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## SOIL POLLUTION BY ARSENIC WITHIN THE ALLOTMENT GARDENS IN ZŁOTY STOK

### ZANIECZYSZCZENIE ARSENIEM GLEB OGRÓDKÓW DZIAŁKOWYCH W ZŁOTYM STOKU

**Abstract:** The aim of the study was to determine arsenic contents in soils of allotment gardens in the town Złoty Stok, which was formerly the greatest European centre of arsenic industry, as well as to assess ecological risk caused by soil contamination. Two complexes of allotment gardens, where soil samples were collected from the depths of 5–15 cm and 30–40 cm, were investigated.

The soils were rich in organic matter and indicated favourable sorption properties. Total contents of arsenic in soils of both garden complexes were extremely high (with the mean  $232 \text{ mg} \cdot \text{kg}^{-1}$  in the surface layers and  $281 \text{ mg} \cdot \text{kg}^{-1}$  in subsurface layers), and exceeded by manifold the value of Polish soil quality standard established as  $20 \text{ mg} \cdot \text{kg}^{-1}$ . Actually soluble forms of arsenic, determined by extraction with  $0.05 \text{ mol} \cdot \text{dm}^{-3} (\text{NH}_4)_2\text{SO}_4$ , proved to be generally low, ie 2.0 % of total on average. At the same time, potentially soluble arsenic content, mainly adsorbed on organic matter and iron oxides, determined by extraction with  $0.05 \text{ mol} \cdot \text{dm}^{-3} \text{NH}_4\text{H}_2\text{PO}_4$ , was relatively high, in the range:  $14.0\text{--}136 \text{ mg} \cdot \text{kg}^{-1}$  (with the mean 17.2 % of total As). The results indicate that certain environmental risk exists and allotment gardens in Złoty Stok should be excluded at least from a home production of vegetables and other edible plants.

**Keywords:** arsenic, solubility, soils, Złoty Stok, allotment gardens

Soil contamination with arsenic does not make, generally, a serious problem in Poland, such as it is in many countries of the world, like in India, China or Chile [1–3], but there are some sites in Poland, where arsenic occurs in the environment, including soils, in high concentrations [4]. Złoty Stok, a former arsenic mining and processing center, belongs to those sites. The town, situated at the foot of Złote Mountains, has a long history of gold and arsenic mining, which began in the thirteenth century. Arsenic processing started there in the seventeenth century and lasted until 1962. Mining generated large quantities of waste materials, including waste rock and slag, which were disposed in nearby valleys. Soils within the mining area have been polluted by air-borne arsenic. Additionally, numerous mine spoils, slag dumps and tailings

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remained in the vicinity of the town, and extremely high concentrations of arsenic in surrounding soils have already been reported [4, 5]. In spite of the fact that environmental pollution in this area has been proved, soil pollution within the town was not closer investigated, and there are no data available on arsenic contents and mobility in soils in home gardens or allotment gardens.

There are two groups of allotment gardens in Zloty Stok, divided into hundreds of parcels cultivated individually, where gardeners not only cultivate grasslands and ornamental plants, but grow vegetable and fruits as well. The risk of arsenic mobilization into groundwater as well as the hazard of its possible plant uptake depends on soil properties, such as pH, contents of iron oxides, organic matter and phosphates, and several other factors including soil redox potential. Environmental risk caused by the presence of arsenic in soils can be assessed by the extraction of its easily soluble forms as well as potentially soluble forms, mainly sorbed specifically by iron hydroxides [5–7].

In this paper, we present the results of the study in which the properties of soils, including total contents of arsenic and its actual and potential solubility were examined in the main complexes of allotment gardens in Zloty Stok. Compared were arsenic contents and soluble forms in the surface and subsurface soil layers, which let us draw some conclusions as to the sources and extent of soil pollution.

## Material and methods

Soil samples were collected from two complexes of allotment gardens Radosc and Relaks, situated in the town of Zloty Stok and indicated in the map (Fig. 1). In each



Fig. 1. Location of allotment garden complexes Radosc and Relaks in Zloty Stok [8]

garden complex, the samples were taken in 6 sites, from two soil layers: surface (at the depth 5–15 cm) and subsurface (at the depth 30–40 cm).

Soil samples were air-dried and sieved to 2 mm prior to analysis. Basic soil properties were determined using standard methods [9]. Particle size analysis of the fraction < 2 mm was carried out by a combined sieve and sedimentation technique, using a hydrometer method. Soil pH was measured potentiometrically in a suspension with  $1 \text{ mol} \cdot \text{dm}^{-3}$  KCl (*m/v*: 1/2.5). Organic carbon was determined oxidometrically with potassium dichromate in a hot sulphuric acid. Alkaline cations were extracted using a batch method with  $0.5 \text{ mol} \cdot \text{dm}^{-3}$   $\text{NH}_4$ -acetate, and exchangeable acidity was determined in  $1.0 \text{ mol} \cdot \text{dm}^{-3}$  KCl, and on that basis, cation exchange capacity CEC and base saturation BS were calculated.

Total concentrations of arsenic in soil were measured after microwave acid digestion of soil samples in the mixture of concentrated nitric(V) and hydrochloric acids ( $\text{HNO}_3 + \text{HCl}$ , 3 + 1). The method yields results comparable to the standard method with *aqua regia*. After filtering, the digests were analysed for arsenic using ICP-AES method (Varian Instrument). Analytical procedures of total arsenic determination were validated using certified reference materials (Montana soils: SRM 2710 and SRM 2711 that contained 626 and 105  $\text{mg} \cdot \text{kg}^{-1}$  As, respectively), as well as with internal standards.

Soluble forms of arsenic in soils were determined in simple extractions with two different solutions, optimised according to the method by Wenzel et al [6]. Easily soluble As was extracted with  $0.05 \text{ mol} \cdot \text{dm}^{-3}$   $(\text{NH}_4)_2\text{SO}_4$  (1:25, 20°C, 4 h), and specifically bound As, believed to reflect potentially soluble pool of these elements was extracted with  $0.05 \text{ mol} \cdot \text{dm}^{-3}$   $\text{NH}_4\text{H}_2\text{PO}_4$ , (1:25, 20 °C, 16 h).

## Results and discussion

The basic properties of all soils did not show great diversity, and proved to match the typical features of soil cover in that region [4] and those of garden soils. All the data on basic soil properties are presented in Table 1.

Table 1

Basic properties of investigated soils, mean values and ranges

Gardens	Depth [cm]	N	Value	Percentage of grains		Organic C	$\text{pH}_{\text{KCl}}$	CEC	BS
				< 0.02 mm	< 0.002 mm				
				[%]					
Radosc	5–15	6	range mean	15–44 26	1–5 3	2.3–5.1 3.9	6.1–7.0 6.6	17.7–28.0 23.6	87–95 92
	30–40	6	range mean	30–61 43	2–18 8	0.1–2.1 1.3	5.9–7.0 6.4	13.1–21.8 18.8	83–95 92
Relaks	5–15	6	range mean	15–26 20	2–4 3	4.3–5.6 4.9	5.0–7.0 6.2	13.5–29.4 22.9	76–94 87
	30–40	6	range mean	20–34 29	0–6 3	1.2–3.3 1.8	5.0–6.6 5.9	12.0–21.4 16.8	78–93 87

Grain size composition of soils, assigned to the textural groups according to USDA [10], was determined as sandy loam, with locally occurring silt loams in the garden complex Radosc. All soil contained low proportion of clay fraction (4 % being the mean value of all samples), and comparable contributions of silt and sand fractions. Soil pH varied in the range of 5.0–7.0, with neutral or slightly acidic reaction in most cases. Higher pH values in the surface soil layers than those in subsurface layer are typical for intensively used and often limed soils, like horticultural soils. High content of organic matter both in surface and subsurface soil layers, are typical for garden soils as well. The soils contained 2.3–5.6 %, and 0.1–3.3 % of organic carbon ( $C_{org.}$ ) in upper and lower soil layers, respectively. High amounts of organic matter went together with beneficial sorption properties. The values of the cation exchange capacity (CEC) were in the ranges  $131\text{--}294 \text{ mmol}^{(+)} \cdot \text{kg}^{-1}$  in the upper soil layer and  $120\text{--}218 \text{ mmol}^{(+)} \cdot \text{kg}^{-1}$  in the lower one. Generally, the basic properties of soils should be described as beneficial for plant cultivation and amateur garden production.

Closer examination of soil chemistry, in particular contents of arsenic, gives however, quite different assessment. Total concentrations of arsenic were extremely high in all investigated soil samples, and ranged from 72 to 451  $\text{mg} \cdot \text{kg}^{-1}$  (Table 2). It is worth mentioning, that Polish soil quality standards define the level of 20  $\text{mg} \cdot \text{kg}^{-1}$  as maximum acceptable arsenic content in soils used for both agricultural or horticultural purposes, as well as for soils in recreational areas [11]. Total arsenic concentrations in subsurface soil layer (74–451  $\text{mg} \cdot \text{kg}^{-1}$ ) were higher even than those in surface soil layer (72–303  $\text{mg} \cdot \text{kg}^{-1}$ ), though the difference was not statistically significant at  $p = 0.95$ . The results characterizing total arsenic in soils of two garden complexes did not significantly differ either. Presumably, air-borne arsenic was not the only source of this element in the soils examined. Such statement may be based on the data on relatively high arsenic concentrations in subsurface soil, matched together with general knowledge on limited mobility of this element in the soil environment [1, 2, 7, 12, 13]. Possible other sources of soil arsenic might have been: 1) either mine water, used there commonly for soil watering and containing high contents of arsenic in easily soluble forms, or 2) high contents inherited in soil parent rock, of either natural or anthropogenic origin. It is also possible, that originally higher arsenic concentrations in the surface soil layer have been “diluted” with foreign material used for cultivation, such as organic fertilizers. Further studies are needed to give better light to the problem of arsenic origin in garden soils.

Table 2

Total content of arsenic [ $\text{mg} \cdot \text{kg}^{-1}$ ]

Gardens	Depth [cm]	N	Value			
			minimum	maximum	mean	SD
Radosc	5–15	6	72	303	213	85
	30–40	6	74	357	251	114
Relaks	5–15	6	211	272	250	23
	30–40	6	237	451	310	83

At this stage of the study, at least preliminary data were required to estimate the environmental risk caused by arsenic presence in soil and to assess related hazards to human health. Therefore, arsenic solubility in soils was determined, including both actual solubility (easily soluble forms) and potential solubility (the forms specifically bound, mainly to organic matter and iron oxides). Actually soluble forms of arsenic, as determined by extraction with  $0.05 \text{ mol} \cdot \text{dm}^{-3} (\text{NH}_4)_2\text{SO}_4$ , proved to be generally low, in the range  $0.7\text{--}11.0 \text{ mg} \cdot \text{kg}^{-1}$ , which corresponded to  $0.3\text{--}3.5 \%$  ( $2.0 \%$  on average) of soluble arsenic contributions to its total pools in soils (Table 3).

Table 3

## Easily soluble arsenic in soils

Gardens	Depth [cm]	N	Contents [ $\text{mg} \cdot \text{kg}^{-1}$ ]			Percent of total As		
			range	mean	SD	range	mean	SD
Radosc	5–15	6	2.5–4.8	3.7	1.2	1.3–3.4	2.5	1.1
	30–40	6	2.6–11.0	6.8	4.2	2.6–3.5	3.1	0.5
Relaks	5–15	6	2.5–3.0	2.8	0.4	1.1–1.2	1.2	0.1
	30–40	6	0.7–9.3	4.3	4.5	0.3–2.1	1.2	0.9

The extent of this study did not allow to find any statistical relationships between soil properties and arsenic solubility, but it should be mentioned that the highest absolute concentrations of easily soluble arsenic were found in the samples collected from the layer 30–40 cm.

The contributions of potentially soluble arsenic, determined by extraction with  $0.05 \text{ mol} \cdot \text{dm}^{-3} \text{NH}_4\text{H}_2\text{PO}_4$ , in soils were relatively high (Table 4), in the range:  $14\text{--}136 \text{ mg} \cdot \text{kg}^{-1}$  (with the mean value  $41.6 \text{ mg} \cdot \text{kg}^{-1}$ , and average contribution to total As:  $17.2 \%$ ).

Table 4

## Potentially soluble arsenic in soils

Gardens	Depth [cm]	N	Concentrations [ $\text{mg} \cdot \text{kg}^{-1}$ ]			Percent of total As		
			range	mean	SD	range	mean	SD
Radosc	5–15	6	14.0–29.3	21.8	7.7	7.5–19.5	14.7	6.3
	30–40	6	22.7–95.3	52.8	37.8	15.0–30.5	24.6	8.4
Relaks	5–15	6	22.8–24.2	23.5	1.0	8.7–11.5	10.1	2.0
	30–40	6	29.8–136	68.4	38.7	11.6–30.1	19.4	6.6

The contents of potentially soluble arsenic were in subsurface layer higher than those in the surface soil, and this difference proved statistically significant at  $p = 0.95$ . The highest contributions of specifically bound arsenic reached the values of  $30 \%$  of total and were found in subsurface soil layer. There were no significant differences between the contributions of potentially soluble arsenic in soils of both garden complexes. Such high contributions of specifically bound arsenic were not found in the other sites in Zloty Stok, affected by arsenic mining and processing activities [4, 5].

The results indicate, that arsenic presence in soils may cause serious environmental risk, as its easily soluble and specifically bound forms may be mobilized, due to strong changes in soil pH, and more likely, because of changing redox conditions [1, 5, 7, 13].

## Conclusions

The soils of two main garden complexes in Złoty Stok, both in their surface and subsurface layers, contained extremely high concentrations of arsenic, by manifold exceeding those established as soil quality standards.

The origin of arsenic in those soils should be closer studied, as it may be crucial for predicting further behaviour and mobility of this toxic element.

Actual solubility of arsenic in soils remains relatively low, but the contributions of potentially soluble, specifically bound forms, are high, and when mobilized may cause serious risk of water pollution and increased plant uptake. The factors maintaining the processes of arsenic mobilization and bioavailability in those specific soils, require thorough examination.

To minimize the risk to human health, at least the production of plants for consumption, such as vegetables or fruits in the allotment gardens in Złoty Stok should be definitely banned.

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## ZANIECZYSZCZENIE ARSENIEM GLEB OGRÓDKÓW DZIAŁKOWYCH W ŻŁOTYM STOKU

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**Abstrakt:** Celem niniejszej pracy było określenie zawartości arsenu w glebach ogródków działkowych Żłotego Stoku, niegdyś największego w Europie ośrodka przetwórstwa arsenu, a także ocena zagrożenia ekologicznego wynikającego z zanieczyszczenia gleb tym pierwiastkiem. Badano gleby dwóch zespołów ogrodów, w których pobrano próbki z głębokości 5–15 cm i 30–40 cm.

Gleby wykazywały znaczną zawartość materii organicznej oraz korzystne właściwości sorpcyjne. Całkowita zawartość As w glebach obu kompleksów była bardzo duża (średnio  $232 \text{ mg} \cdot \text{kg}^{-1}$  w warstwie powierzchniowej i  $281 \text{ mg} \cdot \text{kg}^{-1}$  w podpowierzchniowej) i w obu zespołach ogrodów znacznie przekraczała wartość  $20 \text{ mg} \cdot \text{kg}^{-1}$  określoną w Rozporządzeniu Ministra Środowiska jako standard jakości gleby. Udział łatwo rozpuszczalnych form arsenu, określanych na podstawie ekstrakcji roztworem  $0,05 \text{ mol} \cdot \text{dm}^{-3}$   $(\text{NH}_4)_2\text{SO}_4$ , był mały i wynosił średnio 2% całkowitej zawartości arsenu, ale udział form potencjalnie rozpuszczalnych, związanych z substancją organiczną oraz uwodnionymi tlenkami żelaza, ekstrahowanych  $0,05 \text{ mol} \cdot \text{dm}^{-3}$   $\text{NH}_4\text{H}_2\text{PO}_4$ , był znaczny, w przedziale:  $14,0\text{--}136 \text{ mg} \cdot \text{kg}^{-1}$  (i średnio odpowiadał 17,2 % całkowitej zawartości As w glebach). Uzyskane wyniki wskazują, że istnieje ryzyko środowiskowe związane z zanieczyszczeniem gleb arsenem i dlatego należy ograniczyć użytkowanie gleb ogrodów działkowych w Żłotym Stoku, przynajmniej w zakresie produkcji warzyw i innych roślin na cele konsumpcyjne.

**Słowa kluczowe:** arsen, rozpuszczalność, gleby, Żłoty Stok, ogródki działkowe