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Zinc speciation in soil solution of selected Poland's agricultural soils

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Abstract

The influence of soil properties (pH, organic carbon content, soil texture, content of available zinc (Zn)) on the percentage share of the various forms of Zn in the soil solution of 62 arable soils of Poland were investigated. The soil solution was obtained following the vacuum displacement method. Speciation of zinc ions (Zn^{2+}) was determined with *MINTEQA2* for *Windows* software. The investigation showed that the concentration of active Zn^{2+} in the soil solution and related Zn bioavailability for the most part relies upon soil reaction when compared with other investigated physical and chemical soil properties. The effects of soil texture, and above all those of organic matter contents in soil, are significantly lesser. The results of speciation analysis showed that apart from physical and chemical soil properties active Zn^{2+} are the main forms of Zn occurring in the soil solution. Depending on soil properties these ions add up to from 60% to almost 80% of all Zn forms in the soil solution. Zinc forms can be arranged with regard to their percentage share in the soil solution as follows: $Zn\text{-DOC} > ZnCO_3 > ZnCl^+ > ZnHCO_3^+ > ZnOH^+$.

Key words: organic matter, pH, soil solution, soil texture, speciation, zinc.

Introduction

The soil solution represents the milieu for nutrient uptake, thus it can be used for diagnostics of plant needs for fertilization with microelements, including zinc. The total concentration of a given metal in a sample presents only partial analytical information. It does not specify any environmental processes, which in the element investigated are involved, and for that reason it does not put in the picture information on element mobility and bioavailability as well as its real toxicity (McLaughlin et al., 2000, van Leeuwen et al., 2005). Hydrolysis reactions along with the formation of ion pairs and complexes in the soil solution bring about various ion forms such as free ions, complex ions, neutral complexes (Wolt, 1994). Ion forms of metals in the soil solution are characteristic of differentiated reaction ability (ion activity) which influences ion mobility and bioavailability (Ge et al., 2005). According to numerous authors, the activity of ions in the soil solution is a key aspect in determination of their bioavailability and toxicity for a range of organisms (Weng et al., 2001; Aldrich et al., 2002; Cancés et al., 2003).

Up to date, numerous researchers have showed that zinc concentration in the soil solution depends on soil physical and chemical properties. Higher zinc concentrations have been observed in the soil solution of acidic, sandy soils with low contents of organic matter (Peijnenburg et al., 2000; Lofts et al., 2004). In view of that, in this study a hypothesis was assumed that soil

properties could also influence the percentage share of different zinc forms in the soil solution.

The aim of the present study was to evaluate the effects of selected soil physical and chemical properties, such as: soil texture, soil pH, organic carbon content and content of available Zn in soil, on the concentration of zinc in the soil solution. The trial was undertaken using speciation analysis in order to examine to what extent the above mentioned soil properties determine the incidence of different zinc forms in the soil solution so as to explain differences in zinc availability under various soil and fertilization conditions.

Materials and methods

There were investigated 62 soil samples collected in autumn 2011 from the Polish agricultural soils. With each voivodeship from Poland, soil samples were taken from the following types of soils (FAO, 2006): *Podzol (PZ)* – 17 soil samples, *Umbrisol (UM)* – 17 soil samples, *Luvisol (LV)* – 17 soil samples and *Cambisol (CM)* – 11 soil samples. Soil samples were collected from 0–30 cm layer in the autumn after the harvest of crops (winter wheat, *Triticale*). The soils were air dried and ground in an agate mortar to pass through a 2.0 mm sieve for analysis. The physical and chemical properties such as: pH – by potentiometric method after extraction with 1 mol dm⁻³ KCl, soil texture <0.02 mm

– by laser diffraction method (Ryzak et al., 2007), total organic carbon content – by dry combustion at high (900°C) temperature (Tiessen, Moir, 1993), zinc (Zn) – after extraction in 1 mol dm⁻³ HCl (10 g of soil was shaken with 100 ml HCl on a rotary shaker for 2 hours at 120 revolutions per minute) by inductively coupled plasma atomic emission spectrometry (ICP-AES) were determined in the soil samples. On the basis of available Zn in soil, soil samples were divided into two groups: medium and high content of Zn extractable by 1 M HCl – according to Polish Standard (PN-92 R-04016, 1992).

The soil solution of all observed soils was obtained by modified vacuum displacement method (Wolt, Gravel, 1986). Air dried soil samples (100 g each) were wetted with redistilled water to 100% field water capacity and then incubated at room temperature for 72 hours. Once the balance between solid and liquid soil phases was established the soil solution was obtained with the use of a vacuum pump (“Dynavac OP4”, Australia) under pressure 0.08–0.09 MPa. The obtained soil solution was filtered through filter paper. The total concentration of Zn in soil solution was determined by ICP-AES. Different forms of Zn in soil solution such as: Zn²⁺ (active/free ions), Zn-DOC (organic complexes with zinc), ZnCl⁺ (chloride complexes), ZnCO₃, ZnHCO₃⁺ (complexes with carbonates), ZnOH⁺ (hydroxyl complexes) were calculated with *MINTEQA2* for *Windows* software. *MINTEQA2* is a geochemical speciation model which can be used to calculate the theoretical mass distribution of metals between free ions, dissolved complexes, metals adsorbed on hydrous iron oxide surfaces and solid phases. Adsorption modelling is based on the diffuse layer model, and surface complexation theory. *MINTEQA2* can be used to predict metal behaviour in a variety of experimental and natural systems for which input data, such as trace and major ion concentrations, pH, redox conditions and hydrous iron oxide concentrations, are available. The model makes certain assumptions, such as that: thermodynamic equilibrium has been achieved, all potential ligand groups have been identified and the appropriate thermodynamic data included in the database (Allison et al., 1991).

The results were statistically analyzed with *ANOVA* and simple linear regression. The differences between means were analyzed with Tukey's test at $p = 0.05$.

Table 2. Total concentration of zinc (Zn) and concentration of zinc ions (Zn²⁺) in the soil solution (μmol dm⁻³) according to soil properties

| Zn form | Fine earth fraction % | | | | Soil pH | | | | Organic carbon content g kg ⁻¹ | | Content of zinc extractable by 1 M HCl in soil | |
|---------------------|-----------------------|-------|-------|------|---------|---------|---------|------|---|------|--|------|
| | <10 | 10–20 | 20–35 | >35 | <4.5 | 4.6–5.5 | 5.6–6.5 | >6.6 | <10 | >10 | medium | high |
| Zn | 1.62 | 1.48 | 1.01 | 0.76 | 2.37 | 1.45 | 1.16 | 0.68 | 1.35 | 1.16 | 1.08 | 1.36 |
| LSD _{0.05} | 0.531 | | | | 0.378 | | | | 0.422 | | 0.435 | |
| Zn ²⁺ | 1.43 | 1.14 | 0.79 | 0.48 | 2.08 | 1.15 | 0.89 | 0.55 | 1.10 | 0.90 | 0.83 | 1.12 |
| LSD _{0.05} | 0.469 | | | | 0.331 | | | | 0.380 | | 0.396 | |

Results and discussion

The samples differed in terms of their physical and chemical properties, such as: content of soil particles <0.02 mm, soil reaction, organic carbon content, content of Zn extractable by 1 M HCl in soil (Table 1).

Table 1. Physical and chemical properties of investigated soils samples (n = 62)

| | Content of fraction (%) with particle diameter <0.02 mm | | | |
|------------------------|---|---------|---------|------|
| | <10 | 11–20 | 21–35 | >35 |
| Number of soil samples | 17 | 17 | 17 | 11 |
| | pH _(KCl) | | | |
| | <4.5 | 4.6–5.5 | 5.6–6.5 | >6.6 |
| Number of soil samples | 12 | 17 | 12 | 21 |
| | Content of organic carbon g kg ⁻¹ | | | |
| | <10 | >10 | | |
| Number of soil samples | 33 | 29 | | |
| | Content of zinc extractable by 1 M HCl in soil | | | |
| | medium | high | | |
| Number of soil samples | 35 | 27 | | |

The total concentration of Zn and the concentration of active Zn²⁺ in the soil solution depended on physical and chemical properties of the soils analyzed (Tables 2–3). Total concentration of Zn ranged from 0.68 to 2.37 μmol dm⁻³. The concentration of active Zn²⁺ was somewhat lower and ranged from 0.48 to 2.08 μmol dm⁻³.

For the most part, soil reaction was the factor which influenced the concentration of Zn and free Zn²⁺ in the soil solution. Both the total concentration of Zn and the concentration of free Zn²⁺ were negatively correlated with soil pH (Table 3) According to Tipping et al. (2003) and Tye et al. (2003), soil reaction is the main factor which determines the activity of free Zn²⁺ and related Zn bioavailability. With a decreasing pH value Zn²⁺ are displaced by H⁺ and Al³⁺ in soil sorption complex, then the solubility of Zn compounds in the soil solution increases, and as a result Zn is represented in the solution as readily available free ions (Cancés et al., 2003; Stephan

et al., 2008). According to Burcu Özkaraova Güngör and Bekbölet (2010), the amount of organic matter in soil determines Zn availability for plants. In the present study, no statistical significance was indicated for organic matter effects on the concentration of Zn and free Zn^{2+} in the soil solution (Tables 2–3).

Table 3. Correlation coefficients between total concentration of zinc (Zn) and concentration of zinc ions (Zn^{2+}) and soil properties

| Zn form | Fine earth fraction % | Soil pH | Organic carbon content $g\ kg^{-1}$ | Content of Zn extractable by 1 M HCl in soil |
|-----------|-----------------------|---------|-------------------------------------|--|
| Zn | -0.40* | -0.69** | -0.24 | +0.61** |
| Zn^{2+} | -0.45* | -0.72** | -0.29 | +0.64** |

* – significant at $p = 0.05$, ** – significant at $p = 0.01$

In line with Zn forms complexes with soil organic matter rather fast – on the other hand, definitely slower than copper or calcium (Cancés et al., 2003; Stephan et al., 2008). The total concentration of Zn and the concentration of free Zn^{2+} in the soil solution decreased with increasing share of fine earth fraction. Wolt (1994) believes that nutrient concentration is usually higher in the solutions of light, sandy soils when compared with the solutions of soils with greater fine earth fraction contents. The share of free Zn^{2+} in Zn total concentration in the soil solution decreased from 77% to 68% with increased content of fine earth fraction in soil. Similar dependencies were noted in the case of Zn complexes with organic matter, the share of which decreased from 15.6% to 8.2%. In the soil solution analyzed there dominated free Zn^{2+} , the share of which in the total concentration of Zn was from 67% to 79%. In reference to *MINTEQA2* assessment complex Zn associations with organic matter also represented substantial shares in the soil solution (from 7.3% to 18.5%) (Table 4).

Table 4. Percentage share of individual zinc (Zn) forms in the soil solution according to soil texture

| Fine earth fraction % | Zn^{2+} | Zn-DOC | $ZnCl^+$ | $ZnCO_3$ | $ZnHCO_3^+$ | $ZnOH^+$ |
|-----------------------|-----------|--------|----------|----------|-------------|----------|
| <10 | 76.9 | 15.6 | 3.1 | 2.6 | 1.9 | 0.0 |
| 10–20 | 73.7 | 12.0 | 2.7 | 7.0 | 3.0 | 1.6 |
| 20–35 | 71.2 | 9.9 | 3.8 | 9.6 | 3.7 | 1.8 |
| >35 | 68.3 | 8.2 | 3.6 | 12.9 | 4.3 | 2.7 |

Zn^{2+} – active/free ions, Zn-DOC – organic complexes with zinc, $ZnCl^+$ – chloride complexes, $ZnCO_3$, $ZnHCO_3^+$ – complexes with carbonates, $ZnOH^+$ – hydroxyl complexes

The highest percentage share of Zn^{2+} and Zn-organic matter complexes with reference to the total concentration of Zn was observed in the soil solution of the most acidic soils analyzed (Table 5). With increasing soil pH value there was decreasing the share of Zn^{2+} and metal-organic complexes in the soil solution. Other forms of Zn ($ZnCl^+$, $ZnOH^+$, Zn- CO_3 and $ZnHCO_3^+$)

did not occur in the solutions of examined soils which indicated the lowest pH. In the solution of soils with pH 5.0 and 6.0 the share of other Zn forms in Zn total concentration was relatively low. Zinc complexes with carbonates constituted as much as 14.9% only at soil pH above 6.5 (Table 5).

Table 5. Percentage share of individual zinc (Zn) forms in the soil solution according to soil pH

| pH | Zn^{2+} | Zn-DOC | $ZnCl^+$ | $ZnCO_3$ | $ZnHCO_3^+$ | $ZnOH^+$ |
|---------|-----------|--------|----------|----------|-------------|----------|
| <4.5 | 79.0 | 18.5 | 2.5 | 0.0 | 0.0 | 0.0 |
| 4.6–5.5 | 72.4 | 12.7 | 2.9 | 3.0 | 3.5 | 0.0 |
| 5.6–6.5 | 71.9 | 10.8 | 3.9 | 7.3 | 3.7 | 2.3 |
| >6.5 | 67.0 | 7.3 | 4.1 | 14.9 | 3.7 | 3.0 |

Explanations under Table 4

In the soil solution of analyzed soils with differentiated contents of organic matter there always dominated Zn^{2+} form. The share of free Zn^{2+} was decreasing (from 74.8% to 60.2%) with increasing organic carbon contents in soil. At the same time, the

share of zinc-organic matter complexes increased by 10%, and that of zinc-carbohydrate associations by 3% (Table 6). Other complexes which were formed showed similar incidence degree.

Table 6. Percentage share of individual zinc (Zn) forms in the soil solution according to contents of organic carbon in soil

| Organic carbon content $g\ kg^{-1}$ | Zn^{2+} | Zn-DOC | $ZnCl^+$ | $ZnCO_3$ | $ZnHCO_3^+$ | $ZnOH^+$ |
|-------------------------------------|-----------|--------|----------|----------|-------------|----------|
| <10 | 74.8 | 11.5 | 3.2 | 6.1 | 2.9 | 1.5 |
| >10 | 60.2 | 21.6 | 3.6 | 9.0 | 3.5 | 2.1 |

Explanations under Table 4

Likewise in the above mentioned cases, Zn^{2+} form also dominated in the solution of soils with differentiated contents of plant available Zn (Table 7). Soil differentiation with regard to content of available Zn

did not change relations among Zn forms observed in the soil solution, and these can be arranged in the following order: $Zn^{2+} > Zn\text{-DOC} > ZnCO_3 > ZnCl^+ > ZnHCO_3^+ > ZnOH^+$.

Table 7. Percentage share of individual zinc (Zn) forms in the soil solution according to contents of Zn extractable by 1 M HCl in soil

| Content of Zn extractable by 1 M HCl in soil | Zn^{2+} | Zn-DOC | $ZnCl^+$ | $ZnCO_3$ | $ZnHCO_3^+$ | $ZnOH^+$ |
|--|-----------|--------|----------|----------|-------------|----------|
| Medium | 71.8 | 12.1 | 3.7 | 8.1 | 3.1 | 1.4 |
| High | 72.2 | 9.6 | 3.4 | 7.8 | 3.0 | 1.8 |

Explanations under Table 4

The results of Zn speciation analysis obtained in the present study are in line with those reported by other authors. According to Pérez-Esteban et al. (2013), Zn^{2+} are the main form of Zn incidence in the soil solution, and at the pH value = 6.2 they account for 75% of this element amount in the soil solution. However, the share of this form in the total concentration of Zn in the soil solution decreases with increasing soil pH. This tendency was also confirmed by Dang et al. (1996), Fotovat and Naidu (1997) and Zampella and Adamo (2010) as well Saeki et al. (2002). The study by Stephan et al. (2008) and Hernandez-Soriano and Jimenez-Lopez (2012) conducted on neutral and alkaline soils indicated from 8% to 30% share of Zn^{2+} in the total concentration of Zn in the soil solution. The results of speciation analysis carried out by Dang et al. (1996) with the use of *GEOCHEM* software showed that Zn^{2+} amounted to 30–72% of Zn total concentration in the soil solution. Similar results were obtained by Fotovat and Naidu (1997) who showed with *MINTEQA2* software that even 66% of Zn could occur in the soil solution as Zn^{2+} . Even higher, reaching 90% share of Zn^{2+} form was observed by Pérez-Esteban et al. (2013) in the soil solution of sandy soil with acidic reaction (pH = 5.5).

In the present study, zinc-organic complexes (Zn-DOC) were additionally determined in the soil solution investigated, and these constituted from 7.3% to 21.6% (Tables 4–7). The share of zinc-organic matter complexes in the total concentration of Zn in the soil solution depended on soil reaction as well as the content of organic carbon in soil (Tables 5–6). In research conducted by Hernandez-Soriano and Jimenez-Lopez (2012) Zn complexes with organic matter on average amounted to 5% and 13% of Zn total concentration in the soil solution. In the soil solution analyzed, Zn was also observed as complexes $ZnHCO_3^+$ and $Zn\text{-CO}_3$, the share of which in the total concentration of Zn in the soil solution depended on the value of soil pH. In the solution of soils with pH < 4.5 no incidence of the above mentioned forms was noted but with increasing pH value up to >6.5 there was observed increased incidence of both $ZnHCO_3^+$ (3.7%) and $Zn\text{-CO}_3$ (14.9%) complexes (Table 5). According to Dang et al. (1996), $ZnHCO_3^+$ form constitutes up to 16.8% of the total concentration of Zn in the solution of alkaline soils. Furthermore, according

to the estimates obtained with the use of *MINTEQA2* software reported by Khoshgoftar et al. (2004), this form can amount to even 23% of Zn total concentration in the soil solution.

The results of Dang et al. (1996) and Pérez-Esteban et al. (2013) confirmed that in the soil solution there could occur small amounts of Zn associated with inorganic ligands (e.g., OH^- , NO_3^- , Cl^- , PO_4^{3-}). In the present study on Zn speciation using *MINTEQA2* software there were observed only small ratios of $ZnOH^+$ and $ZnCl^+$ forms, and incidence of other forms was not observed.

Conclusions

1. The concentration of active zinc ions (Zn^{2+}) in the soil solution for the most part relies upon soil reaction when compared with other investigated physical and chemical soil properties. The effects of soil texture, and above all those of organic matter contents in soil, are significantly lesser. Higher Zn concentration can be projected in the soil solution of acidic soils when compared with soils with neutral soil reaction. Moreover, there can also be expected higher Zn concentration in the soil solution of sandy soils in comparison with that in medium and heavy soils.

2. The results of speciation analysis showed that apart from physical and chemical soil properties active Zn^{2+} are the main forms of Zn occurring in the soil solution. Depending on soil properties these ions add up to from 60% to almost 80% of all Zn forms in the soil solution. Zinc forms can be arranged with regard to their percentage share in the soil solution as follows: Zn-DOC > $ZnCO_3$ > $ZnCl^+$ > $ZnHCO_3^+$ > $ZnOH^+$.

3. Because Zn^{2+} dominate in the soil solution, the measurement of Zn concentration in the soil solution can be used in diagnostics of Zn fertilization of cultivated plants.

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References

- Allison J. D., Brown D. S., Novo-Gradac K. J. 1991. *MINTEQA2/PRODEFA2*, a geochemical computer assessment model for environmental systems. EPA/600/3-91/021. Athens, USA.
- Aldrich A. P., Kistler D., Sigg L. 2002. Speciation of Cu and Zn in drainage water from agricultural soils. *Environmental Science Technology*, 36: 4824–4830
<http://dx.doi.org/10.1021/es025813x>
- Burcu Özkaraova Güngör E., Bekbölet M. 2010. Zinc release by humic and fulvic acid as influenced by pH, complexation and DOC sorption. *Geoderma*, 159 (1–2): 131–138
<http://dx.doi.org/10.1016/j.geoderma.2010.07.004>
- Cancés B., Ponthieu M., Castrec-Pouelle M., Aubry E., Benedetti M. F. 2003. Metal ions speciation in a soil and its soil solution: experimental data and model results. *Geoderma*, 113 (3–4): 341–355
[http://dx.doi.org/10.1016/S0016-7061\(02\)00369-5](http://dx.doi.org/10.1016/S0016-7061(02)00369-5)
- Dang Y. P., Tiller K. G., Dalal R. C., Edwards D. G. 1996. Zinc speciation in soil solutions of *Vertisols*. *Australian Journal of Soil Research*, 34: 369–383
<http://dx.doi.org/10.1071/SR9960369>
- FAO 2006. World reference base for soil resources. A framework for international classification, correlation and communication. *World Soil Resources Report*, 103. Food and Agriculture Organization of the United Nations, Rome, 116 p.
- Fotovat A., Naidu R. 1997. Ion exchange resin and *MINTEQA2* speciation of Zn and Cu alkaline sodic and sodic extracts. *Australian Journal of Soil Research*, 35: 711–726
<http://dx.doi.org/10.1071/S96079>
- Ge Y., MacDonald D., Sauvé S., Hendershot W. H. 2005. Modelling of Cd and Pb speciation in soil solutions by WinHumicV and NICA-Donnan model. *Environmental Modelling and Software*, 20: 353–359
<http://dx.doi.org/10.1016/j.envsoft.2003.12.014>
- Hernandez-Soriano M. C., Jimenez-Lopez J. C. 2012. Effects of soil water content and organic matter addition on the speciation and bioavailability of heavy metals. *Science of the Total Environment*, 423: 55–61
<http://dx.doi.org/10.1016/j.scitotenv.2012.02.033>
- Khoshgoftar A. H., Shariatmadari H., Karimian N., Kalbasi M., van der Zee S. E. A. T. M., Parker D. R. 2004. Salinity and zinc application effects on phytoavailability of cadmium and zinc. *Soil Science Society of America Journal*, 68: 1885–1889
<http://dx.doi.org/10.2136/sssaj2004.1885>
- Lofts S., Spurgeon D. J., Svendsen C., Tipping E. 2004. Deriving soil critical limits for Cu, Zn, Cd, and pH: a method based on free ion concentrations. *Environmental Science Technology*, 38: 3623–3631
<http://dx.doi.org/10.1021/es030155h>
- McLaughlin M. J., Hamon R. E., McLaren R. G., Speir T. W., Rogers S. L. 2000. A bioavailability-based rationale for controlling metal and metalloid contamination of agricultural land in Australia and New Zealand. *Australian Journal of Soil Research*, 38: 1037–1086
<http://dx.doi.org/10.1071/SR99128>
- Peijnenburg W., Baerselman R., de Groot A., Jager T., Leenders D., Posthuma L., van Veen R. 2000. Quantification of metal bioavailability for lettuce (*Lactuca sativa* L.) in field soils. *Archives of Environmental Contamination and Toxicology*, 39: 420–430
<http://dx.doi.org/10.1007/s002440010123>
- Pérez-Esteban J., Escolástico C., Moliner A., Masaguer A. 2013. Chemical speciation and mobilization of copper and zinc in naturally contaminated mine soils with citric and tartaric acids. *Chemosphere*, 90: 276–283
<http://dx.doi.org/10.1016/j.chemosphere.2012.06.065>
- PN-92 R-04016. 1992. Chemical and agricultural analysis of soil. Determination of the content of available zinc in mineral soils. Polish Committee for Standardization (in Polish)
- Ryzak M., Bieganowski A., Walczak R. T. 2007. Application of laser diffraction method for determination of particle size distribution of grey-brown podzolic soil. *Research in Agricultural Engineering*, 53 (1): 34–38
- Saeki K., Kunito T., Oyaizu H., Matsumoto S. 2002. Relationship between bacterial tolerance levels and forms of copper and zinc in soils. *Journal of Environmental Quality*, 31: 1570–1575
<http://dx.doi.org/10.2134/jeq2002.1570>
- Stephan C. H., Courchesne F., Hendershot W. H., McGrath S. P., Chaudri A. M., Sappin-Didier V., Sauvé S. 2008. Speciation of zinc in contaminated soils. *Environmental Pollution*, 155 (2): 208–216
<http://dx.doi.org/10.1016/j.envpol.2007.12.006>
- Tiessen H., Moir J. O. 1993. Total and organic carbon. Carter M. E. (ed.). *Soil sampling and methods of analysis*. Florida, USA, p. 187–211
- Tipping E., Rieuwerts J., Pan G., Ashmore M. R., Lofts S., Hill M. T. R., Farago M. E., Thornton I. 2003. The solid-solution partitioning of heavy metals (Cu, Zn, Cd, Pb) in upland soils of England and Wales. *Environmental Pollution*, 125: 213–225
[http://dx.doi.org/10.1016/S0269-7491\(03\)00058-7](http://dx.doi.org/10.1016/S0269-7491(03)00058-7)
- Tye A. M. S., Young D., Crout N. M. J., Zhang H., Preston S., Barbosa-Jefferson V. L., Davison W., McGrath S. P., Paton G. I., Kilham K., Resende L. 2003. Predicting the activity of Cd²⁺ and Zn²⁺ in soil pore water from the radio-labile metal fraction. *Geochimica Cosmochimica Acta*, 67: 375–385
[http://dx.doi.org/10.1016/S0016-7037\(02\)01138-9](http://dx.doi.org/10.1016/S0016-7037(02)01138-9)
- van Leeuwen H. P., Town R. M., Buffle J., Cleven R. F. M. J., Davison W., Puy J., van Riemsdijk W. H. 2005. Dynamic speciation analysis and bioavailability of metals in aquatic systems. *Environmental Science and Technology*, 39: 8545–8556
<http://dx.doi.org/10.1021/es050404x>
- Weng L., Temminghoff E. J., van Riemsdijk W. H. 2001. Determination of the free ion concentration of trace metals in soil solution using a soil column Donnan membrane technique. *European Journal of Soil Science*, 52: 629–637
<http://dx.doi.org/10.1046/j.1365-2389.2001.00416.x>
- Wolt J. D. 1994. *Soil solution chemistry. Application to environmental science and agriculture*. New York, USA, 337 p.
- Wolt J. D., Graveel J. 1986. A rapid routine method for obtaining soil solution using vacuum displacement. *Soil Science Society of America Journal*, 50: 602–605
<http://dx.doi.org/10.2136/sssaj1986.03615995005000030012x>
- Zampella M., Adamo P. 2010. Chemical composition and Zn bioavailability of the soil solution extracted from Zn amended variable charge soils. *Journal of Environmental Sciences*, 22 (9): 1398–1406
[http://dx.doi.org/10.1016/S1001-0742\(09\)60266-7](http://dx.doi.org/10.1016/S1001-0742(09)60266-7)

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Cinko formos Lenkijos žemės ūkio veiklai naudojamų dirvožemių tirpale

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Santrauka

Tirta dirvožemio savybių – pH, organinės anglies kiekio, granulometrinės sudėties, augalų įsisavinamo cinko (Zn) kiekio – įtaka įvairių cinko formų procentinei daliai Lenkijos ariamų dirvožemių 62 ėminių tirpaluose. Dirvožemių tirpalai gauti taikant vakuumo išstūmimo metodą. Cinko jonų (Zn^{2+}) forma nustatyta *MINTEQA2 Windows* programine įranga. Tyrimas parodė, kad aktyvių Zn^{2+} koncentracija dirvožemių tirpale ir su tuo susijęs Zn įsisavinimas, palyginus su kitomis tirtomis dirvožemio fizikinėmis bei cheminėmis savybėmis, labiausiai priklauso nuo dirvožemio rūgštumo. Dirvožemio granulometrinės sudėties ir ypač organinės medžiagos kiekio įtaka yra žymiai mažesnė. Cinko formų analizės rezultatai parodė, kad, nepriklausomai nuo dirvožemio fizikinių ir cheminių savybių, dirvožemio tirpale pasitaikanti pagrindinė Zn forma yra aktyvus Zn^{2+} . Priklausomai nuo dirvožemio savybių, dirvožemio tirpale šie jonai sudaro nuo 60 iki beveik 80 % visų Zn formų. Pagal procentinę dalį dirvožemio tirpale Zn formos išsidėsto taip: $Zn-DOC > ZnCO_3 > ZnCl^+ > ZnHCO_3^+ > ZnOH^+$.

Reikšminiai žodžiai: cinkas, dirvožemio granulometrinė sudėtis, dirvožemio tirpalas, forma, organinė medžiaga, pH.