

## ALUMINIUM AND SELENIUM CONTENT IN SOILS OF INDUSTRIAL AREA IN OPOLE (SOUTHERN POLAND)

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**Abstract:** Aluminium is one of the main soil components. Usually it is a part of non-toxic aluminosilicates but in low pH values its mobility is higher and – especially in monomeric form is toxic for plants. Selenium is an essential element necessary for animals and humans. Its compounds have anticancer and anti mutagenic character. However, its high uptake from environment, e.g. with food or water could lead to various diseases including embryonic deformity, decreased hatchling survival and death to aquatic organisms. Soil contamination with aluminium leads to disturbances in plant growth as a result of low calcium and magnesium uptake. High concentrations of selenium lead to its accumulation in plant tissues what is the beginning of selenium fate in food chain. In this work a cultivated layer of soils located near five industry plants in the town of Opole (southern Poland) were investigated. Aluminium and selenium content in soils is an effect of two factors: its natural occurrence in rocks (natural content) and human activity – especially chemicals from agriculture, industrial and transport pollutants. Aluminium was determined in the range of 3440 to 14804 mg/kg d.w. Obtained results of selenium concentration covered the range from 27.1 to 958.1 µg/kg d.w. These results are slightly higher than concentrations noted in natural or non-polluted soils, but still low. These amounts of selenium could have more positive than negative effects. Aluminium and selenium concentrations were discussed concurrently with base soils parameters, such as pH, EC and granulometric fractions composition.

### INTRODUCTION

Aluminium and selenium content is an important parameter of soils composition. It is especially important in cultivated layer due to bioavailability and potential toxicity of these elements for plants and consequently in food chain what, subsequently, poses a threat for animals and humans. Aluminium, as a basic soil component, could be released to soil solution due to soils acidification but in high concentrations could be toxic especially at pH below 5 [5, 6, 7]. This element has a negative impact on cell proteins, especially on extensines and some enzymatic proteins, e.g. hemicellulases, peroxidases, and expansines what leads to cell growth dysfunction [8]. Some authors suggest that in the case of humans, the high aluminium uptake, in some cases, might be a risk factor of Alzheimer's disease (AD) [13, 23].

Selenium is an essential element necessary for animals and humans. Lack or low selenium concentration in water and food leads to several diseases, e.g. Kashin-Beck and heart disease known as Keshan [20]. Some plant species could accumulate selenium in tissues and are a source of selenium for humans [11]. Its compounds have proved anticancer and anti mutagenic character and could be antagonistic to mercury [8, 10]. However, too high uptake of it from environment, e.g. with food or water, could lead to various diseases including embryonic deformity, decreased hatchling survival and death to aquatic organisms [12, 15, 18, 20]. Strong soil contamination with selenium compounds leads to its accumulation in plant tissues what is the beginning of selenium fate in food chain [14]. In some areas, organic fertilization of soils could be a main source of selenium [17].

## MATERIALS AND METHODS

### *Study area*

In this work we focused on surface layer (30 cm) of investigated soils because this is the most suitable layer for plants roots. All collected samples were taken in Opole (southern Poland). Samples were collected during summer 2008 from 5 points (A–E) around industry plants. The first area (A) was a cement plant “Groszowice” (demolished in 2006), the second area (B) was a covered bitumen plant “Bisek”, the third (C) an agricultural machinery factory, the fourth (D) a covered area around Odra river harbour and a cement plant “Odra” (in operation) formed E. One soil sample was collected from 50 single sampling points, covering the area of about 100 m<sup>2</sup> and was about 5 kg.

### *Methods*

All collected samples from single points were mixed, dried at room temperature to air-dry humidity. Afterwards the samples were well ground and sieved through a 1 mm sieve. For general soils characteristic basic parameters, such as pH, EC (with electrometric method), grain size analysis (Casagrande’s method in Prószyński modification), organic carbon – TOC (by Thiurin’s method) and humus content, were calculated. For aluminium and selenium determination, soil samples (approx. 0.5 g) were mineralised with 12 cm<sup>3</sup> of aqua regia in Teflon® bombs at first in room temperature (12 h) and next in microwave furnace MARS-X at 180°C (15 min). Aluminium and selenium determination was done on Varian SpectrAA 220-FS apparatus. Results correlation and LSD tests were performed using Statgraphics 4.0 software.

## RESULTS AND DISSCUSION

### *General sample characteristic*

Investigated soils are mostly sands and loamy sands with low content of very thick sand (Table 1). This is typical for soils in investigated area where sandy and limestone soils dominate. Values of pH indicate neutral or light alkaline conditions and medium salinity (Table 2). It is typical for investigated soil types [19]. Humus content is low, except for samples 3 and 16, where it exceeds 12%, and sample 21, where it exceeds 11%.

Table 1. Granulometric composition of the investigated soils [%]

Sample	Grain size fraction rate (mm)				
	> 2	< 2	2.00-0.05	0.05-0.002	< 0.002
1	6	94	82	14	4
2	31	69	89	8	3
3	24	76	85	23	2
4	27	63	73	26	1
5	9	91	80	18	2
6	4	96	81	14	5
7	14	86	74	18	8
8	4	96	70	17	13
9	15	85	80	14	6
10	6	94	80	13	7
11	7	93	82	12	6
12	6	94	81	14	5
13	5	95	88	8	4
14	3	97	83	12	5
15	5	95	89	8	3
16	32	67	78	19	3
17	18	82	90	8	2
18	34	66	88	9	3
19	21	79	52	29	19
20	11	89	56	41	3
21	6	94	62	31	7
22	6	94	62	34	4
23	8	92	65	31	4
24	16	84	48	28	24
25	10	90	57	31	12

### *Aluminium and selenium*

Aluminium in soils could be moved to soil solution due to low pH value. Very important for that is total content of this element in soil as its source. In the investigated samples, aluminum concentration was on the medium level and it covered the range from 3440.2 to 14804 mg/kg d.w. (Fig. 1). Concentrations exceeding 10000 mg/kg are high but in observed pH values mobility of this element is low [5]. However, there were observed higher concentrations in two out of five analysed areas. Mean values 9282 and 11466 mg/kg d.w. were obtained in D and E points. The highest value (area E) exceeded 1.7 x value from area A. There were statistical differences observed between areas: A and E and also between C and E (at 95% confidence level). The last observed dependence indicates that the area around historic cement plant (A) and the area near existing cement plant (E) with similar soil composition are completely different. This phenomenon was also observed in the case of selenium content. In area A cement production was stopped about 20 years ago.

Table 2. Basic parameters of investigated soils

Study area	Sample	Sampling depth [cm]	pH		EC (mS/cm)	C <sub>org</sub> (%)	Humus content (%)
			H <sub>2</sub> O	1N KCl			
A	1	0-30	8.16	7.48	0.157	4.15	7.15
	2	0-30	7.81	7.42	0.145	2.21	3.81
	3	0-30	7.38	7.01	0.238	7.01	12.08
	4	0-30	7.75	7.10	0.126	4.58	7.89
	5	0-30	7.56	7.13	0.184	4.44	7.65
B	6	0-30	7.42	7.00	0.116	1.98	3.41
	7	0-30	7.51	6.90	0.134	1.87	3.22
	8	0-30	7.60	6.90	0.139	1.45	2.49
	9	0-30	7.58	7.13	0.149	2.30	3.96
	10	0-30	7.43	7.03	0.126	1.02	1.76
C	11	0-30	7.22	6.75	0.274	5.14	8.86
	12	0-30	7.54	7.09	0.168	2.59	4.46
	13	0-30	7.28	6.83	0.096	2.09	3.60
	14	0-30	7.46	6.98	0.126	2.25	3.88
	15	0-30	7.52	6.98	0.142	3.02	5.21
D	16	0-30	7.57	7.07	0.167	7.49	12.91
	17	0-30	7.30	6.87	0.163	5.34	9.21
	18	0-30	7.43	7.12	0.141	4.23	7.30
	19	0-30	7.42	6.98	0.137	1.85	3.19
	20	0-30	7.41	6.94	0.180	4.78	8.24
E	21	0-30	7.79	7.11	0.154	6.51	11.22
	22	0-30	7.75	7.12	0.137	3.74	6.45
	23	0-30	7.45	7.30	0.972	5.08	8.75
	24	0-30	7.6	7.2	0.132	1.88	3.24
	25	0-30	7.95	9.30	0.285	2.36	4.07

The results of selenium concentration obtained in this work covered the range from 27.1 to 958.1  $\mu\text{g}/\text{kg}$  d.w. (Fig. 2). These results are slightly higher than concentrations noted in natural soils, but they are still low [1, 9]. Typical range for this element content in Polish soils equals 100–200  $\mu\text{g}/\text{kg}$  d.w. [2]. Researches show that the noted concentrations are not toxic but even in this level of selenium content it could be accumulated in plant tissues up to 4–6mg/kg dw [14, 21]. Especially in two points (1 and 8) the selenium content was low and did not exceed 135  $\mu\text{g}/\text{kg}$  d.w. Extremely low selenium content (27.1  $\mu\text{g}/\text{kg}$  d.w.) was observed in point 20. This content is lower than usually noted natural concentration and leads to plants' growth disfunction [4]. High concentrations (614.1, 614.4, 958.1 and 715.8  $\mu\text{g}/\text{kg}$  d.w.) were observed also in points 4, 11, 21 and 23. The highest mean value (623.7  $\mu\text{g}/\text{kg}$  d.w.) was observed in the area close to a cement plant "Odra" – the plant in operation 24h per day. In this case concentrations are 10–12 times higher than those noted in the Yangtze river delta [3], but in neutral pH value still not toxic and occurring in many samples [22]. Extremely low amounts of selenium in cultivated soils could lead to diseases and in this case a fertilization with selenium (e.g.

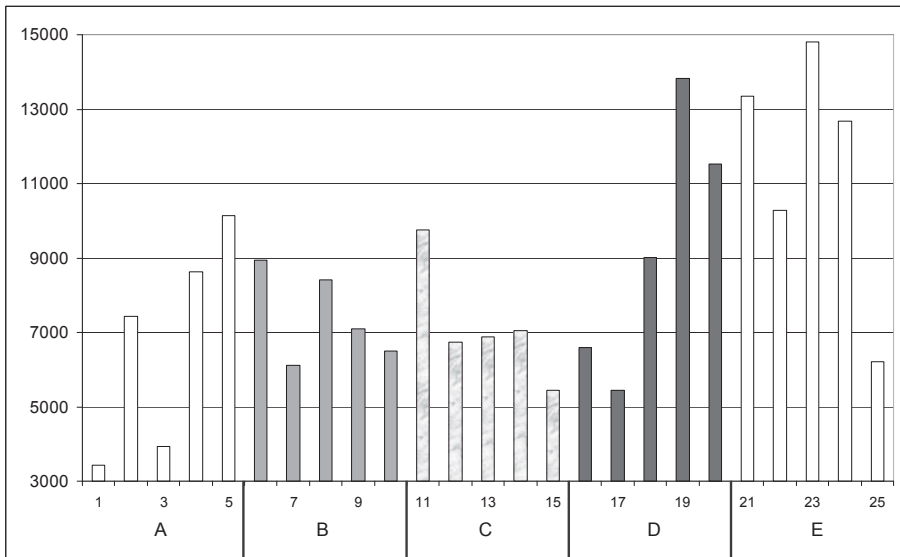


Fig.1. Aluminium content in investigated soils [mg/kg d.w.]

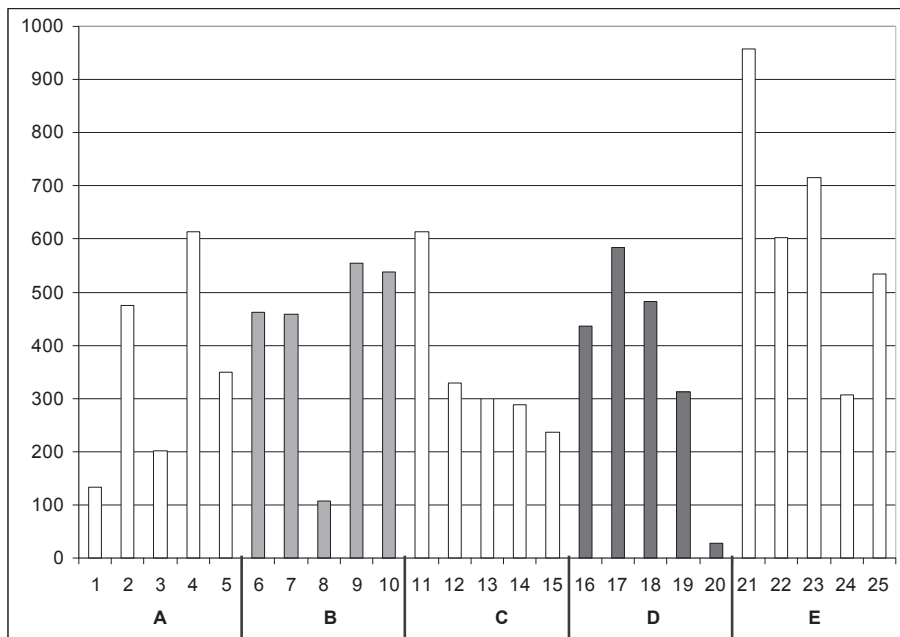


Fig.2. Selenium content in investigated soils [µg/kg d.w.]

manuring) could be necessary [3, 20]. There was no correlation between wind direction and selenium content in soils, so we can exclude investigated industry plants (cement plant “Groszowice”, bitumines factory, agricultural machine park) as selenium pollution source.

Statistically significant differences were observed between areas A and D and also A and E. This confirms an influence of existing cement plant on aluminium and selenium concentration in soils. Selenium as an important micronutrient and essential element for humans could have different effects depending on total content but also on chemical compounds type [8]. Neutral pH (effect of high content of calcium and magnesium carbonates in rocks) of investigated soils minimizes movement of selenium ions from soil to groundwater. The obtained results are in non-toxic range (toxic dose for humans is 5 mg/day) and it is possible to cultivate food plants even if selenium will be accumulated in plant tissues. A maximum level of selenium concentration for soils (incl. agricultural) according to Canadian Quality Guidelines is 1 mg/kg d.w., so all investigated samples are in agreement with this requirement. However, in researches with strawberries and barley, a toxic effect (low leaves growth) of selenium (additionally under UV-B radiation) was observed in concentration 1.0 mg/kg in soil [21]. Low and medium amounts of selenium observed in investigated soils could have more positive than negative effects on plants, animals or humans in the case of using plants raised on these areas for feed or food production. A high correlation (corr.coef. -0.87) between areas A and B in the case of selenium concentrations was observed. The obtained results of aluminium and selenium concentrations were not correlated in the examined areas.

## CONCLUSIONS

In this work a cultivated layer of soils (topsoil layer) located near some industry plants in Opole (southern Poland) were investigated. Aluminium contents were typical for these soils but statistical differences were observed between areas located around a historic cement plant and a plant being still in operation. Aluminium ions in investigated soil are not moved to soil solution in effect of neutral or alkaline pH values. The selenium content in soils is an effect of two factors: natural occurrence in rocks (natural content) and human activity – especially chemicals agriculture use, or as an effect of industry production. The obtained results of selenium concentration covered the range from 108.0 to 614.4  $\mu\text{g}/\text{kg}$  d.w. These results are slightly higher than concentrations noted in non-polluted soils, but still low. These amounts of selenium (taking into account soil conditions, especially neutral pH and low EC) could have more positive than negative effects. Also in the case of selenium, statistical differences were observed between areas A and E – what confirms an influence on close soil environment of cement plant which is still in operation. However, it is necessary to investigate the amount of mobility forms of selenium in these areas.

## REFERENCES

- [1] Borowska K., J. Koper, T. Tykwińska: *Zawartość selenu w wybranych typach gleb mineralnych regionu Kujaw i Pomorza na tle aktywności oksydoreduktaz*. *Ochr. Środ. i Zas. Nat.* **31** (2007) IOŚ Warszawa 18–22.
- [2] Borowska K., J. Koper, H. Dąbkowska-Naskręt: *Zawartość selenu w wybranych typach gleb Pomorza i Kujaw na tle aktywności peroksydaz*. *Roczniki Gleboznawcze* Vol.59 No.1 (2008).

- [3] Cao Z.H., X.C. Wang, D.H. Yao, X.L. Zhang, M.H. Wong: *Selenium geochemistry of paddy soils in Yangtze River Delta*. Environment International, **26**, 335-339 (2001).
- [4] Dhillon S.K., B.K. Hundal, K.S. Dhillon: *Bioavailability of selenium to forage crops in a sandy loam soil amended with Se-rich plant materials*. Chemosphere, **66**, 1734–1743 (2007).
- [5] Gestel C.A.M. G. van, Hoogerwerf: *Influence of soil pH on the toxicity of aluminium for Eisenia andrei (Oligochaeta: Lumbricidae) in an artificial soil substrate*. Pedobiologia, **45**, 385-395 (2001).
- [6] Goransson P., P.A. Olsson, J. Postma, U. Falkengren-Grerup: *Colonisation by arbuscular mycorrhizal and fine endophytic fungi in four woodland grasses – variation in relation to pH and aluminium*. Soil biology and biochemistry, **40**, 2260–2265 (2008).
- [7] Guo J., R.D. Vogt, X. Zhang, Y. Zhang, H.M. Seip, J. Xiao, H. Tang: *Aluminium Mobilization from Acidic Forest Soils in Leigongshan Area, Southwestern China: Laboratory and Field Study*. Arch. Environ. Contam. Toxicol., **51**, 321–328, (2006).
- [8] Huilan Y., S. Liangian: *Vicia root-mirconucleus and sister chromatid exchange assays on the genotoxicity of selenium compounds*. Mutation Research, **630**, 92–96 (2007).
- [9] Jianming Z., Z. Baoshan: *Distribution of selenium in a mini-landscape of Yutangba, Enshi, Hubei Province, China*. Applied Geochemistry, **16**, 1333–1344 (2001).
- [10] Kąklewski K, J. Nowak, M. Ligocki: *Effects of selenium content in green parts of plants on the amount of ATP and ascorbate–glutathione cycle enzyme activity at various growth stages of wheat and oilseed rape*. Journal of Plant Physiology, **165**, 1011–1022 (2008).
- [11] Kita A.: *Oddziaływanie selenu na kumulację K, Na, Ca w roślinach Zea mays L. poddanych działaniu ABA*. Ochr. Środ. i Zas. Nat., **32**, 97–102 (2007) IOŚ Warszawa.
- [12] Kuczyńska J., M. Biziuk: *Selenium biogeochemistry and its monitoring in biological samples*. Ecol. Chem. and Eng., **14** S1, 47–64 (2007).
- [13] Kumar A., S. Dogra, A. Prakash: *Protective effect of curcumin (Curcuma longa), against aluminium toxicity: Possible behavioral and biochemical alterations in rats*. Behav. Brain Res., **205**, 384–390 (2009).
- [14] Moreno D.A., G. Villora, M.T. Soriano, N. Castillab, L. Romero: *Sulfur, chromium, and selenium accumulated in Chinese cabbage under direct covers*. Journal of Environmental management **74**, 89–96 (2005).
- [15] Munier-Lamy C., S. Deneux-Mustin, C. Austin, D. Merle, J. Berthelin, C. Leyval: *Selenium bioavailability and uptake as affected by four different plants in a loamy clay soil with particular attention to mycorrhizae inoculated ryegrass*. Journal of Environmental Radioactivity, **97**, 148–158 (2007).
- [16] Puzanowska-Tarasiewicz H., L. Kuźmicka, M. Tarasiewicz: *Funkcje biologiczne pierwiastków i ich związków. II. Selen, seleniany, związki selenoorganiczne*. Pol. Merk. Lek., XXVII **159**, 249-252 (2009).
- [17] Sager M.: *Trace and nutrient elements in manure, dung and compost samples in Austria*. Soil Biology & Biochemistry, **39**, 1383–1390 (2007).
- [18] Skopikova A., K. Kralova, E. Masarovicova: *Phytotoxic effects of selenium oxoacids and some of their salts on growth of Brassica napus L. seedlings*. Ecological Chemistry and Engineering Vol. 15, no 3221-226 (2008).
- [19] Świerszcz A.: *Heavy metals and selected physicochemical properties of rendzic leptosols of the Poniżnie region (southern Poland)*. Archives of Environmental Protection vol. **35**, no **2**, 97–104 (2009).
- [20] Tan J., W. Zhu, W. Wang, L. Ribang, H. Shaofan, W. Dacheng, Y. Linsheng: *Selenium in soil and endemic diseases in China*. The Science of the Total Environment, **284**, 227–235 (2002).
- [21] Valkama E., M. Kivimäenpää, H. Hartikainen, A. Anu Wulff: *The combined effects of enhanced UV-B radiation and selenium on growth, chlorophyll fluorescence and ultrastructure in strawberry (Fragaria x ananassa) and barley (Hordeum vulgare) treated in the field*. Agricultural and Forest Meteorology, **120**, 267–278 (2003).
- [22] Wang M.C., H.M. Chen: *Forms and distribution of selenium at different depths and among particle size fractions of three Taiwan soils*. Chemosphere, **52**, 585–593 (2003).
- [23] Yun L., N. Fengan, S. Zongzheng, C. Wangsen, Z. Xin, G. Dening, L. Zhimai, Z. Bing, X. Yun: *Altered expression of Ab metabolism-associated molecules from D-galactose/AIC13 induced mouse brain*. Mechać. of Ageing and Develop., **130**, 248–252 (2009).

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### WYSTĘPOWANIE GLINU I SELENU W GLEBACH TERENÓW PRZEMYSŁOWYCH MIASTA OPOLA (POLSKA POŁUDNIOWA)

Glin jest jednym z podstawowych składników gleb. Zazwyczaj jest związany w postaci nietoksycznych glinokrzemianów, jednak przy niskim odczynie gleb jego mobilność wzrasta i zwłaszcza formy monomeryczne mogą oddziaływać toksycznie na rośliny. Selen postrzegany jest jako pierwiastek niezbędny dla zwierząt i człowieka. Jego związki wykazują działanie antynowotworowe i antymutagenne. Jednak pobieranie go ze środowiska w większych ilościach może oddziaływać toksycznie na zwierzęta i człowieka, powodując deformacje, spadek przeżywalności zarodków, także w stosunku do organizmów wodnych. Zanieczyszczenie gleb tym pierwiastkiem prowadzi do kumulacji w tkankach roślinnych, a to powoduje włączenie go do łańcucha pokarmowego.

W pracy badano warstwę orną gleb wokół wybranych zakładów przemysłowych na terenie miasta Opola. Zawartość selenu w glebach jest wynikiem dwóch czynników – uwarunkowań naturalnych oraz gospodarki człowieka w szczególności związanej z rolnictwem (opryski środkami ochrony roślin) lub działalnością przemysłową. Poziomy stężenie glinu były typowe dla typu gleb i obejmowały zakres 3440 to 14804 mg/kg s.m. Zanotowane stężenia selenu nie były wysokie i zawierały się w przedziale od 27,1 do 958,1 µg/kg s.m. Są to jednak wartości nieco podwyższone w stosunku do spotykanych w glebach niezanieczyszczonych zawierających zwykle kilkadziesiąt mikrogramów selenu w kilogramie. Stwierdzone w niniejszej pracy stężenia nie stanowią zagrożenia dla zdrowia ludzi nawet w przypadku uprawy roślin jadalnych na badanych glebach. W przypadku badanych pierwiastków zanotowano różnice statystycznie istotne pomiędzy badanymi obszarami.