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LITHIUM CONTENT
IN SELECTED ROOT VEGETABLES
AGAINST ITS CONTENT IN SOIL

ZAWARTOŚĆ LITU
W WYBRANYCH WARZYWACH KORZENIOWYCH
NA TLE JEGO ZAWARTOŚCI W GLEBIE

Abstract: In the first half of September 2003, 44 samples of cultivated root vegetables *ie* carrot, parsley, celery and beetroot at their consumption maturity, were collected from arable lands in the Miechowski county. Samples were gathered from the fields of considerable area (0.5–2.0 ha) vegetable cultivation. The collected plant material was subjected to dry mineralization, ash was dissolved in HNO_3 and obtained mineralizat was analysed. Soil samples were taken from the same locations as vegetables, from the depth of 0–25 cm. Basic physicochemical properties of the soil samples were determined by means of methods universally applied in agricultural chemistry. Total lithium content in the soils was determined after mineralization at a temperature of 450 $^{\circ}$C, then digestion with a mixture of acids ($HClO_4$ and HNO_3) and dissolving in HCl. Content of this element soluble forms was determined after extraction with 0.1 mol $\cdot$ dm^{-3} HCl solution.

The total lithium content in the examined soils varied widely (2.79 to 12.20 mg $\cdot$ kg^{-1}), with a geometric mean of 7.78 mg $\cdot$ kg^{-1}. The content of the soluble forms of lithium extracted with 0.1 mol $\cdot$ dm^{-3} HCl solution varied from 0.057 to 0.251 mg $\cdot$ kg^{-1}, with a geometric mean of 0.119 mgLi $\cdot$ kg^{-1}. It was fund significant correlation between total lithium content and share of floatable fraction and colloidal clay in studied soils, as well as between content of soluble lithium forms and share of colloidal clay in soil. The lithium content in the vegetables varied depending on species and part of the plant. A geometric mean of lithium content in roots varied from 0.206 mgLi $\cdot$ kg^{-1} (parsley) to 0.365 mgLi $\cdot$ kg^{-1} (beetroot). Tops of vegetables contained 3–5 times more lithium than their roots. It was stated, that physicochemical properties of studied soils not uniformly affected lithium content in vegetables, what demonstrated values of simple correlation coefficients. Lithium content in roots of all vegetables and tops of beetroot and parsley depended on soluble forms of lithium content in soil. Moreover, lithium content in carrot roots as well as parsley roots and tops was affected

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by total lithium content in the soil. However, soil reaction had no significant effect on lithium content in organs of studied root vegetables.

Introduction

Among trace elements microelements present in the natural environment are crucial for the correct growth and development of plants, as well as for the proper functioning of human and animal organisms. Usefulness of some elements (*eg* lithium) has not been fully recognized.

Lithium salts are relatively readily soluble in the soil water, therefore this cation is absorbed by plants proportionately to its concentration in the substratum [1]. The content and uptake of nutrients, including lithium, are determined by the content and form of a given element in soil, soil pH value, soil moistness and organic matter content, but also by heavy metal contents, the temperature and insolation, the kind and amount of applied mineral fertilizers and pesticides, number and composition of microflora present in the soil, the species and variety of plants and finally by other factors [2–6].

Currently, there is a growing interest in possibilities including waste materials of biological origin to the balance of organic fertilization [7]. These materials may be used for fertilization of some plants on condition that they do not contain heavy metals, nor are burdened with sanitary pollutants [8, 9].

Bioavailability of trace elements more or less determines consumptive or fodder value of agricultural products. Lithium salts are widely used in various industries and by modern technologies, so they may cause local pollution with this element and therefore affect plant chemical composition.

The investigations aimed at determining lithium content in root vegetables cultivated for consumption against its content in soil.

Materials and methods

The subject of investigations was selected root vegetables and soils from under their cultivation. In the first half of September 2003, 44 samples of cultivated root vegetables *ie* carrot, parsley, celery and beetroot at their consumption maturity, were collected from arable lands in the Miechowski county. Samples were gathered from the fields of considerable area (0.5–2.0 ha) vegetable cultivation, situated at the distance of more than 50 m from the main traffic routes. The analysed plant sample was an average of 12 individual ones (*ca* 1 kg of fresh mass). The collected plant material, after removing earthy parts, was washed and divided into roots and tops. After drying the examined samples were crushed and dry-mineralized. The obtained ashes were dissolved in nitric acid diluted with water (1 : 2, *v/v* ratio) and obtained solution was analysed.

From the same places as vegetables, soil samples were collected from the depth of 0–25 cm of arable lands. Each soil sample was an average of individual samples (0.5–1.0 kg of soil). Basic physicochemical properties were determined in the soil

material by means of methods universally applied in agricultural chemistry [10]. Analyses comprised: soil texture by aerometric Bouyoucose and Casagrande's method in Proszynski's modification, pH by potentiometer in soil suspension in H_2O and in 1 mol · dm^{-3} KCl solution, and organic carbon content by Tiurin's method.

Total lithium content in the collected soil samples was assessed after previous mineralization at 450 ^oC and subsequent digestion in mineral acids mixture ($HClO_4$ and HNO_3) and dissolving in HCl [11]. The content of soluble forms of lithium was assessed after extraction with 0.1 mol · dm^{-3} HCl solution.

Lithium content was assessed in obtained plant and soil mineralizats and soil extracts by means of ICP AES method on JY 238 Ultrace apparatus.

The obtained results referring to lithium content in soils, plants and physicochemical soil properties were used for statistical computations, *ie* arithmetic and geometric means, standard deviation (SD), relative standard deviation (RSD) and linear correlation coefficients (r).

Results and discussion

Soil properties

The places of vegetable and soil samples collection were described in the first part of the paper [12].

The examined soils differed in respect of their texture, pH value, organic carbon content and the lithium content. pH value, assessed in water suspension fluctuated from 5.14 to 7.64, whereas in 1 mol · dm^{-3} KCl solution from 4.13 to 7.23. On the five degree acidification scale (pH_{KCl}), collected soil samples were divided into two groups: 11 samples were acid and slightly acid soils (pH_{KCl} < 6.6), whereas 33 samples were neutral ones (pH_{KCl} ≥ 6.6).

On the basis of texture, collected soil samples were classified to the following agronomic categories: 5 represented medium soils with floatable particles content from 21 to 35 %, 36 samples were heavy soils with floatable particles content from 35 to 50 % and 3 – very heavy soils with over 50 % of floatable particles.

Total lithium content in the tested soils ranged from 2.79 mg · kg^{-1} to 12.20 mgLi · kg^{-1}, its geometric mean amounts 7.78 mg · kg^{-1}, and RSD = 27 %. The content of lithium soluble forms extracted in 1 mol · dm^{-3} HCl solution ranged from 0.057 mgLi · kg^{-1} to 0.250 mgLi · kg^{-1}, with geometric mean amounting 0.119 mgLi · kg^{-1} and RSD = 62 %. The share of these soluble lithium forms in total lithium content fluctuated from 0.83 to 3.05 %.

Ammari et al [13] revealed that the content of water extracted (soluble) lithium in the topsoil (0–20 cm) ranged from 0.95 to 1.04 mgLi · kg^{-1}, whereas in 20–40 cm layer from 1.06 to 2.68 mgLi · kg^{-1} depending on the region situated along the Jordan River valley.

Total content of lithium and its soluble forms extracted with 1 mol · dm^{-3} HCl solution in the studied neutral soils (pH_{KCl} ≥ 6.6) was higher than in the acid and slightly acid ones (pH_{KCl} < 6.6) (Table 1).

Table 1

Lithium content in soil [mg · kg^{-1} d.m.] depending on soil pH

Parameter	Total content	Content of soluble forms
pH in 1 molKCl · dm^{-3} ≤ 6.5		
Range	4.80–9.30	0.064–0.250
Arithmetic mean	7.42	0.132
Geometric mean	7.28	0.118
RSD [%]	20	52
pH in 1 molKCl · dm^{-3} ≥ 6.6		
Range	2.79–12.20	0.057–0.204
Arithmetic mean	8.52	0.140
Geometric mean	8.14	0.135
RSD [%]	27	26

Explanation for Tables 1, 2 and 4: RSD – relative standard deviation.

Total lithium content dependent on examined soils texture and was twice higher in heavy and very heavy soils (with floatable particles content > 35 %) in comparison with medium soils (with floatable particles content ≤ 35 %) (Table 2).

Table 2

Content of lithium in soils [mgLi · kg^{-1}] depending on the share of soil fractions with ∅ < 0.02 mm

Parameter	Total content	Content of soluble forms
Content of < 0.02 mm fraction ≤ 35 %		
Range	2.79–7.58	0.057–0.202
Arithmetic mean	4.98	0.127
Geometric mean	4.59	0.115
RSD [%]	45	46
Content of < 0.02 mm fraction > 35 %		
Range	4.55–12.21	0.084–0.251
Arithmetic mean	8.54	0.139
Geometric mean	8.32	0.132
RSD [%]	22	31

Kosla [14] stated that heavy loamy soils contained bigger lithium amounts than light ones. The same relationship was confirmed by the research of Rogoz and Tabak [15] who found 14.8 mgLi · kg^{-1} in heavy soils, and 8.86 mgLi · kg^{-1} in light ones.

Statistical analysis of obtained results revealed that the physicochemical properties of the soils in which the vegetables were cultivated affected lithium content to various extent, as evidenced by simple correlation coefficients (Table 3).

Table 3

Simple correlation coefficients (r) between of lithium content in soils and selected physical and chemical properties

Soil property	Beetroot n = 40	Carrot n = 44	Parsley n = 44	Celery n = 32
Total lithium content				
pH$_{KCl}$	ns	ns	ns	ns
Share of fraction				
$\varnothing$ < 0.02 mm	0.5830**	0.6173***	0.6038***	0.6182***
$\varnothing$ < 0.002 mm	0.4278*	0.4058*	0.4034*	0.3369*
Content of soluble lithium forms				
pH$_{KCl}$	ns	ns	ns	ns
Share of fraction				
$\varnothing$ < 0.02 mm	0.2265	0.2036	0.1766	0.1715
$\varnothing$ < 0.002 mm	0.3899**	0.2570	0.2916*	0.1610

Explanation: n = number of soil samples; ns – not significant; r significant at: *p = 0.05; **p = 0.01; ***p = 0.001.

The pH of the studied soils did not have any significant influence either on total or soluble lithium forms content. A positive relationship occurred between total lithium content in the investigated soils and both floatable particles and colloidal clay share. Rogoz in his previous experiments [16] revealed that lithium content obtained in individual fractions in results of sequential fractioning of metals in soils was quite diversified depending on granulometric composition.

A positive dependence was also pointed out between lithium content in soil in forms extracted with 1 mol · dm^{-3} HCl solution and colloidal clay content (Table 3).

Lithium content in vegetables

Among the most valuable and vitamin rich vegetables used by households and possessing culinary values are: beetroot (*Beta vulgaris* var. *esculenta*), carrot (*Daucus carota*), parsley (*Petroselium sativum*) and celery (*Apium graveolens*). Lithium contents in plants depend on: the species, phase of development, analysed plant part, as well as content and forms of lithium present in soil [1, 12].

Plants absorb lithium in ionic form through exchange, proportionately to its content in soil [2, 3]. Ammari et al [13] demonstrated that lithium content was diversified depending on the species, as well as region of investigations. Lithium contents in citrus tree leaves fluctuated from 5 to 20 mgLi · kg^{-1} d.m., whereas in pepper leaves from 3 to 27 mgLi · kg^{-1} d.m.

In the Authors' own research lithium concentrations in the cultivated root vegetables were quite diversified depending on the species and analysed plant part. The arithmetic mean lithium content in roots was the largest in case of beetroot and showed the most changeability (RSD = 102.5 %), while in roots of other vegetables was around 20 to

45 % lower and showed smaller variability (RSD = 58.4–78.9 %) (Table 4). Larger lithium contents were found in the vegetable tops than in the roots, which evidences that this cation is easy subjected to translocation from roots to tops. This cation mean content in beetroot tops was about 5-fold higher than in roots, was the largest among studied vegetables and was the most diversified (RSD = 112.7 %). Arithmetic mean lithium contents in above-ground parts of other vegetables were from 3 to 3.5 times lower than in beetroot tops. Carrot, parsley and celery tops contained on average around thrice bigger amount of lithium than their roots, but showed a bit smaller variability than in beetroot tops (RSD = 78.0–98.0 %) (Table 4).

Table 4

Statistical parameters of lithium content [mg · kg^{-1} d.m.]
in vegetable roots and tops

Parameter	Roots	Tops
	Lithium content [mg · kg^{-1} d.m.]	
Beetroot – *Beta vulgaris* var. *esculenta*		
Range	0.09–2.06	0.22–17.86
Arithmetic mean	0.468	2.741
Geometric mean	0.365	1.801
Standard deviation	0.369	3.088
RSD [%]	78.9	112.7
Carrot – *Daucus carota*		
Range	0.06–0.52	0.16–2.16
Arithmetic mean	0.243	0.775
Geometric mean	0.209	0.641
Standard deviation	0.130	0.500
RSD [%]	62.0	78.0
Parsley – *Petroselium sativum*		
Range	0.08–0.86	0.17–2.72
Arithmetic mean	0.270	0.743
Geometric mean	0.206	0.581
Standard deviation	0.211	0.569
RSD [%]	102.5	98.0
Celery – *Apium graveolens*		
Range	0.11–0.89	0.18–4.11
Arithmetic mean	0.363	0.896
Geometric mean	0.306	0.693
Standard deviation	0.212	0.764
RSD [%]	58.4	85.2

Jurkowska et al [2] and Rogoz [17] revealed that this element transport from stalks to leaves and seeds is weaker in plants growing in soil with higher lithium content than in plants cultivated in soil with natural content of this element.

Malinowska and Kalembasa [18] revealed a diversified lithium content in test plants, *ie* Italian ryegrass, maize and sunflower, depending on fertilization and liming. These authors the highest lithium bioaccumulation stated in sunflower, next in Italian ryegrass and finally in maize. Bibak et al [19] demonstrated that lithium content in of fresh mass of cabbage was on the level of 1.49 μgLi $\cdot$ kg^{-1}, whereas in Brussels sprouts 0.41 μgLi $\cdot$ kg^{-1} of fresh mass.

Physical and chemical properties of the studied soils in different extent affected lithium content in plants, as evidenced by simple correlation coefficients (Table 5).

Table 5

Simple correlation coefficients (r) between lithium content in root vegetables
and selected properties of soil

Property	Beetroot n = 40	Carrot n = 44	Parsley n = 44	Celery n = 32
Roots				
Soil pH in KCl	0.1780	0.034	–0.1277	0.0685
Total content of lithium	0.0185	0.414*	0.2996*	0.3019
Content of lithium soluble forms	0.4690**	0.508**	0.6401***	0.6250**
Tops				
Soil pH in KCl	0.2379	–0.075	–0.1427	0.0901
Total content of lithium	0.2416	0.268	0.346*	0.2547
Content of lithium soluble forms	0.3652*	0.234	0.5514**	0.3202

n = number of soil samples; r significant at: *p = 0.05; **p = 0.01; ***p = 0.001.

Simple correlation coefficients revealed that the reaction of studied soils did not have any significant influence on lithium content both in tops and roots of vegetables. On the other hand, it was established that total lithium content in soil affected its content in roots of carrot, as well as in roots and tops of parsley. Moreover, values of correlation coefficients evidenced that content of lithium soluble forms determined this cation level in roots of all studied vegetables and in tops of beetroot and parsley as well (Table 5).

Bach [20] demonstrated that lithium is the element crucial for proper physical functions in goats and rats, which maintained on low-lithium ratios were shown to exhibit higher mortalities as well as reproductive and behavioral abnormalities. For example rats became less aggressive [21].

Lithium at levels naturally present in the diet may exert a powerful effect on behavior [22]. Dawson informed about evidence of correlation between low lithium contents of tap water and urine with higher mental hospital admissions due to psychosis, neurosis, schizophrenia, personality disorders and homicides [22]. A study carried out in Texas showed significantly more incidences of suicide, homicide and rape in counties where people drink water contained little or no lithium than in those with higher lithium concentration [23]. The animals responded differently to lithium supplement in fodder. Anke et al [24] stated that 20 mgLi $\cdot$ kg^{-1} added to goat or turkey feed led to slight

changes in its consumption and in body weight gains. Ruminants are more sensitive to lithium burden than monogastric animals.

As presented Gupta et al [25] there are evidences that lithium plays an important role during the early fetal development because the high lithium contents were found in the embryo during the early gestational period. Lithium depletion causes low lithium status has a negative impact on homeostasis of glucose and insulin sensitivity in diabetic patients and lithium supplementation may manage this disease [22]. Moreover, 72 % of diabetic patients had low lithium content in serum, and of control ones only 10 % of population.

So far there have been few data on lithium content in food products or its consumption by people available in the literature. For this reason investigation of lithium content in vegetables is very important and may be useful for elucidation this issue.

Długaszek et al [26] suggested allowable lithium contents in 6 groups of food products, ie cereals 4.405 mgLi $\cdot$ kg^{-1}, vegetables 2.327 mgLi $\cdot$ kg^{-1}, potatoes 1.305 mgLi $\cdot$ kg^{-1}, dairy products 0.5 mgLi $\cdot$ kg^{-1} and fish 3.15 mg Li $\cdot$ kg^{-1}. Schrauzer [27] determined considerable amounts of lithium in yeast $Saccharomyces\ cerevisiae$, ie 115–400 mgLi $\cdot$ kg^{-1}.

Daily requirement for lithium of an adult weighing 70 kg is 1000 µg, ie 14.4 µg $\cdot$ kg^{-1} of body weight. Długaszek et al [25] demonstrated also that the results obtained are approximate to results published by Belgian authors. Van Cauwenbergh et al [28] provided that average daily lithium consumption by a group of students participating in the investigations fluctuated from 3.9 in Brussels to 12.2 µg $\cdot$ d^{-1} in Antwerp and Vilwoorde. Lithium intake ranged from 1.2 to 15.2 µg $\cdot$ d^{-1}, and mean value for adult amounted 8.6 $\pm$ 4.6 µg $\cdot$ d^{-1} and was lower than in other countries. In the paper are also presented data concerned daily lithium consumption in various countries, eg Canada 21.6 µg, Germany 182–546 µg and Great Britain 107 µg $\cdot$ d^{-1}. According to Schrauzer [27] considerable quantities of this element are consumed by the citizens of China (1560 $\pm$ 1009 µg $\cdot$ d^{-1}).

Conclusions

1. Lithium content in vegetable roots depended on the species and analysed plant part. Mean geometric lithium content in beetroot was 0.365 mgLi $\cdot$ kg^{-1}, in the roots of carrot 0.209 mgLi $\cdot$ kg^{-1}, parsley 0.206 mgLi $\cdot$ kg^{-1} and celery 0.306 mgLi $\cdot$ kg^{-1}. Lithium content in the cultivated vegetables was determined by the content and form in which it occurred in soil.

2. Larger lithium contents were registered in the tops than in roots of the analysed vegetables, what indicates an easy translocation of this element from roots to above-ground parts.

3. It was demonstrated that physical and chemical properties of the studied soils to various extent influenced lithium content in vegetables as evidenced by values of simple correlation coefficients.

4. Determining lithium contents in food products and its consumption is crucially important because this element participates in many important life processes of humans and animals.

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ZAWARTOŚĆ LITU W WYBRANYCH WARZYWACH KORZENIOWYCH NA TLE JEGO ZAWARTOŚCI W GLEBIE

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Abstrakt: W pierwszej połowie września 2003 r. na terenie powiatu miechowskiego pobrano 44 próbki warzyw korzeniowych, tj. marchwi, pietruszki, selera oraz buraka czerwonego. Próbki pobierano z pól o znaczącym areale (0,5–2,0 ha) uprawy warzyw z przeznaczeniem na cele konsumpcyjne. Zebrane próbki warzyw poddano mineralizacji na sucho, popiół roztworzono w HNO_3, a uzyskane mineralizaty poddano analizie. Z tych samych miejsc, na których uprawiano warzywa korzeniowe, pobrano próbki glebowe z głębokości 0–25 cm. W próbach glebowych oznaczono podstawowe właściwości fizykochemiczne metodami standardowymi stosowanymi w chemii rolnej. Całkowitą zawartości litu w glebach oznaczono po ich wcześniejszej mineralizacji w temperaturze 450 °C, a następnie wytrawieniu w mieszaninie kwasów ($HClO_4$ i HNO_3) i roztworzeniu w HCl. Zawartość rozpuszczalnych form tego pierwiastka oznaczono po ich wyekstrahowaniu roztworem HCl (0,1 mol · dm^{-3}).

Całkowita zawartość litu w badanych glebach wahała się w szerokim zakresie (2,79–12,20 mgLi · kg^{-1}), a średnia geometryczna wynosiła 7,78 mgLi · kg^{-1}. Natomiast zawartość rozpuszczalnych form litu wyekstrahowanych HCl o stężeniu 0,1 mol · dm^{-3} wahała się od 0,057 do 0,251 mgLi · kg^{-1} (ze średnią geometryczną 0,119 mgLi · kg^{-1}). Stwierdzono istotną dodatnią korelacje pomiędzy całkowitą zawartością litu a zawartością części spławianych oraz iłu koloidalnego w badanych glebach, a także pomiędzy zawartością rozpuszczalnych form litu a zawartością iłu koloidalnego.

Zawartość litu w zebranych warzywach była zróżnicowania w zależności od gatunku i organu rośliny. Średnia geometryczna zawartość litu w korzeniach wynosiła od 0,206 mgLi · kg^{-1} (pietruszka) do 0,365 mgLi · kg^{-1} (burak czerwony). Części nadziemne warzyw zawierały 3–5 razy więcej litu niż korzenie. Wykazano, że właściwości fizykochemiczne badanych gleb w niejednakowym stopniu wpływały na zawartość litu w warzywach, czego dowodzą wartości współczynników korelacji prostej. O zawartość litu w korzeniach wszystkich badanych warzyw oraz naci buraka i pietruszki decydowała zawartość rozpuszczalnych form litu w glebie. Ponadto zawartość litu w korzeniach marchwi oraz korzeniach i naci pietruszki zależała od całkowitej zawartość tego pierwiastka w glebie. Natomiast odczyn gleb nie miał istotnego wpływu na zawartość litu w organach badanych warzyw korzeniowych.

Słowa kluczowe: warzywa korzeniowe, gleba, zawartość litu