

Arsenic Distribution in Soils of a Former As Mining Area and Processing

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Abstract

Distribution of As concentrations in soils in the vicinity of Złoty Stok, a historical centre of gold and arsenic mining and processing, was examined on the basis of two regular nets of sampling sites: in a forested mountain valley affected by mining activities, and in a flat river valley polluted by spills from tailing impoundments. The maps of As concentrations in the 0-15 cm soil layer show extremely high levels of soil pollution, with maximum values of 28,300 and 7,860 mg·kg⁻¹, in those areas, respectively. Lower amounts of As in forest litter indicate limited arsenic phytoavailability. Extraction and incubation tests confirm that under certain conditions, considerable amounts of As (up to 93 mg·kg⁻¹) may be released from soils.

Keywords: arsenic, Złoty Stok, soil, mining, tailings

Introduction

Contamination of the environment by arsenic is particularly problematic in the surroundings of arsenic mining areas [1-3]. The town of Złoty Stok in SW Poland (Fig. 1) was in the past an important centre for gold mining and processing. From the 17th century until 1962 it was one of the most important arsenic industry centers in Europe [4-7]. Arsenic-bearing ores are present within the complexes of Proterozoic metamorphic rocks, mainly acidic, such as gneisses and schists, with locally occurring amphibolites and intrusions of crystalline limestone. The main As minerals are loellingite (FeAs₂) and arsenopyrite (FeAsS), formed in the contact zone as a product of hydrothermal processes [4, 7].

Ore mining and processing generated large quantities of waste materials rich in As, such as mine waste rock, slag and tailings, disposed of in nearby valleys [6-8]. Mine spoils of various ages are spread over the forested hilly Valley of Złoty Potok (Golden Creek), situated in a mountainous landscape south of the town, and indicated as area I (Fig. 1).

Most of the mine spoils are in fact hardly distinguishable from natural forms of the slopes. Additionally, ore smelting processes carried out in small facilities that produced gold were the source of As released into the atmosphere and deposited on the earth's surface. According to some estimates, arsenic emissions throughout the 16th century might have been as high as several Mg daily [9].

Tailings, produced in recent centuries by arsenic ore processing plants, were disposed north of the town in the embanked sites situated in the valley of the Trująca (Poisonous River), indicated as area II (Fig. 1). A large part of the valley downstream from the tailings-disposal sites was affected by casual dam overflowing or seepage [3, 9], and in consequence the soils presently contain high As concentrations locally exceeding 1,000 mg·kg⁻¹ [5, 6, 9]. There are also some reports of water contamination with As in that area [7, 9]. In spite of all these facts, the lower part of the Trująca valley (area II) is used for agriculture, as arable fields, meadows, and pastures. It should be stressed that Złoty Stok itself, on account of its scenic surroundings, attracts a lot of tourists, and therefore they should be particularly well protected from the hazard caused by arsenic occurrence in the environment.

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It has been widely proved that total As concentrations in soils do not necessarily reflect environmental risk. Easily mobilizable forms of pollutants are much more important from the standpoint of possible environmental impacts [1, 10, 11]. Single extraction methods may be used for a rough assessment of real environmental risk posed by the presence of toxic elements in soils. Several extracting agents have been proposed for the measurement of bioavailable arsenic in soils [12]. However, none of them is universal to indicate As mobility in various contaminated soils under different conditions [11-14]. Soil incubation tests may be used for examining the potential of arsenic mobilization under reducing conditions [5, 15, 16], as the main pool of As in soils is usually bound to Fe oxides liable to reduction and dissolution [5, 17, 18].

The main objective of this study was to assess the spatial distribution of As concentrations in soils in the vicinity of Złoty Stok – based on two regular nets of sampling sites established in two separate areas, as well as to assess the environmental risk caused by As abundance, based on the results of single extractions and incubation tests applied to representative soil profiles. Several previous papers [5, 6, 15] indicated high soil enrichment in As in selected sites of those areas, whereas this study aims to illustrate the spatial extent of its occurrence.

Experimental Procedures

Soil Sampling

Soil samples were collected from two areas:

- I. Złoty Potok Valley, an abandoned mining zone
- II. Trujača River Valley (Fig. 1).

In both areas, separate nets of soil sampling sites were established, built of 28 and 25 sites respectively. Surface soil material was sampled from a depth of 0-15 cm. In the forested area (I), samples of forest litter also were collected from all the sites. Maps illustrating a spatial distribution of As were then elaborated, as described further.

Based on the maps, eight locations (four in each area, I and II) were chosen as representative for various ranges of As concentrations in soils. In those locations, 2-3 soil samples were taken from deeper soil profiles in order to describe a profile distribution of As in soils. The depth of sampling varied among the sites and was determined by the morphology of soil horizons. The samples were examined by single extraction tests to assess the potential for As mobilization and bioavailability.

Basic Soil Properties

All the samples were air-dried, sieved to 2 mm and stored at room temperature in polypropylene containers until analysis. Morphological features and mineralogical composition of the soil skeleton (stones and gravels) were roughly described and that fraction was discarded. Particle size analysis of the fraction <2 mm was carried out via a combined sieve-and-sedimentation technique. Basic chemical properties of soils were determined using standard methods [19]. Soil pH (in suspension with 1M KCl, 1:2.5 / m:v) was measured after 8 h of equilibration, using a combined pH electrode. Organic carbon was determined by a combustion method with a Ströhlein CS-MAT 5500 automatic analyzer.

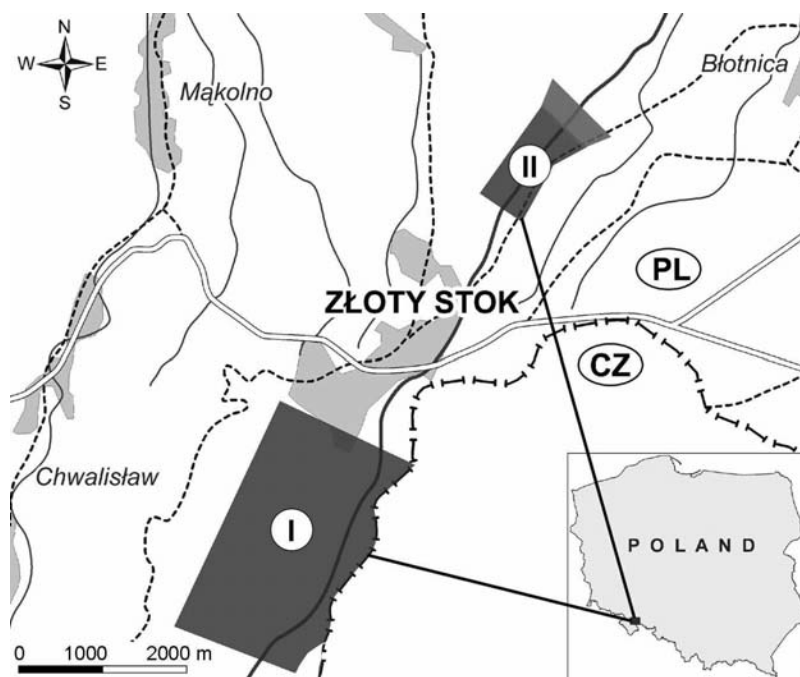


Fig. 1. Situation of the investigated area. A simplified map derived from the topographic map 1:25,000, in a raster form [20]. (Created by authors).

I, II – two separate areas considered in the study: I – Złoty Potok Valley, an abandoned mining zone, II – Trujača River Valley. More details are given in the text.

Analysis and Mapping of Total Arsenic in Soils

Total concentrations of As in soil samples were measured after acid digestion under reflux in the mixture of concentrated nitric and perchloric acids ($\text{HNO}_3 + \text{HClO}_4$), which gives results comparable to the method with aqua regia. The digests were filtered and analyzed for As using ICP-AES, Varian. Deionized water was used throughout during the laboratory tests. All reagents were of analytical grade purity. All analytical procedures were validated using internal and certified reference materials: WEPAL RSM 2709 (San Joaquin soil), RTH 912 (Swiss Loess Soil), and SRM 2711 (Montana Soil). The recoveries of As were in the range 93-116%, most satisfying in the case of standard RSM 2711, which contained the highest As concentration.

Numerical maps of arsenic concentrations in soils were created with ArcEditor 10.0 software, using the Geostatistical Analyst application. Images of spatial variability of arsenic concentrations in the soils of both studied areas were obtained by the interpolation method of inverse distance weighting type (IDW). Topographic maps in a raster form, in the scale 1:25,000, in the Polish system of mappings "1965" [20], were applied as background data.

Single Extractions and Incubation Tests

All soil samples collected from 8 representative soil profiles were extracted using 0.05 M $(\text{NH}_4)_2\text{SO}_4$, which is believed to release non-specifically-bound As. This reagent, employed as a single extractant, has been shown to correlate well with As in soil solutions collected in the field, and hence can be used for predicting As solubility [21]. Ammonium sulphate extractability is a suitable parameter used to assess the risk assessment of As to the groundwater and to estimate readily bioavailable As fractions. In order to determine the susceptibility of arsenic to mobilization under reducing conditions, incubation-extraction tests were carried out in two versions: 1-day incubation without additives supporting reductive processes (1d-0), and: 7-day incubation with the addition of glucose (7d-G). The recommendations for such procedures were adapted from Glinski et al. [22], and were described in detail by Krysiak and Karczewska [5, 15]. Soil samples were fully saturated with background electrolyte 0.1 M $\text{Ca}(\text{NO}_3)_2$ at a soil to solution ratio of 1/2.5 (wt./v.), tightly closed and incubated over a period of 1 or 7 days. Glucose (0.1 g per 100 g of soil) was applied to soils as a source of carbon for soil microorganisms to promote the development of reducing conditions [22]. After incubation, the samples were centrifuged (1,100 g) and filtered. Arsenic concentrations in supernatants were then measured with ICP-AES.

Results and Discussion

Basic Soil Properties

All soils in the valley of Złoty Potok (I) contained substantial amounts of coarse fractions, and usually had the texture of gravely sandy loams, silty loams, and loams.

Table 1. Basic soil properties and arsenic concentrations in the layers 0-15 cm, in areas I and II. All the properties, including clay content, refer to fine earth (<2 mm). Most soil samples contained high amounts (up to 85%) of gravel and stones.

Area	No. of samples	Clay <0.002 mm %	pH 1M KCl	C _{org.} %	Total arsenic mg·kg ⁻¹
I	27	5-17	3.2-4.3	3.2-20.2	194-2,960
	1 ^a	4	6.3	3.5	28,300
II	25	7-18	4.2-6.8	1.1-6.8	190-7,860

^a Site indicated with asterisk in the map (Fig. 2a).

The exception was a soil sample collected from one site (marked on the map with an asterisk) that had the texture of gravely sand described separately in Table 1). The basic chemical properties of that soil sample were also considerably different from those in the other sampling sites, i.e. the skeleton contained admixtures of limestone, and soil pH was much higher than that in other sites. These properties, together with an extremely high concentration of As, indicate that in that particular site the slope of the valley was covered by, or built of, the waste rock material from mining activities.

In the valley of the Trująca River (II) soils differed considerably in their textures; however, they contained, in general, higher amounts of clay fraction than those in area I (Table 1). In some sites, particularly in the area directly adjacent to the river, the soils contained relatively high admixtures (up to 30%) of skeletal grains, with varying mineral compositions. The pH of soils was close to neutral or slightly acidic. Organic carbon content in the layer 0-15 cm varied substantially (in the range 1.1-6.8 %), depending on site position in the valley and was the highest in its central parts.

Spatial Distribution of Arsenic in the Surface Soil Layers

The concentrations of As in soils in the Złoty Potok valley were in the ranges 194-28,300 mg·kg⁻¹ and 23-9,990 mg·kg⁻¹ for mineral levels (0-15 cm) and the forest litter samples, respectively (Table 1). The highest concentrations of As in the layer 0-15 cm occurred in the lower (NE) part of the valley (Fig. 2a), i.e. in the zone of most intensive mining documented by historical sources [7-9]. Values gradually decreased toward SW, but on the border of the examined area they still considerably exceeded the levels typical for uncontaminated areas, remaining usually below 5 mg·kg⁻¹ [1, 11]. Extremely high concentrations of As (2.8%) in the layer 0-15 cm were found at the site (marked with an asterisk) in which soil properties were quite different from the others. Such a high arsenic content in soil in this site undoubtedly resulted from the fact that the soil parent rock was composed of waste material anthropogenically disposed of during mining operations. Very high levels of As (1,880 and 2,960 mg·kg⁻¹) also were found in two other sites situated in the same part of the investigated area,

which probably indicates that those sites also were situated on slopes covered with mining waste material.

Arsenic concentrations in forest litter in Złoty Potok (area I) were significantly lower than those in mineral soils. Surprisingly, the highest content of As in litter (nearly 1.0%) was found in a different site from that with maximum As concentrations in the mineral soil layer (Fig. 2b). Generally, As concentrations in mineral soil layers and in the forest litter did not correlate well, although the tendency of decreasing values toward SW, i.e. with the increasing distance from the centre of mining and smelting activities, was observed in both cases. The Pearson's correlation coefficient (determined for the sets of log values, calculated to obtain near-normal distributions) was high at $R=0.616$; however, the correlation did not prove significant at $p=0.95\%$. Relatively low concentrations of As in forest litter indicate that there is a limited bioavailability of As in the highly enriched forest soils and that factors other than total As have a decisive impact on As uptake or absorption from the air by the aboveground parts of trees and other plants. The lack of significant correlation between As concentrations in mineral and forest litter layers should probably be attributed to the mechanical pollution of tree leaves by mineral particles removed from the uncovered soil surface.

The concentrations of As in the surface soil layer (0-15 cm) of Trująca Valley (area II) varied in the range of 190-7,860 $\text{mg}\cdot\text{kg}^{-1}$ (Table 1) and were assessed as extraordinarily high. There was a clear tendency of decreasing As concentrations in soils toward N (Fig. 3), i.e. with increasing distance from tailing impoundments, believed to be the main source of soil As enrichment. On the outskirts of the valley, at the sites situated at higher locations, As concentrations in soils were much lower than those in the immediate vicinity of the impoundments or river bed, but they still considerably exceeded the values accepted as safe for agricultural use, i.e. 20 $\text{mg}\cdot\text{kg}^{-1}$.

Profile As Distribution in Soils

Profile distribution of soil properties and As concentrations in soils in areas I and II are illustrated on the basis of examples from 8 sites located in zones with various ranges of As enrichment. Basically, in all the sites chosen as representative, total As concentrations in soils decreased soil profiles (Table 2). This tendency, typical for both areas (I and II), seems to confirm that As-rich material (mine wastes in area I or tailings transported by water due to the spills or dams overflowing – in area II) was in the past mechanical-

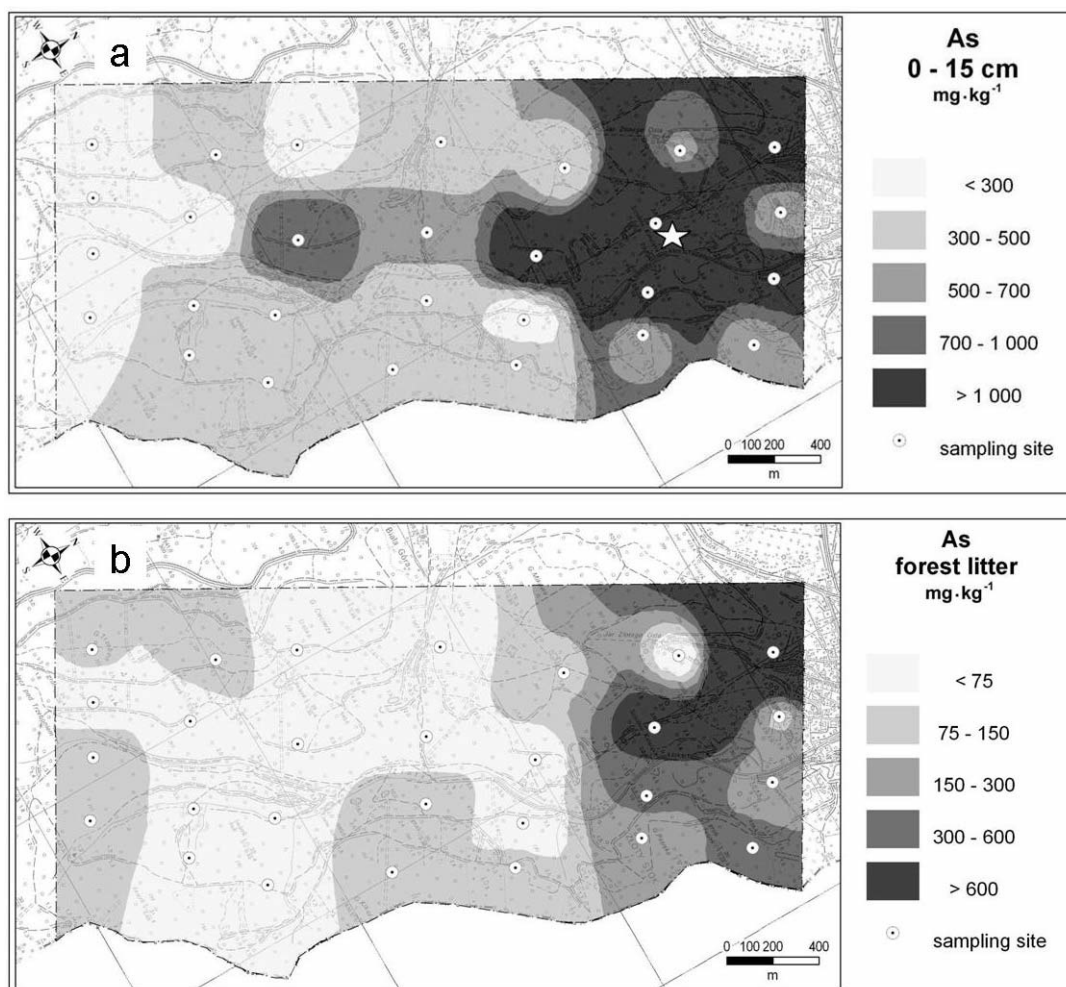


Fig. 2. Spatial distribution of arsenic a) in the mineral surface soil layer (0-15 cm) and b) in forest litter, in the area of Złoty Potok Valley (I). Numerical maps created with ArcEditor 10.0 software, on the background of topographic map 1:25,000, in a raster form [20].

ly disposed of on the soil surface. Undoubtedly, those effects were overlapped by generally high concentrations of As in the whole area, caused both by airborne pollution [9] as well as natural environmental enrichment in As, typical for gold mining areas (the so-called “halo” effect) [1]. Other studies carried out in areas I and II [9], however, indicate that soil profiles in large parts of both areas, and particularly in the Trujaca Valley (II), were mechanically disturbed due to mining activities and land reclamation measures, and that the layers highly enriched in As may locally be present very deep in the soil profiles, which is an important factor for planning future land management.

Mobilization Potential

The results of single extraction tests performed with 0.05 M ammonium sulfate according to Wenzel et al. [21] provided information about easily soluble forms of As in soils. Their amounts in mineral layers of soils in area I were low, in the range <0.02-1.05% of total As, which corresponded to the concentrations from <0.1 to 10 mg·kg⁻¹ As. The highest amount of soluble As (10 mg·kg⁻¹) was extracted from the soil I-1 that contained in mineral horizons a very high total As, over 5,000 mg·kg⁻¹ (Table 2). The shares

of readily soluble As in the forest litter were slightly higher than those in mineral soils in area I, but only in the case of the most enriched soil, I-1, should ammonium sulphate-soluble As in the forest litter (20 mg·kg⁻¹) be considered problematic. The potential for arsenic mobilization from forest litter in such extremely enriched sites, as well as the subsequent fate of released As, should be subject to closer examination in a future study.

Extraction of As from samples collected from area I, incubated for a period of 7 days in the presence of glucose, proved that the amounts of As released from soils in reducing conditions increased in comparison with those extracted after a 1-day incubation without this additive (Fig. 4). While the maximum amount of As released after a 1-day incubation without glucose did not exceed 5 mg·kg⁻¹, those obtained after a 7-day incubation with glucose in a number of samples were higher than 10 mg·kg⁻¹, and the amount of As mobilized from the most polluted forest litter sample reached 30 mg·kg⁻¹, i.e. 6.9% of total As. This effect may be attributed to the decreasing sorption capacity of solid phase caused by the transformation of organic matter, as well as to the mobilizing effect of low-weight organic compounds rather than to possible solubilization of Mn-Fe oxides.

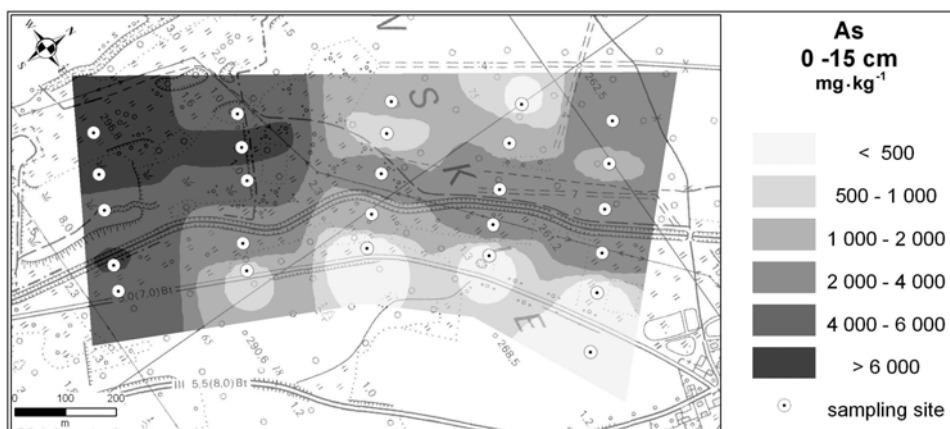


Fig. 3. Spatial distribution of arsenic in the surface soil layer (0-15 cm) in the area of Trujaca Valley (II). Numerical map created with ArcEditor 10.0 software, on the background of topographic map 1:25,000, in a raster form [20].

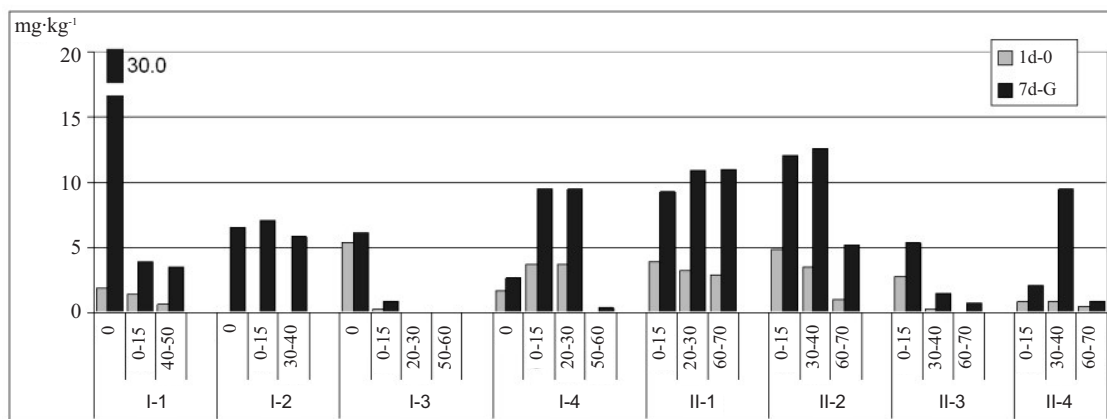


Fig. 4. The amounts of arsenic released from soils in incubation-extraction tests. 1d-0: 1 day incubation without additives, 7d-G: 7 day incubation with the addition of glucose.

Table 2. Basic soil properties and soluble arsenic concentrations in selected sites. All the properties, including clay content, refer to fine earth (<2 mm). Most soil samples contained high amounts (up to 85%) of gravel and stones.

Site No.	Depth cm	Clay <0.002 mm %	pH 1M KCl	C _{org.} %	Total As, mg·kg ⁻¹	0.05 M (NH ₄) ₂ SO ₄ soluble As	
						mg·kg ⁻¹	Percent of total
I-1	O	-	3.3	35.5	460	20	4.35
	0-15	4	4.1	4.1	5,730	8.3	0.14
	40-50	4	5.0	0.8	5,470	10.0	0.18
I-2	O	-	3.8	23.1	270	0.2	0.07
	0-15	6	3.8	3.9	880	0.2	0.02
	30-40	7	4.0	0.9	420	<0.1	<0.02
I-3	O	-	2.8	43.7	57	2.1	3.68
	0-15	5	3.3	3.2	460	0.2	0.04
	20-30	6	3.9	1.5	300	<0.1	<0.03
	50-60	6	3.8	0.8	240	<0.1	<0.04
I-4	O	-	2.9	40.8	29	0.3	1.03
	0-15	9	2.9	20.2	190	2.0	1.05
	20-30	11	3.7	2.8	260	2.4	0.92
	50-60	8	3.7	1.1	320	0.3	0.09
II-1	0-15	12	6.7	3.4	6,030	68	1.13
	20-30	8	6.2	1	1,670	59	3.53
	60-70	11	5.8	0.4	1,170	52	4.44
II-2	0-15	14	6.1	5.6	4,970	93	1.87
	30-40	17	5.8	2.4	4,640	81	1.75
	60-70	13	5.5	0.4	1,130	25	2.21
II-3	0-15	15	5.9	4.1	2,960	41	1.39
	30-40	7	5.5	0.4	730	0.4	0.05
	60-70	11	5.4	0.2	430	0.3	0.07
II-4	0-15	14	4.5	1.3	373	2.0	0.54
	30-40	12	5.0	0.4	232	5.2	2.24
	60-70	9	5.2	0.3	118	3.4	2.88

The amounts of As released in the single extraction tests with (NH₄)₂SO₄ from the soil samples collected in the Trująca Valley (area II) were in general considerably higher than those described above for area I, and varied in the range 0.3-93 mg·kg⁻¹. The highest amounts of As were extracted from the samples of the two most polluted soil profiles. Also, the incubation-extraction tests yielded results higher than those obtained from the soils of area I. Potential mobilization of As from soils of the Trująca valley under reducing conditions should be taken into account when preparing the recommendations for future land management in that area. It is crucial to take precautions against soil flooding in the valley, particularly if organic amend-

ments, favouring a drop in redox potential [16, 23-25], are considered for soil fertilization in that area.

Conclusions

This study confirmed that both areas, i.e. the valleys of Złoty Potok (I) and Trująca (II) are heavily contaminated with As. The highest concentrations of As in area I occur mainly in the surface soil layers and are undoubtedly associated with the historical influence of ore mining and processing. The much lower concentrations of As in forest litter than those in the mineral soil layers prove the limited

phytoavailability of As and indicate that As remains relatively stable in soils of that area. However, certain amounts of As may be potentially released from the forest litter in highly polluted locations, and this matter requires closer examination.

The analysis of spatial and profile distribution of As in soils of Trujaca Valley (II) confirmed the long-range impact of tailing impoundments and indicated extremely high concentrations of As in soils. Its considerable amounts may get mobile at reducing conditions. Therefore, special care should be taken to prevent soil flooding. Further study is needed to assess the actual risk of As mobilization from that area.

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