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MOBILITY AND PHYTOAVAILABILITY OF LEAD IN URBAN SOILS

DOSTĘPNOŚĆ OŁOWIU DLA ROŚLIN NA TERENACH UPRZEMYSŁOWIONYCH

Abstract: Lead belongs to a group of the most commonly man distributed heavy metals. The reason lies in a dynamic development of transportation but also in development of industry and municipal economy. In bibliography it is referred as a chemical element which is relatively stable in soil - captured in surface layers, and in a high reaction conditions with good sorption qualities it is almost unavailable for live organisms. The paper proves that the problem is more complicated due to various geneses and man's pressure towards soil. Only small anthropogenic pressure affects lead content and mobility. Soils under big anthropogenic pressure - urban, industrial and those within communication route areas - can be characterized for their increased lead content, its solubility and phytoavailability.

Keywords: heavy metals, lead, plants, industrial zones

Lead is a chemical element often referred in bibliography. This is definitely a result of prevalence on Earth and its potential toxicity for organisms [1-4].

The communication used to be recognized as the main source of this element - lead petrol which ceased to be used not a long time ago [5, 6], industry - mainly steel industry, metallurgy, power engineering [7, 8], municipal economy, wastes, landfill effluents, wastewaters and sludge, composts [8]. Sometimes, attention is directed to installations and other elements of infrastructure [5, 9]. Effects from particular sources have changed in time, which illustrates the typical history of development of the most of European cities. Until the 19th century first there were farming and craftsmen's settlements with a great part of activities focused on gardening. In the 19th century and the first part of the 20th century their character changed into typically industrial. In the end of the 20th century industry fell substituted by development of services and dynamic growth of city areas followed by an increase of the number of cars.

In the majority of references lead mobility is described as relatively low, which results from this element chemical and replacement sorption in soils [10]. Many authors also stress a great importance of other soil qualities, mainly reaction. High, neutral or alkaline reaction is indicated as a factor immobilizing lead in soil environment which causes that it becomes practically unavailable to live organisms [1, 11, 12]. Researchers also point at the phenomenon of accumulation of this element in surface soil levels, rich in organic matter. Most of these observations have already been reflected in border figures fixed for lead content in particular elements of natural environment.

As long as researchers' analyses concerning lead behavior are generally right, they rarely touch the problem of time necessary for permanent absorption of this element. Not

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often do they indicate disturbances in soil profile structure being a result of urban pressure as a potential reason for variation of sorption performed. Important within this context is behavior of the constantly mobile part of soil lead. The tests carried out in Zielona Gora by the authors of this paper show that lead deposition in urban soils is often a result of the history of their transformations, and not of a directly treated surface deposition (for example, industrial or communication).

In Europe the problem of lead sorption by plants growing in urban areas has two meanings. One is a result of the condition of decorative plants in urban green areas [13, 14]. The other issues from growing fruit and vegetable in urban vegetable gardens which are then designed for human consumption [15, 16]. Recently, as part of waste management, attention is also focused upon the so called green wastes generated by plant care. The latter problem is related to the possibility of using compost made of urban plant residue as a fertilizer [8, 14].

Methods

The tests were carried out in the commune of Zielona Gora in the areas used for farming, agriculture and forests, in the outskirts and within the town of Zielona Gora (120 thousand inhabitants, west of Poland, Lubuskie Region). Sample collection locations were chosen in the areas illustrating particular stages of human pressure made on natural environment - 105 soil profiles at the depth of 150 cm (samples from each of the genetic levels) + 32 collective surface samples (area of approximately 20 m^2 each, samples from humus levels). In total, 562 samples were subject to the tests. Soils were classified according to the classification of the WRB [17]. Lead content in soil samples was determined by means of atomic absorption FAAS (Varian, λ = 283.3 nm, 0.7 mm slit).

Extracts in aqua regia ($3HCl:HNO_3$) were made by burning 10 g of airy dry soil in a furnace at temperature of 550ºC (12 hours), and then at a sand bath by heat digesting ash in aqua regia (20 cm^3) [18]. Extracts in 0.1 M HCl - the fraction potentially available to plants [19] was prepared by cool digesting airy dry soil in 100 cm^3 of the solution and by shaking for 1 hour. *Cation Exchange Capacity* (CEC) was determined by the Kappen method, pH in 0.01 M $CaCl_2$ potentiometrically, Ca content according to the flame photometry in aqua regia extract and the humus content by means of the Tiurin method.

Leaves were collected in the places with versatile urban, industrial and transportation pressure. The samples included: Black Locust (*Robinia pseudoacacia* L), Small-leaved Lime (*Tilia cordata* L), Wild Privet (*Ligustrum vulgare* L) and grasses (*Graminae*). Collection of leaves was carried out in July and October 2007 (in total 80 samples). Tree leaves were collected from the level of 1.5÷2 m above the ground, whereas leaves of shrubs were collected at the height of approximately 1 m above the ground. Grass was cut when the leaves were approximately 20 cm long. For the tests only well-formed leaves were selected that did not show any damages or disease symptoms. Leaf lead content analysis was carried out in an extract obtained by burning 5 g of dry matter in a furnace at the temperature of 550ºC (12 hours), and then by heat digesting ash in aqua regia.

Statistic analysis was made using the software Statistica for Windows 9.1a. The basic statistic figures were defined together with correlations between soil condition indices at levels α = 0.01 and 0.05.

Results and discussion

The average lead content in the Lubuskie Region soils is approximately 11.3 mg·kg^{-1} (at the range of 0.6÷81.8 mg·kg^{-1}). About 1.0% of the samples from out-of-town areas show anthropogenic increase of the overall Pb content - 20÷70 mg·kg^{-1}, the other fall within the geochemical background - below 20 mg·kg^{-1} [20]. As far as Zielona Gora is concerned, higher concentrations of this element are noted in the soils within the city as well as in its suburbs (Table 1).

Table 1

Lead content and its potential availability in out-of-town, urban and suburban areas

Description of the area and soils	Lead form (dissolved in:)		0.1 M HCl / aqua regia ratio	pH in 0.01 M $CaCl_2$	CEC
	0.1 M HCl	aqua regia			
	[mg·kg^{-1}]		[%]		[cmol·kg^{-1}]
Out-of-town areas					
Haplic Podzols	2.40÷7.00	3.97÷9.88	63.43÷70.85	4.10÷4.91	1.18÷4.92
Haplic Arenosols	2.40÷5.86	7.62÷10.20	32.48÷57.45	3.52÷4.22	1.97÷8.96
Cambic Arenosols	2.80÷16.80	6.47÷24.11	43.28÷69.68	4.62÷5.12	3.48÷8.22
Suburban areas					
Haplic Podzols	3.19÷17.32	4.40÷59.20	7.89÷72.50	5.57÷7.24	3.36÷26.30
Technosols	3.20÷27.13	4.14÷90.40	4.50÷77.30	6.92÷7.42	2.00÷24.71
Urban areas					
Urbi-Anthropic Regosol	1.80÷6.31	4.76÷22.80	19.76÷59.43	7.21÷7.49	14.02÷24.04
Anthropic Regosol	3.20÷23.18	7.27÷57.00	44.01÷90.33	6.04÷6.59	3.32÷13.21
Cumulic Anthrosol	4.35÷9.09	6.20÷17.40	31.79÷84.44	6.84÷7.31	16.36÷27.77
Anthrosols	3.53÷6.20	8.20÷197.20	2.93÷42.99	6.71÷6.90	2.07÷21.60
Technosols	4.83÷18.85	6.90÷52.40	17.63÷93.93	5.31÷6.80	3.18÷21.83
Technosols	3.19÷36.09	4.40÷171.40	21.06÷72.50	6.80÷8.01	3.88÷25.05
Technosols	4.82÷16.55	22.00÷48.00	21.93÷62.69	6.30÷7.28	9.75÷24.94

When comparing samples from out-of-town areas with those experiencing strong urban pressure we can note several regularities. Enriching soils with various foreign materials, including wastes, results in transferring their reaction and sorption qualities. The dependence among those factors is referred to by numerous researchers, among others: [1, 11, 12]. Others, like Dragovic et al [21], did not show any relation between lead content and soil pH, however indicated a strong correlation between lead content and CEC. This also means a new approach towards the problem of lead mobility in soils. The results of the present paper indicate, that soil sorption along with bringing calcium carbonate into soil are a condition for lowering Pb solubility, which was proved statistically (Figs. 1-3). This is especially clear with respect to strongly limed garden soil/hortisoles, which is referred to in the works of, among others: [22] and [23].

Soil genesis as well as the range and type of transformations they have undergone are very diversified, thus a particular soil cannot be related automatically to an increased or decreased lead content. Furthermore, the test results also show that a factor conditioning lead content, solubility as well as bioavailability in urban soils can be time of soil form occurrence - shorter in anthropogenic transformed areas, especially within a young territory of a developing city. This was also indicated by Bretzel and Calderisi [10].

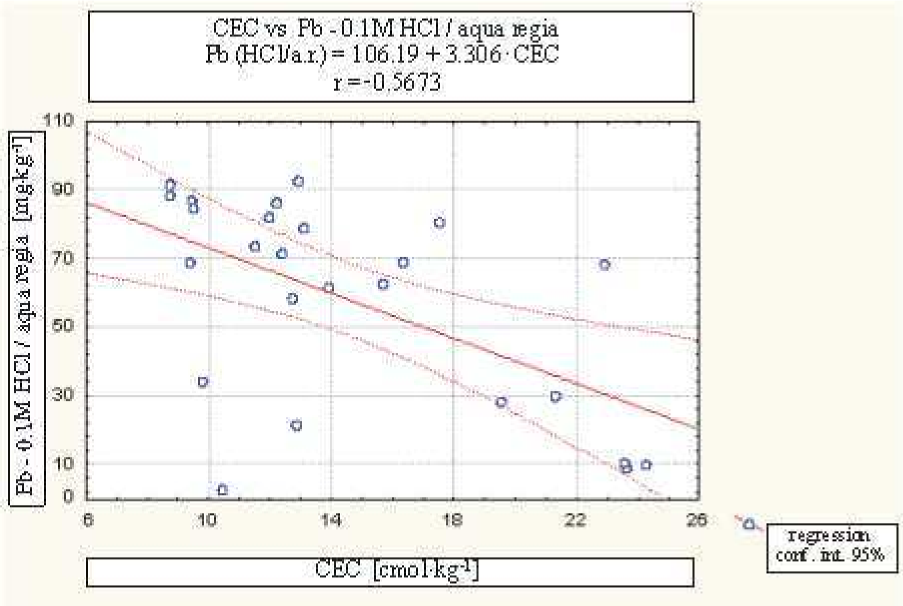

Fig. 1. Effect of CEC on potential Pb availability in urban soils

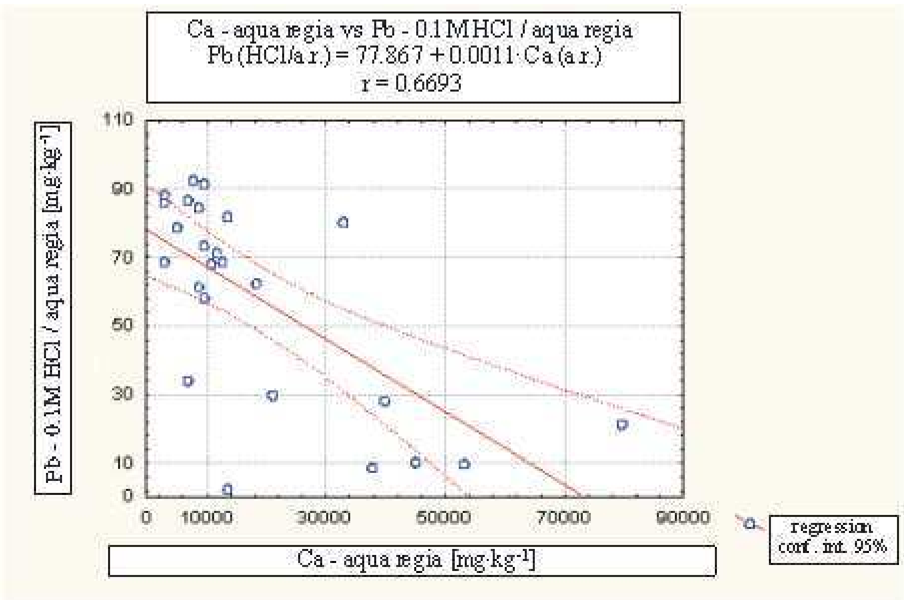

Fig. 2. Effect of Ca content on potential Pb availability in urban soils

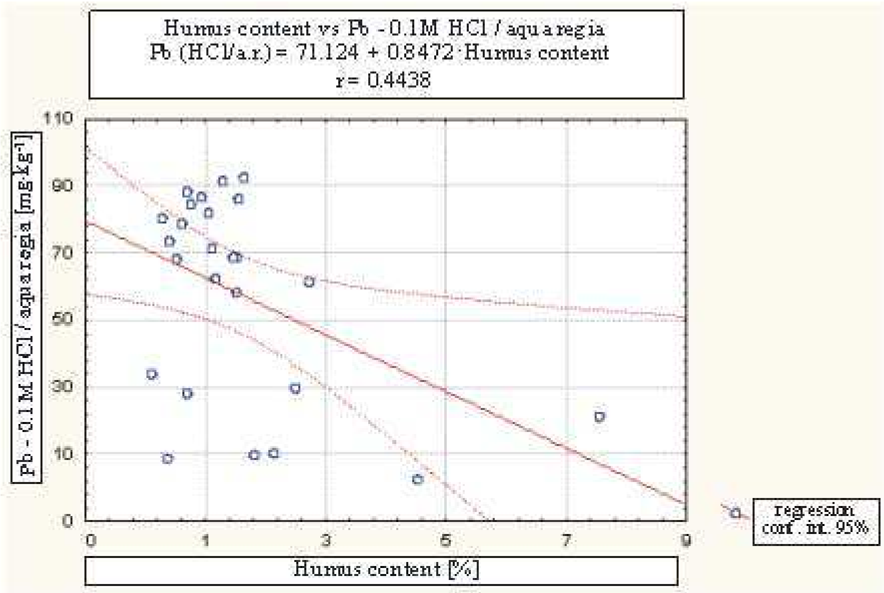

Fig. 3. Effect of humus content on potential Pb availability in urban soils

City is a complex system as far as paths of lead expansion is concerned. This results in both an area surface deposition, as well as in a unit underground deposition - "hot points"! It has been found out that in many parts of cities it is difficult to maintain decorative plants. Only a few of them, however, have a direct relation with emission of toxins, including heavy metals. The majority of problems result from incorrect, other than settlement and microclimate, conditions. Nevertheless, it was noticed that plants of different species and different growth character vary in lead absorption. As far as trees often grown in the cities of Eastern Europe, Small-leafed Lime absorbs more lead than Black Locust. One of the most commonly grown hedge shrubs - Wild Privet - shows the average quantity of Pb absorption in comparison with the above-mentioned tree species. On the other hand, grass specimens have a very wide reaction spectrum.

Table 2

Lead content in leaves of plants from urban green areas

Location	Black Locust	Small-leaved Lime	Wild Privet	Grasses (Grass mix)
	[mg·kg^{-1}]			
Centre	3.82÷7.98	7.36÷31.50	4.26÷12.74	3.54÷24.28
Areas along transit routes	4.58÷15.22	5.64÷21.94	4.36÷20.16	1.76÷17.62
Areas along city roads	7.32÷31.30	9.14÷24.60	9.28÷16.50	3.00÷27.08
Housing estates	3.98÷13.88	6.86÷22.20	3.44÷15.26	9.30÷18.94
Parks	1.10÷11.98	7.94÷28.00	3.42÷13.56	6.80÷18.72

It is quite interesting to compare lead absorption by plants growing along newly constructed roads (transit roads built in 1980-2007) and along old routes (city roads built before 1980). Lead absorption, as it is shown, is bigger in the latter situation. It is a clear picture of plant growth under conditions in which soil has been recently transformed along new communication routes (reference to Urbi-Anthropic Regosol and Cumulic Anthrosol). As far as the old roads are concerned, their surroundings used to be for a long time exposed to immissions at the time when the basic fuel was leaded petrol. This also illustrates a new technology of road building based on clear mineral materials. In the past roads were constructed on the foundation made from waste materials. Smaller lead content is presented by plants growing in some housing estates or park locations, however, also here big diversification can be noticed. This partially depends on the period of time in which housing estates and parks were built, thus on various approaches towards forming their soils and a different time of their deposition.

Conclusions

1. Behavior of lead in urban soils depends on their sorption capacity and reaction.
2. Due to a strong diversification of the genesis and the qualities of urban soils, potential lead availability from soils varies within wide range.
3. It is not possible to indicate automatically a biological risk resulting from lead deposition in a real place in a city, relating it with a form of use or taxonomic soil unit.
4. Absorption of lead by plants depends, to a great extent, on age of the soil cover and an approach to its formation.

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DOSTĘPNOŚĆ OŁOWIU DLA ROŚLIN NA TERENACH UPRZEMYSŁOWIONYCH

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Abstrakt: Ołów należy do grupy metali ciężkich najbardziej rozpowszechnionych przez człowieka. Przyczyną takiego stanu rzeczy jest dynamiczny rozwój transportu, przemysłu i gospodarki komunalnej. W literaturze jest przedstawiany jako pierwiastek stabilny w glebach - kumulowany głównie w wierzchnich warstwach, gdzie w warunkach wysokiego odczynu i dobrych właściwości sorpcyjnych jest właściwie niedostępny dla żywych organizmów. W artykule zwrócono uwagę na fakt, że problem jest jednak bardziej skomplikowany, głównie ze względu na genezę i antropopresję, która, jak się okazuje, podnosi zawartość ołowiu, a także zwiększa jego rozpuszczalność i fitoprzyswajalność.

Słowa kluczowe: metale ciężkie, ołów, rośliny, strefy przemysłowe