

Antoni ROGÓŻ¹

**EFFECT OF SOIL PROPERTIES
ON LITHIUM PHYTOAVAILABILITY
Part 2. LITHIUM CONTENT IN SOIL AFTER COMPLETION
OF MAIZE AND RYE VEGETATION**

**WPLYW WŁAŚCIWOŚCI GLEBY
NA FITOPRZYSWAJALNOŚĆ LITU
Cz. 2. ZAWARTOŚĆ LITU W GLEBIE PO ZAKOŃCZENIU
WEGETACJI KUKURYDZY ORAZ OWSA**

Abstract: Soil samples were collected from each series after the end of rye vegetation in order to follow changes which occurred in physical and chemical properties. Increasing doses of organic matter and applied two doses of lithium affected changes of soil physical and chemical properties. Applied doses of lithium and organic matter influenced the values of pH and hydrolytic acidity, organic carbon content and the content of lithium in soil. Metal sequential extraction with solutions of various leaching power: H₂O; 2.5 % CH₃COOH; 0.1 mol K₂P₄O₇ · dm⁻³; 0.1 mol H₂C₂O₄ · dm⁻³ + 0.175 mol (NH₄)₂C₂O₄ · dm⁻³ was used to determine lithium content and its forms in soil. In result of sequential extraction were lithium forms extracted from easily soluble, ie bioavailable, through weakly bound to sorption complex to sparingly soluble and immobilized, therefore unavailable to plants. Lithium content in individual fractions was quite diversified. The factor determining this element level in the analyzed soil was applied lithium dose and increasing doses of organic matter, one of many factors affecting the size of sorption complex. Lithium doses of 10 and 20 mg Li per pot very distinctly affected the amount of lithium extracted using 2.5 % CH₃COOH as F-2 form. In this case a similar dependence occurred as in F-1 fraction. The content of lithium bound to organic matter (F-3), extracted with 0.1 mol K₂P₄O₇ · dm⁻³ ranged from 0.212 to 0.340 mg Li · kg⁻¹. The quantity of cation bound to organic matter extracted using 0.1 mol K₂P₄O₇ · dm⁻³ was visibly increasing on treatment with growing lithium doses.

Keywords: lithium forms in soil, sequential extraction, soil properties

Natural content of lithium in soil is diversified, fluctuating from several to many mg Li · kg⁻¹. The main factors determining the level of this cation in soil comprise the kind of parent rock, soil forming processes, climate, soil pH, organic matter content, degree of moistening, content of floatable particles and anthropogenic factors [1–6].

¹ Department of Agricultural Chemistry, University of Agriculture in Krakow, al. A. Mickiewicza 21, 31–120 Kraków, Poland, phone +48 12 662 4348, fax +48 12 662 4341, email: rrogoz@cyf-kr.edu.pl

On the basis of his investigations Rogóż [6] revealed that the content of individual lithium forms obtained with the method of metal sequential extraction was quite diversified depending on the content of floatable particles but to a lesser degree on pH value. He also demonstrated a significant dependency between organic carbon content in the researched soils and lithium contents in water soluble forms and exchangeable non-specifically adsorbed form.

The research was conducted to compare the effect of increasing doses of organic matter on the content and forms of lithium in soil polluted with this metal.

Materials and methods

The pot experiment was set up in 2006 in the design comprising the following combinations:

A. Control treatment:

- 1 – soil with natural lithium and organic matter contents,
- 2 – soil with a supplement of 10 mg Li · pot⁻¹ with natural content of organic matter,
- 3 – soil with a supplement of 20 mg Li · pot⁻¹ with natural content of organic matter,

B. Treatments with increasing lithium and organic matter supplements (as compost):

- 4 – with 10 mg Li · pot⁻¹ and 26 g of organic matter,
- 5 – with 20 mg Li · pot⁻¹ and 26 g of organic matter,
- 6 – with 10 mg Li · pot⁻¹ and 52 g of organic matter,
- 7 – with 20 mg Li · pot⁻¹ and 52 g of organic matter,
- 8 – with 10 mg Li · pot⁻¹ and 78 g of organic matter,
- 9 – with 20 mg Li · pot⁻¹ and 78 g of organic matter.

Maize (*Zea mays* L.) and rye (*Secale cereale* L.) were cultivated as test plants. After completed vegetation of both plants soil samples were collected from each series. The samples were left in linen bags in rooms with free air movement and when dried they were ground in a porcelain mortar and sifted through a sieve with 1 mm² mesh. Detailed method and the course of the experiment were presented in the “Material and methods” section in the 1st part of this paper [7].

Basic physicochemical properties were determined in air-dried soil samples with methods commonly used in agricultural chemistry [8]:

- granulometric composition with Bouyoucose-Casagrande method in Proszynski modification,
- pH with potentiometric method in soil suspension in H₂O and in 1 mol KCl · dm⁻³,
- organic carbon content with Tiurin method,
- hydrolytic acidity with Kappen method,
- lithium forms in the analysed soils were assessed with a method of metal sequential extraction [9] modified by Bogacz [1, 10],
- total lithium content was determined as a sum of extracted fractions from F-1 to F-5 (Fig. 1).

The content of individual lithium forms obtained in result of metal sequential extraction was assessed in an acetylene-air flame with ICP AES method on JP238.

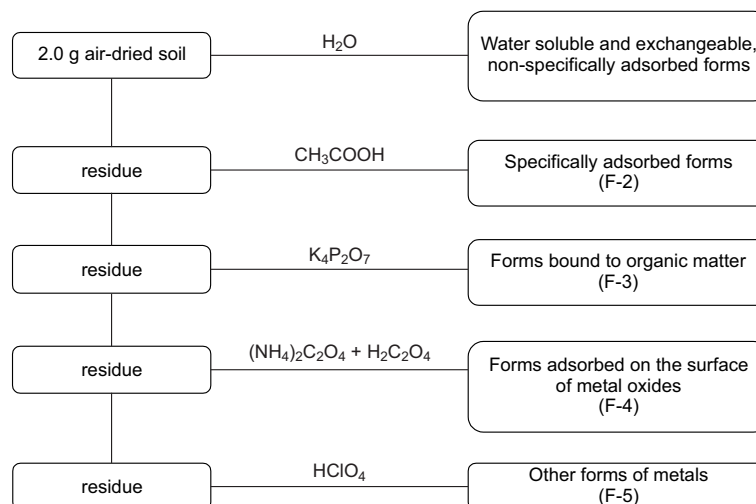


Fig. 1. Scheme of sequential extraction of the lithium fraction in soil [1]

Results and discussion

When rye vegetation was completed soil samples were collected from each series in order to follow changes which occurred in physical and chemical properties. Increasing doses of organic matter and applied two doses of lithium affected changes of soil physical and chemical properties. Applied doses of lithium and organic matter influenced the values of pH and hydrolytic acidity, organic carbon content and the content of lithium in soil after completion of plant vegetation. The soil pH after completed vegetation period assessed in water suspension fluctuated from 5.96 to 6.26, while measured in $1 \text{ mol} \cdot \text{dm}^{-3}$ KCl from 5.59 to 5.94. Organic C content in the soil used for the experiment was 1.33 %. Increasing doses of organic matter: 26, 52 and 78 $\text{g} \cdot \text{pot}^{-1}$ caused an increase in organic C. Assuming eg the control treatment with natural content of organic carbon as 100, it may be concluded that applied doses of organic matter 26, 52 and 78 g led to an increase in organic C from 1.5 to 10.4 % (Table 1). These dependencies confirmed the results obtained by Mazur [11].

Lithium content and its forms in soil were determined using metal sequencing extraction with solutions of various leaching power: H_2O ; 2.5 % CH_3COOH ; $0.1 \text{ mol K}_2\text{P}_4\text{O}_7 \cdot \text{dm}^{-3}$; $0.1 \text{ mol H}_2\text{C}_2\text{O}_4 \cdot \text{dm}^{-3} + 0.175 \text{ mol (NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{dm}^{-3}$. In result of sequential extraction were extracted lithium forms from easily soluble, ie bioavailable, through weakly bound to sorption complex to sparingly soluble and immobilized, therefore unavailable to plants. Lithium content in individual fractions was quite diversified. The factor determining this element level in the analyzed soil was the applied lithium dose and increasing doses of organic matter, one of many factors affecting the size of sorption complex.

Table 1

Soil properties after the end of plant vegetation period

Series	Li supplement [mg · pot ⁻¹]	Dose of organic matter [g · pot ⁻¹]	pH		Hh [mmol(+) · kg ⁻¹]	Organic C [g · kg ⁻¹]
			H ₂ O	KCl		
1	0	0	5.96	5.59	22.0	1.505
2	10	0	6.17	5.71	14.2	1.481
3	20	0	6.08	5.65	15.1	1.515
4	10	26	6.18	5.76	11.2	1.567
5	20	26	6.15	5.72	13.8	1.523
6	10	52	6.23	5.94	13.8	1.614
7	20	52	6.26	5.83	21.2	1.615
8	10	78	6.19	5.86	14.7	1.636
9	20	78	5.97	5.90	12.5	1.656

The quantity of lithium extracted using H₂O comprised water soluble fractions present in the soil solution and the non-specifically adsorbed exchangeable form (weakly bound to the soil sorption complex), thus bioavailable to plants. The amount of lithium extracted with H₂O as F-1 form depended on the natural content of this element in soil, lithium dose and the applied dose of organic matter, and ranged from 0.26 mg to 0.98 mg Li · kg⁻¹.

Lithium doses of 10 and 20 mg Li per pot markedly affected the quantity of lithium as F-1 form extracted using H₂O. Assuming lithium content extracted in F-1 form on the control treatment with natural content of this element as 1, it may be seen that lithium amounts extracted with increasing doses, ie 10 and 20 mg Li · pot⁻¹ were twice and four fold bigger.

Applied growing doses of organic matter had an inhibitory effect on the quantity of lithium extracted as F-1 form using H₂O. Assuming eg lithium content extracted as F-1 form on the treatment with elevated lithium content (10 mg Li · pot⁻¹) as 100, it may be seen that growing doses of organic matter 26, 52 and 78 g · pot⁻¹ caused the decrease of lithium amounts extracted as F-1 fraction by 9, 15 and 2 %, respectively. On the other hand, increasing doses of organic matter in case of 20 mg Li · pot⁻¹ addition affected the amount of extracted metal in various directions (Table 2).

On the basis of previous investigations Rogóż [6] revealed that the amount of lithium extracted using 0.05 mol BaCl₂ · dm⁻³ fluctuated from 0.020 to 0.370 mg Li · kg⁻¹ soil at geometric mean 0.109 mg Li · kg⁻¹, comprising the total of two fractions, ie water soluble and exchangeable, non-specifically adsorbed F-1.

The amounts of lithium in the other fractions extracted by means of the other extractors with various power depended on the natural content of this cation in the soil, applied lithium dose and the dose of organic matter.

This element content extracted with 2.5 % CH₃COOH determined as a form specifically adsorbed by soil colloids F-2 fluctuated from 0.140 to 0.780 mg Li · kg⁻¹.

Table 2

Contents of individual lithium forms after the end of plant vegetation [mg Li · kg⁻¹]

Series	Li addition [mg · pot ⁻¹]	Dose of organic matter [g · pot ⁻¹]	Forms of lithium				
			F-1	F-2	F-3	F-4	F-5
1	0	0	0.260	0.140	0.212	0.709	6.36
2	10	0	0.515	0.406	0.238	0.822	9.71
3	20	0	0.931	0.671	0.242	1.224	6.95
4	10	26	0.472	0.393	0.212	0.446	8.14
5	20	26	0.976	0.664	0.226	0.415	7.72
6	10	56	0.440	0.444	0.299	0.362	7.66
7	20	56	0.972	0.780	0.340	0.462	7.76
8	10	78	0.507	0.437	0.310	0.468	8.08
9	20	78	0.810	0.735	0.340	0.349	7.82

Lithium doses of 10 and 20 mg Li per pot very distinctly affected the amount of lithium extracted using 2.5 % CH₃COOH as F-2 form. In this case a similar dependence occurred as in F-1 fraction.

The content of lithium bound to organic matter F-3, extracted with 0.1 mol K₂P₄O₇ · dm⁻³ ranged from 0.212 to 0.340 mg Li · kg⁻¹. The quantity of cation bound to organic matter extracted using 0.1 mol K₂P₄O₇ · dm⁻³ was visibly increasing on treatment with growing lithium doses. Assuming eg the amount of lithium bound to organic matter extracted on the control treatment with natural content of this element as 100, one may conclude that at increasing lithium doses the amount of extracted cation was greater by 12 and 14 %.

Application of organic matter dose of 52 and 78 g per pot on treatments with elevated lithium content caused an increase of the quantity of extracted cation bound to organic matter which was between 26 and 40 % bigger in relation to the control treatments with the same lithium level. This problem may be explained by the fact that in result of organic matter application sorption ability towards metals increases thus limiting their uptake by plants. The strength of metal bonding by organic matter is different for individual metals. Forming and durability of chelate bonds depend on the kind and molecular weight of humic acids [12]. Dziadowiec et al [13] declared that complexes of fulvic acids, due to smaller molecular weight and greater content of functional groups, are better soluble than humic acid complexes.

Lithium content in F-4 fraction extracted with Tamm reagent (0.1 mol H₂C₂O₄ · dm⁻³ + 0.175 mol (NH₄)₂C₂O₄ · dm⁻³) determined as the form adsorbed on the surface of Fe, Mn and Al oxides fluctuated from 0.349 to 1.224 mg Li · kg⁻¹. The amount of cation extracted using this reagent rose by 16 and 73 % with increasing doses of organic matter. Increasing doses of organic matter ie 26, 52 and 78 g per pot on treatments with growing lithium doses caused a decrease of the quantity of lithium extracted with Tamm reagent (0.1 mol H₂C₂O₄ · dm⁻³ + 0.175 mol (NH₄)₂C₂O₄ · dm⁻³) which was between 2 and 3.5 times smaller on these treatments (Table 5).

Conclusions

1. Contents of individual lithium forms obtained in result of metal sequencing extraction depended on natural content of this element in soil, lithium dose and the dose of applied compost (organic matter).

2. Increasing lithium doses applied as soluble salt (LiCl) in the amounts of 10 and 20 mg Li · pot⁻¹ positively affected the amounts of cation extracted in individual forms in result of metal sequencing extraction.

References

- [1] Bogacz W.: Zesz. Probl. Post. Nauk Rol. 1996, **434**, 1011–1015.
- [2] Kabata-Pendias A. and Pendias H.: Wyd. Nauk. PWN, Warszawa 1999, p. 103–106.
- [3] Gambuś F. and Gorlach E.: Zesz. Nauk. A.R. Szczecin, 172, Rolnictwo 1996, **62**, 131–137.
- [4] Jurkowska H.: Zesz. Probl. Podst. Nauk. Rol. 1997, **448** b, 101–109.
- [5] Motowicka-Terelak T., Terelak H. and Pietruch Cz.: Zesz. Probl. Post. Nauk. Rol. 1997, **448** b, 211–216.
- [6] Rogóż A.: J. Elementol. 2004, **9**(4), 717–725.
- [7] Rogóż A.: Ecol. Chem. Eng. (in press in this volume).
- [8] Praca zbiorowa: Przewodnik do ćwiczeń z chemii rolnej, E. Gorlach (ed.), Wyd. AR Kraków, 1999.
- [9] Iu K.L., Pulford I.D. and Duncan H.J.: Plant Soil, 1981, **59**, 317–326.
- [10] Bogacz W.: Zesz. Probl. Post. Nauk Rol. 1996, **434**, 1017–1023.
- [11] Mazur T.: Zesz. Probl. Post. Nauk. Rol. 1995, **422**, 9–19.
- [12] Mercik S. and Kubiak I.: Zesz. Probl. Post. Nauk. Rol. 1995, **422**, 19–30.
- [13] Dziadowiec H.: Zesz. Probl. Post. Nauk Rol. 1993, **411**, 269–282.

WPLYW WŁAŚCIWOŚCI GLEBY A FITOPRZYSWAJALNOŚĆ LITU Cz. 2. ZAWARTOŚĆ LITU W GLEBIE PO ZAKOŃCZONYM OKRESIE WEGETACJI

Katedra Chemii Rolnej i Środowiskowej
Uniwersytet Rolniczy im. Hugona Kołłątaja w Krakowie

Abstrakt: Po zakończonym okresie wegetacji żyta pobrano próbki glebowe z każdej serii w celu prześledzenia zmian, jakie zaszły we właściwościach fizycznych i chemicznych. Wzrastające dawki materii organicznej oraz zastosowane dwie dawki litu powodowały zmiany właściwości fizycznych i chemicznych gleby. Zastosowane dawki litu oraz materii organicznej wpływały na wartość pH, wartość kwasowości hydrolitycznej, zawartość C-organicznego oraz na zawartość litu w glebie. W celu określenia zawartości litu oraz jego form w glebie wykorzystano metodę sekwencyjnej ekstrakcji metali, stosując roztwory o różnej sile ługowania: H₂O; 2,5 % CH₃COOH; 0,1 mol K₂P₄O₇ · dm⁻³; 0,1 mol H₂C₂O₄ · dm⁻³ + 0,175 mol (NH₄)₂C₂O₄ · dm⁻³. W wyniku sekwencyjnej ekstrakcji oznaczono formy litu od łatwo rozpuszczalnych, czyli dostępnych dla roślin, przez słabo związane z kompleksem sorpcyjnym, po trudno rozpuszczalne, nieuruchamiane, a więc niedostępne dla roślin. Zawartość litu w poszczególnych frakcjach była dość zróżnicowana. Czynniki decydującymi o poziomie tego pierwiastka w poszczególnych formach w glebie były zastosowana dawka litu oraz wzrastające dawki materii organicznej, jednego z parametrów wpływających na kompleks sorpcyjny.

Zastosowane dawki litu w ilości 10 i 20 mg Li · wazon⁻¹ wpływały bardzo wyraźnie na ilość wyekstrahowanego litu przy użyciu H₂O – formy F-1, a zastosowane wzrastające dawki materii organicznej wpływały ograniczająco na ilość litu wyekstrahowanego przy użyciu H₂O. Zawartość litu związanego z materia organiczną F-3, ekstrahowanego 0,1 mol K₂P₄O₇ · dm⁻³, wahała się od 0,212 do 0,340 mg Li · kg⁻¹. Ilość kationu związanego z materia organiczną wyekstrahowanego 0,1 mol K₂P₄O₇ · dm⁻³ wyraźnie wzrastała w obiektach ze wzrastającymi dawkami litu.

Słowa kluczowe: formy litu w glebie, sekwencyjna ekstrakcja, właściwości gleby