1 mg/kg of DM – were barium, copper, manganese, rubidium, strontium and zinc (see Table II).

TABLE II

CONTENT OF TRACE ELEMENTS THAT EXCEEDED 1 MG/KG DRY MASS IN ONION BULBS AND CARROT ROOTS, MG/KG DRY MATTER

Element	Content by species: min – max (mean)	
	Onion, <i>Allium cepa</i> (n=30)	Carrot, <i>Daucus carota</i> (n=30)
Ba	0.53 – 25.05 (2.56)	4.54 – 61.64 (21.26)
Cu	0.95 – 6.50 (3.10)	1.53 – 6.67 (3.76)
Mn	4.52 – 33.56 (11.28)	2.77 – 24.15 (8.47)
Rb	0.76 – 14.17 (4.06)	0.71 – 24.34 (7.44)
Sr	2.16 – 12.25 (6.77)	6.75 – 31.47 (15.52)
Zn	8.11 – 40.66 (15.54)	7.58 – 26.81 (13.67)

While the mean values of Cu, Mn, Rb and Zn concentrations did not differ significantly between the analyzed species, the amount of Ba was eight times higher, and the amount of Sr was twice higher in carrot roots than in onions. These differences could be explained by distinct plant metabolism processes of species. However, it is likely that

carrots have a greater tendency to uptake and accumulate trace metals than onions.

Data from similar studies revealed that onions grown in Finland contained Cu 4-5 mg/kg DM, Mn 8-18 mg/kg DM and Zn 13-22 mg/kg DM, but carrots grown in Finland contained Cu 5-6 mg/kg DM, Mn 12-27 mg/kg DM and Zn 10-23 mg/kg DM [1]. These values are slightly higher than levels of the same trace elements detected in the current study and indicate the importance of geographical differences.

Particular importance should be paid to the potentially toxic element assessment. Commonly known potentially toxic metals were detected in the following mean amounts: Ni 0.25 mg/kg DM and 0.28 mg/kg DM, Cr 0.09 mg/kg DM and 0.16 mg/kg DM, Pb and Cd each 0.05 mg/kg DM and 0.12 mg/kg DM in onions and carrots grown in Latvia, respectively. The obtained data showed slightly lower values than reported in literature. For example, onions and carrots grown in Finland contained Ni 0.15-0.38 mg/kg DM and 0.48-0.60 mg/kg DM, Pb 0.09-0.11 mg/kg DM and 0.10-0.13 mg/kg DM, Cd 0.03-0.15 mg/kg DM and 0.12-0.28 mg/kg DM, respectively [1]. Information about onions and carrots grown in Pakistan showed that amounts of chromium were 1.1 mg/kg DM and 0.8 mg/kg DM, respectively [9], that is much higher than revealed in the Northern countries.

Other trace elements in onions and carrots were detected in relatively small amounts: Co 0.018 mg/kg DM and 0.026 mg/kg DM, As 0.014 mg/kg DM and 0.012 mg/kg DM, Ce 0.006 mg/kg DM and 0.018 mg/kg DM, La 0.005 mg/kg DM and 0.018 mg/kg DM, Ag 0.003 mg/kg DM and 0.013 mg/kg DM, respectively. Only the mean amount of vanadium was higher in onions than in carrots, respectively 0.024 mg/kg DM and 0.006 mg/kg DM. An important element for human health is selenium, which was detected in onions and carrots in the amounts of 0.018 mg/kg DM and 0.014 mg/kg DM, while the values reported by Finnish scientists reached even 0.11 mg/kg DM in onions, but in carrots Se concentration (<0.01-0.02 mg/kg DM) was similar as detected in the current study [1]. Possible soil replenishment by selenium compounds in agriculture, that is a common approach for selenium enrichment in food in areas with low natural geochemical concentration of Se, obviously can be a reason for increasing the Se amount in vegetables, especially in onions, while plants of *Allium sp.* are predisposed to accumulate selenium. It should be noted that soils of the territory of Latvia are considered as "selenium deficient" [11].

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. 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.

Regarding the analysis of onion bulbs, significant differences between the mentioned subgroups were detected for several trace elements. Strontium, nickel, cadmium, selenium and cobalt were the elements the amounts of which were significantly higher in onions grown in farmlands, while rubidium 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 trace elements – carrot samples grown in allotment gardens were significantly richer in zinc, manganese and rubidium. These coherences purport the fact that farmlands are more likely influenced by possible contamination sources, mainly such as agrochemical impact, that can result in increased amounts of potentially toxic metals in vegetables, but the trace element analysis of vegetables grown in rural allotment gardens may reveal possible influence of geochemical background.

B. Content of major elements in root vegetables

Analysis of major elements in root vegetables revealed that potassium and calcium were the most abundant elements in both species. Data showed that carrots were about twice richer in potassium and calcium than onions. Also the amounts of sodium and magnesium in carrot roots were significantly higher than in onion bulbs, while iron in both species was detected in similar quantities (see Table III).

TABLE III
CONTENT OF MAJOR ELEMENTS IN ANALYZED SAMPLES OF ONION BULBS AND CARROT ROOTS, MG/KG DRY MATTER

Element	Content by species: min – max (mean)	
	Onion, <i>Allium cepa</i> (n=30)	Carrot, <i>Daucus carota</i> (n=30)
Ca	605.71 – 2402.63 (1381.81)	2314.81 – 3915.92 (3085.46)
Fe	9.47 – 45.66 (18.57)	11.44 – 34.71 (19.07)
K	9851.21 – 28417.50 (16961.10)	9178.36 – 47979.73 (27839.29)
Mg	610.26 – 1458.50 (923.12)	461.65 – 3097.23 (1365.19)
Na	8.70 – 783.87 (143.67)	150.40 – 4989.68 (1761.11)

The sequence of major elements K > Ca > Mg > Na of onions grown in Latvia refers to literature data where onion cultivars grown in United Kingdom [12] and Finland [1] were analyzed. However, in research done by Mohamed with colleagues [13], who investigated element content of vegetables from Saudi Arabia, the major elements ranked in a

different sequence, *i.e.* Ca > K > Mg > Na. Conditions in Saudi Arabia differs 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 major element content of onions and carrots grown in Latvia is comparable with results from other countries, *e.g.* carrots in Finnish research contained K 2330-2650 mg/100g, Ca 214-225 mg/100g, Mg 121-150 mg/100g, but the amount of Fe 3.0-3.4 mg/100g [1] is significantly higher than observed in the current study. This reveals the influence of site specific geological peculiarities.

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 the performed appropriate t-tests for samples of onion bulbs, only the content of sodium was significantly different in the selected subgroups. The mean score for the subgroup of samples grown in farmlands (M=186.59, n=17) was significantly higher than the scores for the subgroup of samples grown in allotment gardens (M=87.55, n=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 potassium (M=1641.64, n=12) and magnesium (M=31643.9, n=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=18 and for K were M=25302.9, n=18 detected by t-tests for unequal variances and t-test for equal variances, respectively. Results of the 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 [14].

IV. CONCLUSIONS AND FUTURE WORK

The quantitative analysis of trace and major elements of selected species of root vegetables confirmed that element uptake is dependent on the kind of species even in similar growing conditions, but different agrochemical conditions give a much greater impact. In general, the content of trace and major elements in carrot roots were higher than element content of onion bulbs. The higher content of potentially toxic metals (Cd, Cr, Ni, Pb) makes to think that carrots uptake and accumulate elements easier than onions and, therefore, can be affected by impact of pollution that may result with potentially toxic element penetration into animal and human food chains.

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 a significantly less amount of rubidium. For carrots, significantly higher amounts of some elements (K, Mg, Mn,

Rb, Zn) are contained in samples from allotment gardens. Differences between selected subgroups may arise, as well as entailed by natural geochemical background peculiarities as from the use of soil fertilizers that can influence the 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.

The overall data assessment and the comparison with worldwide literature information show that element content of root vegetables can be influenced not only by agricultural or gardening practices, but also is dependent on site specific geographical, geological, climatic conditions and detailed nuances have to be studied deeper by taking into account more influencing factors.

Further studies will involve a quantitative analysis of additional samples of carrots, onions and other food articles from Latvia with the aim to find out the intensity of geochemical impact, as well as the geographical dissemination of element content.

It is foreseen that the data obtained can be used for the consumer risk assessment, respecting possible impact of potentially toxic elements as potentially toxic metals are, as well as the benefit assessment of essential micro- and macronutrients in human daily diet can be performed. Therefore, assessment of daily intake of vegetables should also be under the scope of interest.

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Zane Vincēviča-Gaile, Māris Kļaviņš, Vita Rudoviča, Arturs Viksna. Mikro- un makroelementi pārtikā Latvijā: sakņu dārzeņu analīze

Uzturproduktu ķīmiskā sastāva izpēte ir komplicēts process, kas kā pētniecības metode tiek pielietota galvenokārt pārtikas ķīmijas nozarē. Ir zināms, ka ķīmisko elementu saturu augos ietekmē dažādi faktori, tādi kā suga, augsnes īpašības, laika apstākļi, mēslošana un augu aizsardzības līdzekļu lietošana, kā arī augu attīstības stadija, tāpēc pārtikas produktu analīze var būt nozīmīga arī citu nozaru kontekstā. Pētījuma mērķis – iegūt informāciju par Latvijā audzētu sakņu dārzeņu (sīpolu un burkānu), mikro- un makroelementu sastāva īpatnībām, ņemot vērā dārzeņu paraugu izcelsmi. Pētījuma ietvaros no dažādiem Latvijas reģioniem, precizējot paraugu izcelsmi no zemnieku saimniecībām vai piemājas dārziem, tika ievākti sīpolu un burkānu paraugi. Pēc paraugu apstrādes un mineralizācijas tie tika analizēti ar tādām kvantitatīvās analīzes metodēm kā atomabsorbcijas spektrometrija un induktīvi saistītās plazmas masas spektrometrija. Iegūtie dati par mikroelementu (Ag, As, Ba, Cd, Ce, Co, Cr, Cu, La, Mn, Ni, Pb, Rb, Se, Sr, V, Zn) un makroelementu (Ca, Fe, K, Mg, Na) saturu dārzeņos tika statistiski apstrādāti, savstarpēji salīdzināti, kā arī izvērtēti kontekstā ar līdzīgiem citu valstu pētījumiem. Kopumā tika konstatēts, ka burkānos vairāku elementu saturs ir augstāks nekā sīpolos, kamēr citi elementi abos dārzeņu veidos ir vienlīdzīgā apjomā. Apakšgrupu analīze atklāja statistiski nozīmīgas vairāku elementu īpatnības starp zemnieku saimniecībās mazdārziņos audzētiem sakņu dārzeņiem. Piemēram, Cd, Co, Na, Ni, Rb, Se un Sr koncentrācijas sīpolu paraugos no mazdārziņiem bija statistiski būtiski zemākas nekā sīpolos, kas audzēti zemnieku saimniecībās. Datu analīze ļauj secināt, ka vides faktoru ietekmei ir būtiska nozīme uz elementu saturu dārzeņos.

Зане Винцевича-Гайле, Марис Клявинш, Вита Рудовича, Артурс Вилксна. Микро- и макроэлементы в продуктах питания в Латвии: корнеплодные овощи

Исследование химического состава продуктов питания представляет собой сложный процесс, который в основном используется в пищевой химии в качестве исследовательского метода. Известно, что содержание химических элементов в растениях зависит от различных факторов, таких как вид

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растения, характеристика почвы, условия погоды, продукты для удобрения и защиты растений, а также стадия развития растения, поэтому анализ продуктов питания растительного происхождения может иметь важное значение в контексте разных отраслей науки. Цель исследования - получить информацию о корнеплодных овощах, таких как репчатый лук и морковь, местного латвийского происхождения относительно микро- и макроэлементов, с учетом происхождения с образцов. Образцы были собраны по всей территории Латвии. Происхождение образцов было выяснено при покупке, получая образец из сельскохозяйственного предприятия или из садово-огородного участка. После обработки и минерализации образцов растворы были анализированы такими методами, как: атомно-абсорбционная спектрометрия и масс-спектрометрия индуктивно-связанной плазмы. Полученные данные о содержании микроэлементов (Ag, As, Ba, Cd, Ce, Co, Cr, Cu, La, Mn, Ni, Pb, Rb, Se, Sr, V, Zn) и макроэлементов (Ca, Fe, K, Mg, Na) в овощах статистически обработаны, сравнены между собой, а также в контексте подобных исследований в других странах. В целом, было установлено, что несколько элементов в составе моркови выше, чем у лука, в то время как другие элементы входят в состав обоих видов в одинаковом количестве. Анализ подгрупп показал статистически значимые особенности многих элементов в корнеплодах, выращенных в условиях садово-огородных участков и сельскохозяйственных условиях. Например, концентрации Cd, Co, Na, Ni, Rb, Se и Sr в образцах лука были статистически значимо ниже, чем у лука, выращенного при сельскохозяйственных условиях. Анализ данных показал, что факторы окружающей среды играют важную роль в содержании элементов в овощах.