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CONTENT OF LEAD IN MAIZE AND SOIL FERTILIZED WITH ORGANIC MATERIALS DERIVED FROM WASTE

ZAWARTOŚĆ OŁOWIU W KUKURYDZY I GLEBIE NAWOŻONEJ MATERIAŁAMI ORGANICZNYMI POCHODZENIA ODPADOWEGO

Abstract: The research was conducted to determine the influence of fertilization with waste organic materials on the content and uptake of lead by maize as well as on the total content of lead in soil. The three-year field experiment comprised 7 treatments: a non-fertilized soil (control treatment) as well as a soil fertilized with mineral fertilizers, cattle manure, green waste compost, sewage sludge, compost from sewage sludge and straw as well as with a mixture of sewage sludge and hard coal ash. Maize cultivated for silage was the test plant. The lead content in the above-ground parts of plants and in the soil was determined using ICP-AES method. During the research, no lead pollution of the soil or the above-ground parts of the maize was found. No statistically significant effect of fertilization on the lead content in the maize was found or the fertilized plants contained considerably less of the element than the control plants. The lowest weighted mean content of lead was found in the maize fertilized with the green waste compost, sewage sludge as well as with the compost from sludge and straw. Soil with the lowest lead content was the soil of the treatment fertilized with organic materials. The soil fertilized with the green waste compost (all the years), sewage sludge (2nd year) as well as with the mixture of sludge and ash (1st and 2nd year) contained significantly more lead than the soil fertilized with mineral fertilized.

Keywords: waste organic materials, sewage sludge, compost, lead, maize, soil

Introduction

One of the ways of lead penetrating into animal and human organisms is through food. Lead, like other heavy metals, accumulates in successive links of the "soil-plant-

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-animal-human" food chain. Introducing high doses of lead to soil translates into an increased risk of accumulating this element in plant, animal and human organisms.

According to the current state of knowledge, lead is not an element which has physiological functions in living organisms, whereas its harmful effect is well known. Lead shows genotoxic effect (by inhibiting the processes of DNA repair and generating free radicals) as well as neurotoxic and teratogenic effects [1–3, based on different sources]. It also impairs the effect of the vascular and immunological systems [2, based on different sources]. Having an impact on the human organism, lead is particularly dangerous for small children. In plants, excessive exposition to this element inhibits total chlorophyll level and disturbs the photosynthesis, nitrogen transformation (hampering the activity of nitrate reductase), and cell division processes as well as disturbs water management [4, 5 based on different sources]. Kurtyka et al [6] found that exposition to lead leads to diminishing growth of maize coleoptile segments.

The aim of the research was to determine the influence of fertilization with waste organic materials on the content and uptake of lead by maize as well as on the total lead content in soil.

Material and methods

The three-year field experiment was set up in 2008 at an experimental station of the University of Agriculture in Krakow, located in Krakow-Mydlniki. The experiment was conducted on brown soil typical proper, with graining of light soil. It was an acid soil $(pH_{KCl} = 5.40)$, with a very high content of available phosphorus and potassium (94.9 mgP and 219.2 mgK \cdot kg⁻¹ d.m.). The soil contained 9.88 gC_{org} \cdot kg⁻¹ d.m., 1.07 gN_{total} \cdot kg⁻¹ d.m. and 26.5 mgPb \cdot kg⁻¹ d.m. The content of trace elements in the soil did not exceed the limit values established for agricultural use of sewage sludge, neither did the pH_{H2O} value of the soil make fertilization with sewage sludge impossible [7].

The experiment comprised of 7 objects: a non-fertilized soil (control) as well as a soil fertilized with mineral fertilizers, cattle manure, green waste compost (the waste came mainly from the maintenance of urban green areas), municipal sewage sludge, compost from sewage sludge and straw as well as with a mixture of sewage sludge and ash. Each treatment was carried out in 4 replications. Pioneer 'PR 39F58' maize, cultivated for silage and harvested at the wax maturity stage of the grain, was the test plant in all years of the research. In the first year, 160 kgN, 168 kgP₂O₅ (that is 73 kgP) and 140 kgK₂O (that is 116 kgK) per ha were introduced to the soil of fertilized treatments (except the control). To the soil fertilized with the manure and organic materials the whole nitrogen dose was introduced in that fertilizer and those materials. Mineral fertilizers: ammonium nitrate (34 % N), enriched superphosphate (40 % P₂O₅) and potassium chloride (60 % K₂O) were used in order to introduce nutrients to the soil fertilized with mineral fertilizers as well as to even up the doses of phosphorus and potassium in the soil of the remaining fertilized treatments. These fertilizers were also used to conduct fertilization in the second and third year of the experiment, introducing 100 kgN, 30 kgP₂O₅ (13 kgP) and 110 kgK₂O (91 kgK) per ha to the soil each year. Accurate data regarding conditions of conducting the experiment are included in the papers of Tabak and Filipek-Mazur [8, 9].

The content of trace elements in the organic materials used for fertilization did not exceeded the limit values established for agricultural use of sewage sludge [7]. Table 1 shows the lead content in the manure and in the organic materials used in fertilization as well as doses of lead introduced to the soil.

Table 1

Material	Content $[mgPb \cdot kg^{-1} d.m.]$	Dose $[gPb \cdot ha^{-1}]$	
Manure	5.59	31	
Green waste compost	61.33	680	
Sewage sludge	73.50	582	
Compost from sewage sludge and straw	59.50	389	
Mixture of sewage sludge and ash	38.73	428	

Lead content in manure and in waste-derived organic materials as well as doses of lead introduced to soil with manure and materials

The manure was a material which had a significantly different lead content than the other materials. It contained the least of this element (5.59 mgPb \cdot kg⁻¹ d.m.), and as a result the dose of the element introduced with the manure to the soil was also the lowest. The other materials contained between 38.7 mg and 73.5 mgPb \cdot kg⁻¹ d.m. The content of this element in the organic materials increased in the following order: mixture of sludge and ash < compost from sludge and straw \approx green waste compost < sewage sludge. Along with the organic materials, between 389 g and 680 g Pb \cdot ha⁻¹ was introduced to the soil; the highest dose was introduced with the green waste compost and with the sewage sludge.

After harvest, the plant material was dried at 70 °C in a hot air dryer, milled and mineralized in a muffle furnace (8 hours, 450 °C). The residue was evaporated with hydrochloric acid solution, and then diluted in nitric(V) acid solution [10]. The total lead content in the air-dry soil sieved through a sieve with a mesh size of 1 mm was determined after incineration in a furnace (8 hours, 450 °C), evaporation with a mixture of concentrated nitric(V) and chloric(VII) acids, and dilution of the residue in hydrochloric acid solution [10]. The lead content in the above-ground parts of the maize and in the soil was determined with inductively coupled plasma atomic emission spectrometry (ICP-AES) on JY 238 Ultrace apparatus [Jobin Yvon].

Statistica software, version 10 (StatSoft, Inc.), was used for statistical elaboration of the results. A univariate analysis of variation was carried out, and the significance of differences between the mean values was estimated using the Duncan test ($\alpha \le 0.05$).

Results and discussion

Depending on the year of the research and on the treatment in the experiment, between 0.34 and 1.12 mgPb \cdot kg⁻¹ d.m. was determined in the above-ground parts of the maize (Table 2). This means that there was no lead pollution of the above-ground

parts of the maize, since the permissible lead content in plants intended for feed amounts to 10 mg \cdot kg⁻¹ d.m. [11].

Table 2

Fertilization treatment	1 st year	2 nd year	3 rd year	Weighted mean content
No fertilization	$0.87^{d^*} \pm 0.06$	$1.12^{\text{b}}\pm0.13$	$0.39^{ab}\pm0.10$	0.80
Mineral fertilizers	$0.80^{cd} \pm 0.04$	$0.96^{\text{b}} \pm 0.24$	$0.45^{ab}\pm0.11$	0.77
Manure	$0.77^{bcd} \pm 0.09$	$1.01^{\text{b}}\pm0.02$	$0.50^{\rm b}\pm0.14$	0.79
Green waste compost	$0.60^{\mathrm{a}} \pm 0.02$	$1.01^{\text{b}}\pm0.06$	$0.40^{ab}\pm0.08$	0.68
Sewage sludge	$0.62^a \pm 0.13$	$0.74^{a}\pm0.07$	$0.45^{ab}\pm0.04$	0.62
Compost from sewage sludge and straw	$0.67^{ab}\pm0.09$	$0.92^{ab}\pm0.02$	$0.34^{a}\pm0.07$	0.66
Mixture of sewage sludge and ash	$0.70^{abc}\pm0.10$	$1.06^{\text{b}}\pm0.16$	$0.40^{ab}\pm0.02$	0.74

Lead content in above-ground parts of maize [mgPb \cdot kg⁻¹ d.m. ±SD]

* Mean values in columns marked with the same letters do not differ statistically significantly at $\alpha = 0.05$, according to the Duncan test.

Maize accumulates uptaken trace elements mainly in roots [4, 12], hence the low lead content in the above-ground parts. For example, the obtained by Sekara et al [12] ratio value of the lead content in the above-ground parts of maize to the lead content in roots was 0.21. Bi et al [13] state that lead located in maize leaves and grains comes mainly from foliar uptake of atmospheric Pb, whereas lead taken up by plant from soil is accumulated mainly in stalk and root tissues.

In all years of the research, the fertilized plants contained statistically significantly less lead than the control plants or the differences in the lead content in the biomass were not statistically significant. In the 1st year of the experiment, the lead content in the maize fertilized with materials derived from waste was 20–31 % lower than in the non-fertilized plants. In the following year, the plants fertilized with sewage sludge again contained significantly less (by 34 %) of the element than the control plants. In the third year of the experiment, all the plants contained significantly less lead than the plants harvested in the two previous years. At the same time, the applied fertilization did not lead to statistically significant changes in the control plants. The weighted mean content of lead in the fertilized plants was by 1–22 % lower than the content in the plants cultivated on non-fertilized soil. The lowest mean lead content (0.62 mg \cdot kg⁻¹ d.m.) was found in the plants harvested from the treatment with sewage sludge fertilization.

In the authors' own research, no increase in the lead content in the plants as a result of fertilization with organic materials derived from waste was found. Labetowicz et al [14] showed, however, that soil fertilization with compost generated from unsegregated municipal waste results in an increase in lead content in plants (fodder beet roots and leaves, barley grains and straw as well as grass). Similarly to the authors' own research, Akdeniz et al [15] did not show a statistically significant effect of fertilization with sewage sludge on lead contents in sorghum leaves and grains. Jamali et al [16] as well as Singh and Agrawal [17, 18] obtained different results. They found an increase in content lead in wheat grain, chard leaves and roots as well as in bean seeds. In one part of the research, however, the authors used a large addition of sewage sludge, amounting to 20–40 % of the soil mass [16, 17].

The amount of the element collected with the plant yield was calculated as a product of the content of that element in the yield and the amount of that yield. In the authors' own research, despite a relatively high lead content in the control plants, the lead uptake from the fertilized soil was generally higher than from the soil of the control treatment (as a result of low yield from the non-fertilized plants [9]), as shown in Fig. 1.

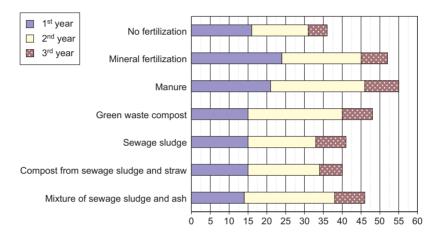


Fig. 1. Amount of lead taken up by maize $[gPb \cdot ha^{-1}]$

The non-fertilized plants took up in total 36.6 g lead from 1 ha of soil. The total uptake of the element from the fertilized soil was between 109 and 148 % of the uptake from the control soil.

The lead content in the soil from the experimental field was between 22.9 and 29.3 mg \cdot kg⁻¹ d.m. (Table 3). As specified by Kabata-Pendias et al [16], natural lead content in medium soil (which was examined in the authors' own experiment) is up to 40–60 mg \cdot kg⁻¹ d.m., depending on soil pH values. The soil from the experimental field contained less lead, so it was not polluted with this element. The lead content in the studied soil also did not exceed the permissible content in soils of agricultural lands, established in the regulation on soil and earth quality standards [20] amounting to 100 mg \cdot kg⁻¹ d.m. In addition, the lead content in the soil was lower than 60 mg \cdot kg⁻¹ d.m., which is the permissible content established for fertilizing use of sewage sludge [7].

The lowest lead content was found in the soil fertilized with mineral fertilizers. In the 1st year of the research, the soil fertilized with the green waste compost and with a mixture of sewage sludge and hard coal ash contained significantly more of the element (by 23–28 % more). In the following year, soil of the four treatments was

characterized by a significantly higher lead content than the soil fertilized with mineral fertilizers – it applied to the non-fertilized soil as well as the soil fertilized with the mixture of sludge and ash, the green waste compost and sewage sludge (16–24 % more lead).

Fertilization treatment	1 st year	2 nd year	3 rd year
No fertilization	$26.5^{ab^*}\pm3.3$	$27.1^{b} \pm 1.9$	$27.0^{ab}\pm2.9$
Mineral fertilizers	$22.9^{\rm a}\pm0.6$	$23.2^{\rm a}\pm2.4$	$24.8^{\rm a}\pm2.3$
Manure	$25.6^{ab}\pm2.4$	$25.6^{ab}\pm1.9$	$27.8^{ab}\pm0.1$
Green waste compost	$29.3^{\text{b}} \pm 5.1$	$28.1^{\text{b}} \pm 4.1$	$29.2^b\pm3.5$
Sewage sludge	$27.1^{ab}\pm3.0$	$28.8^{b} \pm 1.3$	$28.0^{ab}\pm2.4$
Compost from sewage sludge and straw	$26.5^{ab}\pm1.8$	$25.8^{ab}\pm1.1$	$26.6^{ab}\pm1.2$
Mixture of sewage sludge and ash	$28.2^{\text{b}}\pm1.0$	$27.0^{b} \pm 1.3$	$28.2^{ab}\pm0.7$

Content of total forms of lead in soil [mgPb \cdot kg⁻¹ d.m. \pm SD]

Table 3

* See Table 2.

In the authors' own research, the non-fertilized soil did not differ significantly in the lead content from the fertilized soil. However, Jamali et al [16], Singh and Agrawal [17] as well as Weber et al [21] point out to a possibility to increase total content of lead in soil as a result of fertilization with sewage sludge and compost from municipal sewage coming from a heavily industrialized area. Otherwise, Antonkiewicz [22] did not find a statistically significant effect of using mixtures of sewage sludge and fly ash on the lead content in soil.

As highlighted above, in the authors' own research no soil or plant pollution with lead as a result of using the green waste compost, sewage sludge or sludge-containing materials was detected. Application of relatively small doses of those materials was one of the causes. The risk of environmental pollution with heavy metals increases if applied doses of these materials are higher and because of those doses of individual heavy metals introduced to soil are also high. Availability of elements in soil and sludge, dependent on their form of occurrence [23], is also important.

Conclusions

1. During the three-year field research, fertilization with mineral fertilizers, manure and waste-derived organic materials, no pollution of the soil or the above-ground parts of maize with lead was found.

2. When comparing to the lead content determined in the non-fertilized plants, no statistically significant effect of fertilization on the lead content in the maize was found or the fertilized plants contained considerably less of the element than the control plants. The fertilized plants had a lower mean content of lead than the non-fertilized ones.

3. The lowest lead content was found in the soil fertilized with mineral fertilizers. The soil fertilized with compost from green waste (all the years), sewage sludge $(2^{nd}$ year) as well as with a mixture of sludge and ash $(1^{st} \text{ and } 2^{nd} \text{ year})$ contained significantly more lead than the soil fertilized with mineral fertilizers.

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References

- García-Lestón J, Méndez J, Pásaro E, Laffon B. Genotoxic effects of lead: an updated review. Environ Int. 2010;36:623-636. DOI:10.1016/j.envint.2010.04.011.
- [2] Johnson FM. The genetic effects of environmental lead. Mutat Res. 1998;410:123-140.
- [3] Meyer PA, Brown MJ, Falk H. Global approach to reducing lead exposure and poisoning. Mutat Res. 2008;659:166-175. DOI:10.1016/j.mrrev.2008.03.003.
- [4] Kabata-Pendias A, Pendias H. Biogeochemia pierwiastków śladowych. Warszawa: Wyd Nauk PWN; 1993.
- [5] Singh RP, Tripathi RD, Sinha SK, Maheshwari R, Srivastava HS. Response of higher plants to lead contaminated environment. Chemosphere. 1997;34:2467-2493. DOI:10.1016/S0045-6535(97)00087-8.
- [6] Kurtyka R, Małkowski E, Burdach Z, Kita A, Karcz W. Interactive effects of temperature and heavy metals (Cd, Pb) on the elongation growth in maize coleoptiles. C R Biologies 2012;335:292-299. DOI:10.1016/j.crvi.2012.03.012.
- [7] Rozporządzenie Ministra Środowiska z dnia 13 lipca 2010 r. w sprawie komunalnych osadów ściekowych. DzU 2010, Nr 137, poz 924.
- [8] Tabak M, Filipek-Mazur B. Formation of maize yield as a result of fertilization with organic materials. Ecol Chem Eng A. 2011;18(9-10):1355-1362.
- [9] Tabak M, Filipek-Mazur B. Content and uptake of nitrogen by maize fertilized with organic materials derived from waste. Ecol Chem Eng A. 2012;19(6):537-545. DOI:10.2428/ecea.2012.19(06)054.
- [10] Ostrowska A, Gawliński S, Szczubiałka Z. Metody analizy i oceny właściwości gleb i roślin. Katalog. Warszawa: Wyd. IOŚ; 1991.
- [11] Kabata-Pendias A, Motowicka-Terelak T, Piotrowska M, Terelak H, Witek T. Ocena stopnia zanieczyszczenia roślin metalami ciężkimi i siarką. Puławy: IUNG; 1993.
- [12] Sękara A, Poniedziałek M, Ciura J, Jędrszczyk E. Cadmium and lead accumulation and distribution in the organs of nine crops: implications for phytoremediation. Pol J Environ Stud. 2005:14(4):509-516.
- [13] Bi X, Feng X, Yang Y, Li X, Shin GPY, Li F, Qiu G, Li G, Liu T, Fu Z. Allocation and source attribution of lead and cadmium in maize (*Zea mays* L.) impacted by smelting emissions. Environ Pollut. 2009;157:834-839.
- [14] Łabętowicz J, Rutkowska B, Ożarowski G, Szulc W. Możliwości wykorzystania w rolnictwie kompostu ze śmieci miejskich "Dano". Acta Agrophys. 2002;70:247-255.
- [15] Akdeniz H, Yilmaz I, Bozkurt MA, Keskin B. The effects of sewage sludge and nitrogen applications on grain sorghum grown (Sorghum vulgare L.) in Van-Turkey. Pol J Environ Stud. 2006;15(1):19-26.
- [16] Jamali MK, Kazi TG, Arain MB, Afridi HI, Jalbani N, Kandhro GA, Shah AQ, Baig JA. Heavy metal accumulation in different varieties of wheat (*Triticum aestivum* L.) grown in soil amended with domestic sewage sludge. J Hazard Mater. 2009;164:1386-1391. DOI:10.1016/j.jhazmat.2008.09.056.
- [17] Singh RP, Agrawal M. Effects of sewage sludge amendment on heavy metal accumulation and consequent responses of *Beta vulgaris* plants. Chemosphere. 2007;67:2229-2240. DOI: 10.1016/j.chemosphere.2006.12.019.
- [18] Singh RP, Agrawal M. Effect of different sewage sludge applications on growth and yield of *Vigna radiata* L. field crop. Metal uptake by plant. Ecol Eng. 2010;36:969-972. DOI:10.1016/j.ecoleng.2010.03.008.

- [19] Kabata-Pendias A, Piotrowska M, Motowicka-Terelak T, Maliszewska-Kordybach B, Filipiak K, Krakowiak A, Pietruch Cz. Podstawy oceny chemicznego zanieczyszczenia gleb. Metale ciężkie, siarka i WWA. Warszawa: PIOŚ, IUNG; 1995.
- [20] Rozporządzenie Ministra Środowiska z dnia 9 września 2002 r. w sprawie standardów jakości gleby oraz standardów jakości ziemi. DzU 2002, Nr 165, poz 1359.
- [21] Weber J, Karczewska A, Drozd J, Licznar M, Licznar S, Jamroz E, Kocowicz A. Agricultural and ecological aspects of a sandy soil as affected by the application of municipal solid waste composts. Soil Biol Biochem. 2007;39L1294-1302. DOI:10.1016/j.soilbio.2006.12.005.
- [22] Antonkiewicz J. Wpływ komunalnego osadu ściekowego, popiołu paleniskowego, torfu i ich mieszanin na właściwości fizykochemiczne oraz zawartość metali ciężkich w glebie. Roczn Glebozn. 2008;59(1):18-28.
- [23] Merrington G, Oliver I, Smernik RJ, McLaughlin MJ. The influence of sewage sludge properties on sludge-borne metal availability. Adv Environ. Res. 2003;8:21-36. DOI:10.1016/S1093-0191(02)00139-9.

ZAWARTOŚĆ OŁOWIU W KUKURYDZY I GLEBIE NAWOŻONEJ MATERIAŁAMI ORGANICZNYMI POCHODZENIA ODPADOWEGO

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Abstrakt: Celem badań było określenie wpływu nawożenia materiałami organicznymi pochodzenia odpadowego na zawartość i pobranie ołowiu przez kukurydzę oraz na ogólną zawartość ołowiu w glebie. Trzyletnie doświadczenie polowe obejmowało 7 obiektów: glebę nienawożoną (kontrola) oraz glebę nawożoną nawozami mineralnymi, obornikiem bydlęcym, kompostem z odpadów zielonych, osadem ściekowym, kompostem z osadu ściekowego i słomy oraz mieszaniną osadu ściekowego i popiołu z węgla kamiennego. Rośliną testową była kukurydza uprawiana na kiszonkę. Zawartość ołowiu w częściach nadziemnych roślin i glebie oznaczono metodą ICP-AES.

W trakcie prowadzenia badań nie stwierdzono zanieczyszczenia gleby i części nadziemnych kukurydzy ołowiem. Nie wykazano istotnego statystycznie wpływu nawożenia na zawartość ołowiu w kukurydzy lub rośliny nawożone zawierały istotnie mniej pierwiastka niż rośliny z obiektu kontrolnego. Najmniejszą średnią ważoną zawartość ołowiu stwierdzono w kukurydzy nawożonej kompostem z odpadów zielonych, osadem ściekowym oraz kompostem z osadu i słomy. Gleba nawożona nawozami mineralnymi zawierała najmniej ołowiu. Gleba nawożona kompostem z odpadów zielonych (wszystkie lata), osadem ściekowym (II rok) oraz mieszaniną osadu i popiołu (I i II rok) zawierała istotnie więcej ołowiu niż gleba nawożona nawozami mineralnymi.

Słowa kluczowe: odpadowe materiały organiczne, osad ściekowy, kompost, ołów, kukurydza, gleba