

## ARSENIC CONTENT IN ARABLE LAND OF THE ZĄBKOWICE DISTRICT

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### Abstract

The aim of this study was to determine the content of arsenic in soils used for agriculture in the Ząbkowicki district. The content of arsenic in collected soil samples ranged 1.1-569.5 mg·kg<sup>-1</sup>. The standard for arable lands of Group B has been exceeded in 24 out of 231 test points. The highest concentrations occurred in the Złoty Stok commune. This is due to the output of arsenic and gold in this area. Exceeding the standard also occurred in neighboring communes: Kamieniec Ząbkowicki and Ziębice. This is due to the blowing and washing pollutions from the source of contamination, the arsenic mines in the Złoty Stok commune.

Keywords: arsenic, arable land, Ząbkowicki district

### 1. INTRODUCTION

Arsenic is a highly toxic element [1,11], causing cancer of the skin and internal organs [20,23]. Its toxicity depends primarily on the concentration and forms of occurrence [19]. The absorption of this element can occur by ingestion, inhalation and through the skin [6]. Exceeding the limit values for arsenic in soil causes a small number of trees and bushes, discoloration, stunting, and even deformation of the whole plant [4]. Typical contents of arsenic in soil is in the range of 0.2 to 16 mg·kg<sup>-1</sup>. The highest concentrations found in soils with a high

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content of clay fraction and organic soils [6]. The performance of arsenic in soil is usually associated with the weathering of rocks. Anthropogenic activities such as mining, metallurgy of nonferrous metals, coal burning, or use of pesticides containing arsenic can cause increased concentration of this element in the water and soil [1]. Currently, high concentrations of arsenic were recorded in 21 countries, including Poland [15]. The Ząbkowicki district has the oldest mining and metallurgical center in Poland - Złoty Stok. The last arsenic ore mine in this area was closed in 1961[14]. The aim of this study was to analyze the content of arsenic in soils used for agriculture in the Ząbkowicki district.

## 2. DESCRIPTION OF THE RESEARCH OBJECTS

The Ząbkowicki district is located in south-western Poland, in the Dolny Śląsk province. It is located at the foothills of the Sudeten and covers 802 km<sup>2</sup> [12]. In the complex of the district there are four urban-villages (Bardo, Ząbkowice Śląskie, Ziębice and Złoty Stok) and three village communes (Ciepłowody, Kamieniec Ząbkowicki and Stoszowice).

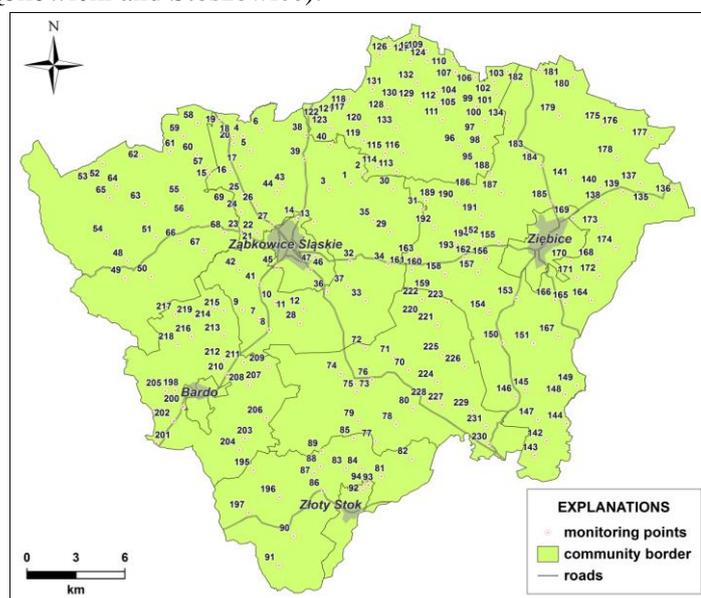


Fig. 1. Location of soil sampling points

Mild weather conditions [5], and the presence of very good soils (Ciepłowody and Ząbkowice Śląskie) cause that a larger area of the district is used for agriculture (Fig. 2) [2]. Arable land in the Ząbkowicki district is formed in a

vast majority of loess and silt of water origin. The contribution of these formations in the total area of arable land in the district is 44.1%, and in the communes ranges from 5.1% in Bardo, to 96.2% in Ciepłowody. A similar share of the total arable land in the district has loam, 41.9%. However, in the communes, loams occupy arable lands from 3.1% in Ciepłowody to 98.4% in Złoty Stok. Water origin silty loams are of a certain significance. Their share in the total area of the district is 7.8%, while in the communes amounted from 1.6% in Złoty Stok, to 17.1% in Ziębice. Sandy soils in the district occupy 5.2% of the arable land. In the communes it is an area from 0.1% in Cieplice to 11.0% in Kamieniec Ząbkowicki.

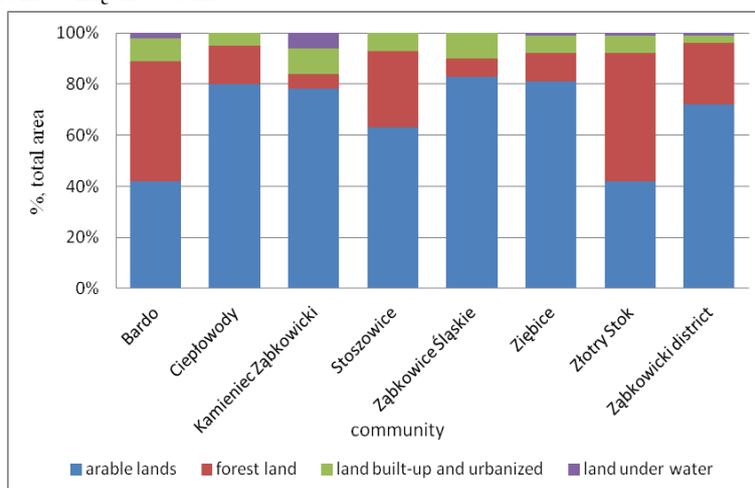


Fig. 2. The structure of land use in the communes of the Ząbkowicki district

There are tens of hectares of clay soils in small enclaves in the four communes where the surface varies from 0.1% (12ha) in the commune of Ząbkowice Śląskie, to 21.2% (330ha) in Ziębice.

### 3. RESEARCH METHODS

The study was conducted on arable land of 7 communes and 2 cities in the Ząbkowicki district. For the analysis 231 samples were collected (Fig.1). The summary of sampling sites is shown in table 1. Material for the study was collected from a depth of 0-30 cm of the few places directly adjacent to the point of the test (located at a distance of less than 5m). In order to control the depth, the samples were taken with the use of a soil core sampler. The samples were mixed directly in the field, and possible excess was removed.

Table. 1 Summary of soil sampling sites

Community	Ambit	Number of samples
Ząbkowice	Bobolice, Brodziszów, Braszowice, Grochowiska, Jaworek, Koziniec, Kluczowa, Olbrachcice, Pawłowice, Sieroszów, Stolec, Strąkowa, Sulisławice, Szklary, Tarnów, Zawrócona	44
Ząbkowice city	Ząbkowice city, Sadłów	3
Stoszowice	Budzów, Grodziszczce, Jemna, Lutomierz, Przedborowa, Różana, Rudnica, Stoszowice	22
Kamieniec Ząbkowicki	Byczeń, Kamieniec Ząbkowicki, Sławęcín, Sosnowa, Topola, Starczów, Doboszowice, Pomianów Górny, Mrokocin, Chałupki	23
Złoty Stok	Błotnica, Płonica, Mąkolno, Chwalisław, Laski	14
Złoty Stok city	Złoty Stok city	3
Cieplowody	Muszkowice, Czesławie, Stary Henryków, Wilamowice, Targowica, Janówka, Jakubów, Cienkowice, Baldwinowice, Piotrowie Polskie, Karczowice, Kobyla Głowa, Koźmice, Tomice, Dobrzenice, Brochocin, Cieplowody	39
Ziębice	Brukalice, Wigańcice, Kalinowice Dolne, Kalinowice Górne, Pomianów Dolny, Lubnów, Głęboka, Niedźwiedź, Biernacice, Służejów, Niedźwiednik, Starczówek, Osina Wielka, Osina Mała, Dębowiec, Nowina, Bożnowice, Raczyce, Witostowice, Wadochowice, Henryków, Nowy Dwór, Krzelków, Czerńczyce, Rososznica	61
Bardo	Opolnica, Dębowina, Laskówka, Dzbanów, Przyłek, Potworów, Grochowa, Brzeźnica	22

For laboratory tests, soil material was dried at room temperature. In determining the proportion of a particle size of soil skeleton, the samples were sieved through sieves with a mesh diameter of 2 mm and 1mm. Fine earth separated in this way (<1 mm) was subjected to further analysis. Soil research included: granulometric composition by the aerometric-sieve method, soil reaction (pH in distilled water and 1 M KCl - by potentiometry), organic carbon content by the Tiurin method. The determination of arsenic was made by GFAAS after mineralization in aqua regia. For the assessment of the correctness of the determinations, certified reference materials and internal standards were used. Maps were prepared in the scale of 1:50 000. In the development of maps Inverse Distance interpolation type Weighting (IDW) was used.

#### 4. RESULTS

Table 2 summarizes the median content of each granulometric fraction in arable soils for each community of the Ząbkowicki district. Granulometric composition is shown in Fig. 3. The analyzed soils showed little soil skeleton (more than 80% of the analyzed soils samples was less than 1%), so this fraction has been omitted.

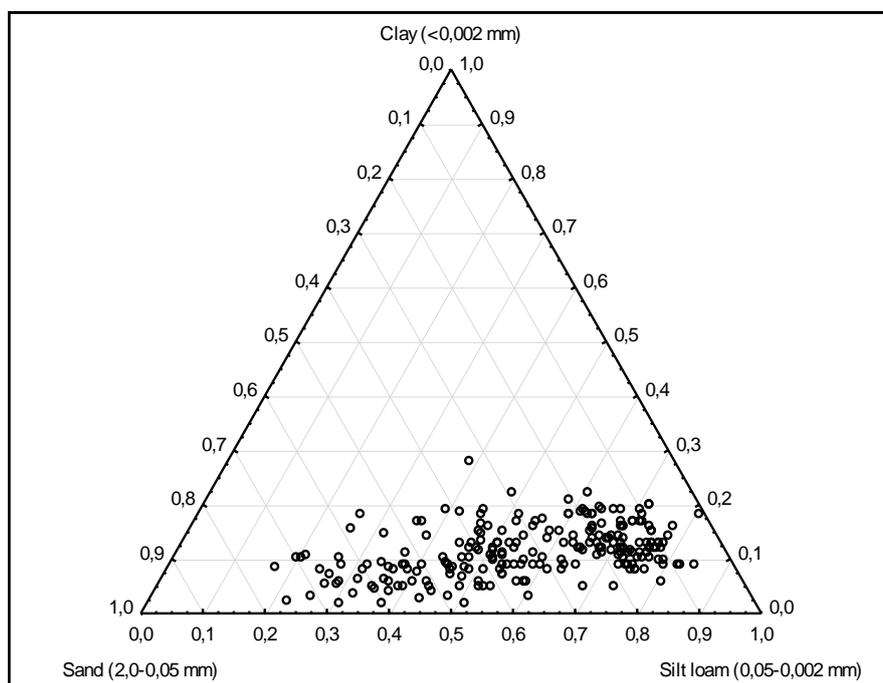


Fig. 3. Granulometric composition of soils from the area of the communities of the Ząbkowicki district

Among the collected soil samples silt loam dominated (169 samples). In a smaller amount there was loam (63 attempts). The fractions of silt loam (0.05-0.002mm) and sand (2.0-0.05mm) have a largest share in granulometric composition of the examined soils. Clay fraction occurred in the least number of samples.

The pH values of soil samples, measured in 1 M KCl solution, ranged in 3.5 - 7.6. The median for all the soil samples was 5.2. In terms of the reaction classification, 52 samples were very acidic, 101- acidic, 62 - slightly acidic, 10 - neutral, and 6 - alkaline.

Table. 2. Particle size of the tested soil samples

Community	Median of fraction content, %		
	2.0-0.05 mm	0.05-0.002 mm	<0.002 mm
Ciełowody	11.0	74.0	14.0
Ziębice	35.0	54.0	10.0
Złoty Stok	51.0	45.0	7.3
Bardo	36.5	51.0	11.5
Kamieniec Ząbkowicki	46.0	44.5	9.8
Ząbkowice Śląskie	18.3	68.4	10.9
Stoszowice	37.5	49.7	11.8

The pH median values for individual communes and the percentage share of soil reaction are shown in Tab.3. Organic carbon content ranged from 0.27% (Ząbkowice) to 5.37% (Bardo), with an average content of 1.12%. The average content of humus was 1.93% (range 0.62 - 9.26%).

Table. 3. Reaction and pH of soil tested samples

Commune	participation of soils, %					pH 1 M KCL	
	very acidic	acidic	slightly acidic	neutral	alkaline	range	median
Ciełowody	17.9	48.7	25.6	5.1	2.6	3.5-7.2	5.4
Ziębice	26.2	37.7	23.0	6.6	6.6	3.5-7.5	5.2
Złoty Stok	35.3	47.1	11.8	5.9	0.0	3.6-7.5	5.1
Bardo	27.3	54.5	18.2	0.0	0.0	3.6-7.5	5.1
Kamieniec Ząbkowicki	30.4	34.8	30.4	4.3	0.0	3.6-7.6	4.8
Ząbkowice Śląskie	8.5	46.8	38.3	4.3	2.1	3.8-7.5	5.4
Stoszowice	27.3	40.9	31.8	0.0	0.0	3.8-6.5	5.2

Acceptable arsenic content, defined for agricultural land in the Regulation of the Minister of Environment of 9 September 2002 on the soil quality standards, for lands from the B Group is 20 mg·kg<sup>-1</sup>. The content of arsenic in the collected soil samples ranged 1.1-569.5 mg·kg<sup>-1</sup>. The limit value was exceeded in 24 out of 231 test points. The average content of arsenic in the studied samples was 32.35 mg·kg<sup>-1</sup>, and the median 20.45 mg·kg<sup>-1</sup>.

Fig. 4 shows the total arsenic content in agricultural soils in the Ząbkowicki district. The standard was exceeded in three communes: Kamieniec Ząbkowicki (8 samples of 23 - range of exceeding 20.5-46.4 mg·kg<sup>-1</sup>), Złoty Stok (16 samples of 17 - range of exceeding 22.0-569.45 mg·kg<sup>-1</sup>), and Ziębice (1 trial of 61.0-25.1 mg·kg<sup>-1</sup>). The elaborated map shows that maximum levels of arsenic

were exceeded only in the southern part of the Ząbkowicki district. The range of arsenic contamination of soil is 12 km from the source, which was the mine in Złoty Stok. Other areas are not contaminated with As.

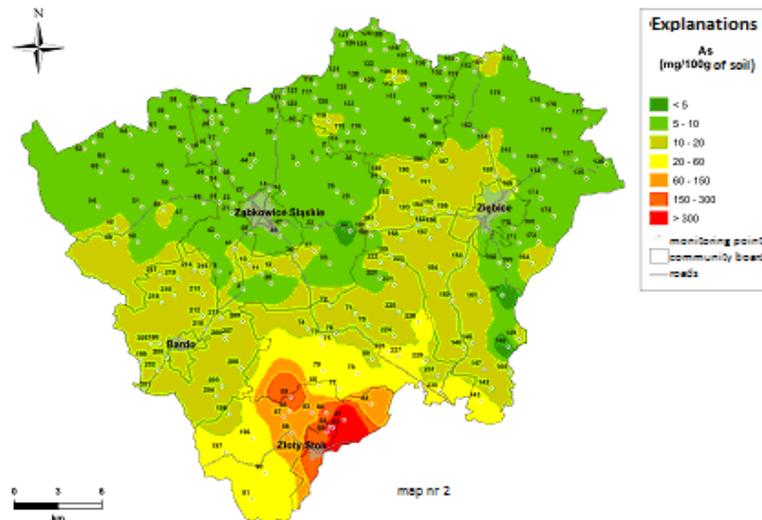


Fig. 4. Spatial distribution of total arsenic in soils of the Ząbkowicki district agricultural lands

In addition to the standards set out in the Regulation, multi-step evaluation of arsenic in the soil can be made on the basis of the geoaccumulation index [16] according to the equation:

$$I_{\text{geo}} = \log_2(C_{\text{As}}/1,5 B_{\text{As}})$$

where:  $C_{\text{As}}$  is the measured concentration of arsenic

$B_{\text{As}}$  is the geochemical background value

the constant 1.5 allows us to analyze natural fluctuations in the content of a given substance in the environment and very small anthropogenic influences.

Assessment is based on a comparison of current levels of heavy metals in the geochemical background (element contents in parent rock) [13]. Background level for arsenic is taken as  $9.02 \text{ mg}\cdot\text{kg}^{-1}$ . This is the average concentration of arsenic in soils of the 9 districts of the Sudeten and the foothills of Sudetenland [10].

Table. 3 Determination of arsenic accumulation classes in communes of the Ząbkowicki district based on geoaccumulation index

Commune	Classes of index						
	0*	1	2	3	4	5	6
Cieplowody	38	1	-	-	-	-	-
Ziębice	53	8	-	-	-	-	-
Złoty Stok	0	4	2	3	3	3	2
Bardo	10	12	-	-	-	-	-
Kamieniec Ząbkowicki	8	10	5	-	-	-	-
Ząbkowice Śląskie	47	-	-	-	-	-	-
Stoszowice	21	1	-	-	-	-	-

\*Class 0- practically uncontaminated, 1- uncontaminated to moderately contaminated, 2- moderately contaminated, 3- moderately to heavily contaminated, 4- heavily contaminated, 5- heavily to extremely contaminated, 6- extremely contaminated.

## 5. DISCUSSION

Arsenic is used in many industries: semiconductor industry, pesticides production, materials for wood preservation, metal alloys, glass, pigments and pharmaceuticals [3]. The presence of this metal can have a natural source (related to parent rock) or anthropogenic (fossil fuel combustion, smelting Cu, Pb, nickel ore, as well as an improper use or overuse of pesticides). Geological risks related to the soil load of heavy metal are considered lower than anthropogenic pollution [21]. Soil pollution with heavy metals in Lower Silesia is primarily associated with the mining and processing of metal ores (current or historical), and the proximity of urban areas and post [8]. A study done by the Plak [18] show that the total arsenic content in soils of Lublin agglomeration ranged from 0.42 - 19.62 mg·kg<sup>-1</sup>. Arsenic concentration in soils of the Ząbkowicki district is much higher: 1.1-569.5 mg·kg<sup>-1</sup>. From 231 examined soil samples, 25 exceeded the legal limit of arsenic for agricultural land. They were the soil of the three communes: Złoty Stok, Kamieniec Ząbkowicki and Ziębice. In the other communes this metal content was within the standard. The largest accumulation of arsenic in soils (569.5 mg·kg<sup>-1</sup>), was found in a sample from the Złoty Stok (Fig. 5). This is due to the presence in this area of arsenic and gold deposits that have been exploited since the '90 of thirteenth century [14]. Similar results were obtained by Kicińska[11], who examined the soil adjacent to the Mining and Metallurgical Bets in the Bukowno region. She meant the arsenic content in the whole soil profile.

The largest concentration of metal appeared in the surface layer of soil ( $1900 \text{ mg}\cdot\text{kg}^{-1}$ ), and at a depth of 30 cm arsenic content was four times less:  $467 \text{ mg}\cdot\text{kg}^{-1}$ . In the commune of Kamieniec Ząbkowicki, adjacent to Złoty Stok, 34.0% of the samples exceeded the limit values of arsenic. Its highest concentration was  $46.4 \text{ mg}\cdot\text{kg}^{-1}$ . In this area, there are no industrial centers. According Niedzielski [17] soils which are not in contact with the anthropogenic sources of pollution show that the content of this element does not correspond to the background. This is related to the widespread pollution. Moreover, all communes in the Ząbkowicki district have predominantly acidic soils, which increase the mobility of metallic elements [9]. Exceeding the standards may be associated with inappropriate agricultural practices, the bedrock [24] or soils rich in organic matter [7]. Arsenic mobility is also connected with the presence of silicate minerals and hydroxides Fe, Al and Mn [22]. In the Ząbkowice commune only one trial (on 44) exceeded the standard. Exceeding was low ( $5.1 \text{ mg}\cdot\text{kg}^{-1}$ ).

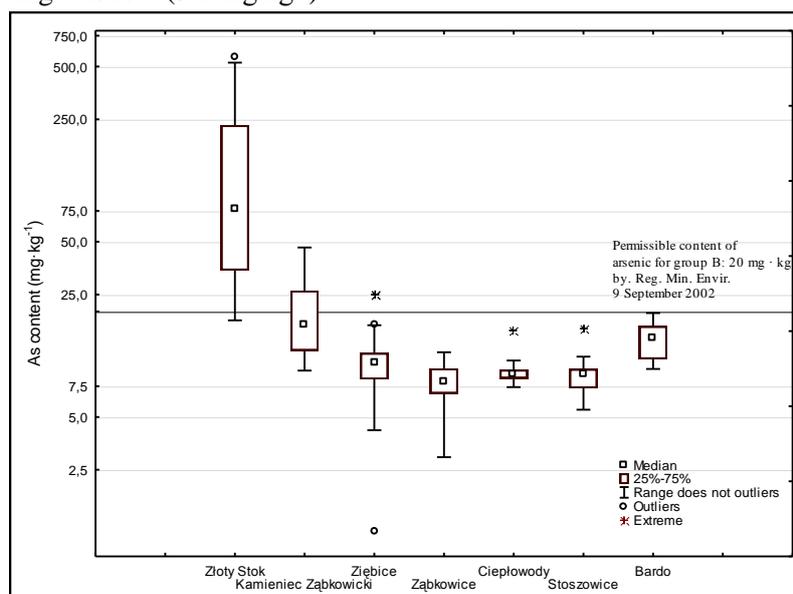


Fig. 5. Arsenic content in arable land of the Ząbkowicki district

The reason for this phenomenon is the same as in the case of Kamieniec Ząbkowicki. The analysis of the arsenic concentration in soils on the basis of geoaccumulation index (tab. 3, Fig.6) shows that the soils are the cleanest in the commune of Ząbkowice Śląskie (47 samples practically uncontaminated). In the communes of Cieplice, Ziębice, Bardo, Stoszowice soils are uncontaminated to moderately contaminated. Moderately contaminated soils are located in

Kamieniec Ząbkowicki while in Złoty Stok there are all classes of pollution (including class 6, which is extremely contaminated soils).

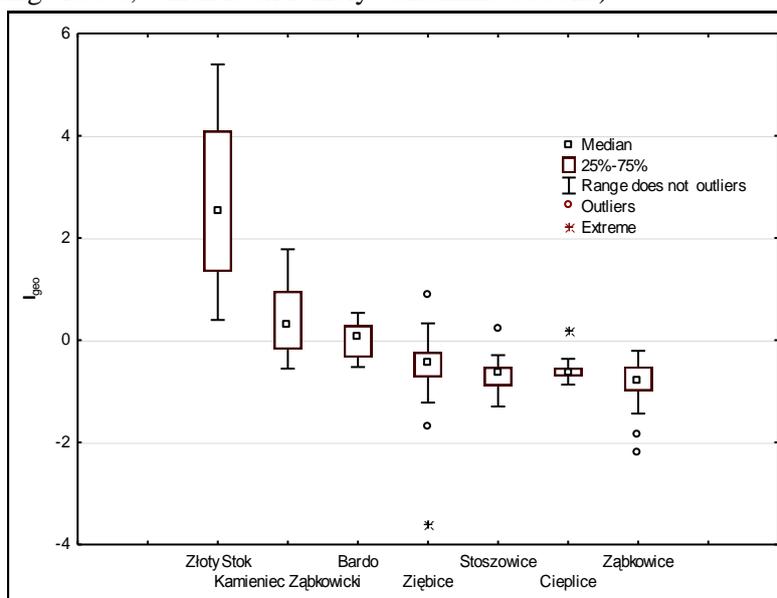


Fig. 6. Geoaccumulation index in communes of Ząbkowicki district

## 6. CONCLUSIONS

1. In terms of the geoaccumulation index, the soils in Złoty Stok commune are extremely contaminated.
2. Pollution appears even in the area of 12 km away from the source of contamination, which is the mine in Złoty Stok.
3. Soils contaminated with arsenic occur in the southern part of the Ząbkowicki district. Exceeding the standards related to the area of arsenic and gold mining is conducted in this area.
4. In the Ząbkowicki district there are mostly very acidic, acidic and slightly acidic soils. This reflects the nature of the host rock. It will also contribute to increase the mobility of arsenic in the soil.

## ADDITIONAL INFORMATION

The study was performed on the basis of Silesian Arable Land Protection Fund.

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## ZAWARTOŚĆ ARSENU W GRUNTACH ORNYCH POWIATU ZĄBKOWICKIEGO

### Streszczenie

Celem publikacji było określenie zawartości arsenu w glebach wykorzystywanych rolniczo w powiecie ząbkowickim. Zawartość arsenu w pobranych próbach gleb mieściła się w granicach 1,1-569,5 mg·kg<sup>-1</sup>. Przekroczenie normy zawartości arsenu w gruntach ornych, określone w Rozporządzeniu, występuje w południowej części powiatu. Wartość dopuszczalna została przekroczona w 24 spośród 231 badanych punktów. Największa koncentracja tego pierwiastka wystąpiła w gminie Złoty Stok. Związane jest to z eksploatacją na tym terenie rud arsenu i złota. Przekroczenie dopuszczalnej zawartości wystąpiło również w sąsiednim Kamieńcu Ząbkowickim oraz w Ziębicach. Jest to

wynikiem występowania na tym terenie gleb kwaśnych, które zwiększają mobilność metali ciężkich.

Słowa kluczowe: arsen, grunty orne, powiat Ząbkowicki

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