



Union of Chemists
in Bulgaria

B U L G A R I A N

Chemistry and Industry

FOUNDED 1922

Volume 78, Numbers 1–4
January–December 2007

Bulgarian Chemistry and Industry

Editor-in-Chief:

D. Tsalev

Editors:

Ch. Bonev, N. Naydenov

Editorial Board:

I. Havezov, S. Ivanov, N. Kolev, Ch. Kratchanov, L. Petrov,
I. Schopov, N. Tyutyulkov, G. Vissokov

Advisory Board:

G. Andreev, S. Armyanov, V. Beschkov, L. Boyadzhiev, D. Elenkov,
D. Kamenski, D. Klissurski, V. Konsulov, S. Manev, M. Mitewa,
M. Natov, Yo. Pelovski, P. Petkov, S. Popov, N. Raev, R. Raicheff,
B. Samuneva, K. Stanulov, S. Stoyanov, D. Stratiev, Ch. Tsvetanov

Founding Editor:

I. Tomov

Manuscripts should be sent to:

Prof. D. L. Tsalev, D.Sc.
Editor-in-Chief
Bulgarian Chemistry and Industry
Faculty of Chemistry, University of Sofia
1 James Bourchier Blvd., 1164 Sofia, Bulgaria
Tel: +359-2-8161318; fax: +359-2-9625438
E-mail: tsalev@chem.uni-sofia.bg

Editorial office:

N. Naydenov, Dip. Eng.
Bulgarian Chemistry and Industry
Union of Chemists in Bulgaria
108 G. Rakovski St.
1000 Sofia, Bulgaria
Tel/fax: +359-2-9875812
E-mail: chem@fnts-bg.org

© Union of Chemists in Bulgaria

Star Press
Printed by M. Drinov Academic Publishing House

ISSN 1311-1663
Printed in Bulgaria

Arsenic speciation in soils in the vicinity of a copper smelter in Pirdop, Bulgaria

Y. Bohari^{1,2}, T. Stoichev^{1,3}, D. L. Tsalev^{4*}, A. Bosev³

¹ LCBIE, CNRS UMR 5034, UPPA, Hélioparc, 64053 Pau, France

² Department of Chemistry, Mulawarman University, Samarinda, Indonesia

³ National Centre of Public Health Protection, 1431 Sofia, Bulgaria

⁴ Faculty of Chemistry, University of Sofia, 1164 Sofia, Bulgaria

Fax: +359-2-9625438, e-mail: tsalev@chem.uni-sofia.bg

Received 24 July 2007, revised 7 August 2007

Abstract

Arsenic can be present in soils in various chemical forms with different mobility and toxicity. Concentrations of four arsenic species (inorganic As(V), inorganic As(III), monomethylarsonic acid, MMA, and dimethylarsinic acid, DMA) in soils around a copper smelter near Pirdop (Bulgaria) were measured. Arsenic species were extracted with 0.3 mol l⁻¹ phosphoric acid in open-focused microwave field. The analysis was achieved by high performance liquid chromatography followed by post column hydride generation and detection by flame atomic fluorescence spectrometry. The soils near the copper smelter in Pirdop (Bulgaria) are heavily polluted with arsenic, which is present there in the form of two species. As(V) is the main form ranging from 3.0 to 206.5 µg g⁻¹ dry weight but the levels of inorganic As(III) are not negligible (0.03–6.50 µg g⁻¹ dry weight). The pollution seems localized near the smelter being a source of As(III). The concentrations of MMA and DMA were below the detection limits of the method. These initial results for the arsenic speciation in soils from Pirdop region have to be extended in the future to water and cultivated plants in order to assess the risk for humans for arsenic intoxication.

Keywords: Arsenic speciation analysis; Soil pollution; High performance liquid chromatography; Hydride generation; Flame atomic fluorescence spectrometry; Soil extract; Copper smelter.

Introduction

An important feature of soil pollution with heavy metals and metalloids is its long duration, because these pollutants are not easily transformed into non-toxic compounds. The main source of pollution is industry, while the chemical forms of the metals depend on the type of contamination. Copper smelting is known to be an important source of soil pollution with heavy metals and arsenic [1]. The knowledge of the toxicity and environmental pathways is essential for better understanding the ecological situation in the region. The inorganic (i-) forms of arsenic are very toxic, especially the i-As(III), arsenite [2–4]. Arsenic enters the environment via coal combustion and sulphidic ores roasting mainly as i-As(III) [5]. In soils, however, it is mostly converted to i-As(V), arsenate, which is retained on hydrated oxides of Al(III) and Fe(III) as well as on humus and Ca(II); the most typical oxidation state is As(V) but As(III) and As(0) could be present in reducing environment. Mobile forms of arsenite and arsenate in soil are AsO₂⁻, AsO₄³⁻, HAsO₄²⁻, H₂AsO₃⁻, [6]. The presence of arsenic in phosphate fertilizers and some pesticides also contributes to soil pollution. In soils the inorganic forms of arsenic may be partly methylated to monomethylarsonic acid and dimethylarsinic acid [7].

Typical As levels in uncontaminated soils are ranging between <1 and 95 µg g⁻¹ [6], with average values of 8.7 µg g⁻¹ (world), 6.7 µg g⁻¹ (USA) and 5.8 µg g⁻¹ (world) [8], with a range of <0.2 µg g⁻¹ to tens of µg g⁻¹ [8]. Contaminated surface soils may reach as high 0.1–0.2% As levels [6]. Plants are relatively tolerant to high As concentrations and may accumulate up to a few tenths % of As on contaminated sites versus normal range from a few ng g⁻¹ to ca. 1.5 µg g⁻¹ As (dry weight) [6,8].

Since arsenic can be present in soils in chemical forms with different mobility and toxicity, revealing the arsenic speciation in soils around a copper smelter has been the aim of this study. Additionally, the authors looked for a relationship between the contamination with arsenic species and the levels of some heavy metals like copper, zinc and lead in order to determine the role of the smelting in soil pollution of the region with arsenic species.

Study area

The map of the study area is presented in figure 1. The valley of Zlatitsa and Pirdop in Bulgaria has been subject to important pollution with heavy metals due to Cu smelting activities for several decades. The Balkan Mountains bor-

ders the valley to the North and Sredna Gora Mountain – to the South. The twin towns of Zlatitsa and Pirdop are bordered to the West by Koznitsa and Galabets hills. The valley is 29 km long and only 4 km wide. Its surface area is 116 km² and the altitude is 730 m. Surrounding hills are about 1500 m high. The Brown Forest type of soil is dominating in the region.

The spreading of contaminants, coming from a point source, is related to the wind direction and force. The rise of winds, according to the meteorological station in Pirdop, is determined by the geographical characteristics of the valley. Winds from north-east are most frequent (22.4%), followed by winds from west (20%). Much lower frequencies have the winds from north-west (7.8%), north (7.8%) and south-west (6.5%). Winds from other directions (east, south and south-east) are rare, their occurrence being within 1.8–2.7%.

The level of the topographic reticence of the valley of Zlatitsa and Pirdop is of prime importance for contaminants transport and soil pollution. Temperature inversions in the valley are the reason for a stable stratification of the atmosphere, which hinders air dynamics and prevents transportation of dust particles to the upper layers, thus contributing to pronounced pollution in the region.

Experimental

Sampling

Fig. 1 displays locations of 14 surface soil sampling sites examined in September 1998 in the vicinity of a copper smelter in Pirdop (Bulgaria). One of the samples (No. 15) was taken at a 25 km distance from the plant in the west direction. Samples were immediately frozen and transported to the laboratory in a frozen state, where they were lyophilized, crashed and stored in double plastic bags until analysis.

Arsenic speciation

The arsenic species were extracted from the soil matrix in open-focused microwave field (40 W, 20 min) with 0.3 mol l⁻¹ H₃PO₄ and the extracts were immediately analyzed in order to decrease i-As(III) oxidation. Separation of the arsenic species was achieved by high performance liquid chromatography (HPLC) with Hamilton PRP-X100 anion-exchange column and injected volume of 100 µl. Additionally, the chromatographic column separates the anionic species from heavy metal interference from these metal-rich soils. After gradient elution with ammonium phosphate solutions the arsenic species were separated from the liquid phase by post column hydride generation (HG). Detection was accomplished by means of flame atomic fluorescence spectrometry (FAFS). The detection limits of the HPLC-HG-FAFS method in case of solid samples are 0.02 µg kg⁻¹ (as As) for i-As(III), MMA and DMA and 0.03 µg kg⁻¹ (as As) for i-As(V). The relative standard deviation is 4–5% for the studied arsenic

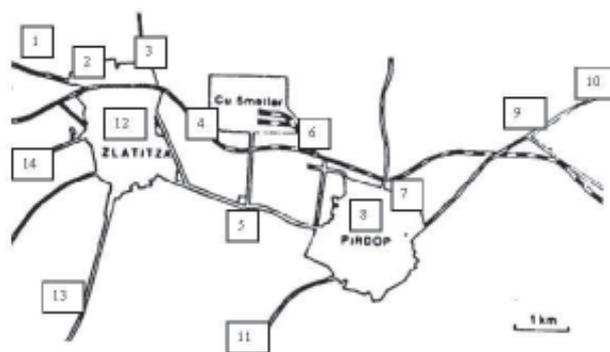


Fig. 1. Map of the study area of the copper smelter, Pirdop and Zlatitsa (Bulgaria) with indication of sampling sites Nos. 1–14.

species. The analytical procedure has been described in detail elsewhere [9–11]. Only anionic arsenic species, like arsenite, arsenate MMA and DMA can be measured by this technique.

Other parameters

An aliquot of each sample was leached with 6 mol l⁻¹ HNO₃ in a microwave oven powered at 60 W for 3 min. Copper, zinc and lead were determined in the leachates by means of inductively coupled plasma mass spectrometry (ICPMS) (Perkin-Elmer ELAN 6000). Noteworthy, this fraction accounts for more available forms (pseudo-total amount) and does not include metals in the silicate lattice of the soil. Anthropogenic constituents are most probably leached there. These acid-leachable forms of metals could be expected to correlate better than the total amounts with the forms of arsenic derived from the smelting activity.

Results and discussion

Table 1 presents results of arsenic speciation and the concentration of some heavy metals that are extractable with 6 mol l⁻¹ HNO₃ in the soil samples. The dominating arsenic species is As(V), ranging from 3.0 to 206.5 µg g⁻¹, with an average value of 66.6 µg g⁻¹ and an average of 26.6 µg g⁻¹. Background levels of arsenic in non-polluted soils in Bulgaria are much lower, being between 2.0 and 11.2 µg g⁻¹ [12,13]. Measured concentrations of arsenic in soils around this copper smelter are similar to those found in other contaminated areas world over [12,14]. There is a relation between similar levels of arsenic in the soils and various arsenic-born diseases in humans [14]. Some of these As concentrations are higher than the maximum tolerable concentration of As in agricultural soils in Bulgaria of 25 µg g⁻¹ [15] and versus remediation levels of µg g⁻¹ As quoted for the Netherlands [8]. These initial results of arsenic speciation in soils have to be extended in the future to water, sediments and plants in the region in order to assess the risk for humans for arsenic intoxication.

Table 1. Arsenic speciation and heavy metal concentrations in soils near the copper smelter in Pirdop (Bulgaria)

Sample No.	Cu ^a , %	Pb ^a , µg g ⁻¹	Zn ^a , µg g ⁻¹	As(V) ^b , µg g ⁻¹	As(III) ^b	As(III)/As _{tot} %
1	0.0480	47	45	13.0	0.10	0.8
2	0.1400	62	124	17.9	0.29	1.6
3	0.0240	49	77	14.1	0.16	1.1
4	0.1100	185	102	161.3	2.99	1.8
5	0.5100	295	375	138.1	2.35	1.7
6	1.0100	371	296	144.9	4.77	3.2
7	0.6100	1191	449	86.4	2.05	2.3
8	0.0420	49	72	19.9	0.17	0.8
9	0.0130	29	60	10.5	0.26	2.4
10	0.0550	81	88	26.6	0.12	0.4
11	0.0300	32	100	6.7	0.10	1.5
12	0.6600	281	527	90.3	6.50	6.7
13	0.3800	140	227	60.5	1.27	2.1
14	0.4600	355	429	206.5	4.01	1.9
15	0.0054	29	63	3.0	0.03	1.0

^a microwave leaching with 6 mol l⁻¹ HNO₃, determination by ICP-MS;

^b microwave extraction with 1 mol l⁻¹ H₃PO₄, determination by HPLC-HG-AFS.

The i-As(III) species was also detected in all samples at a lower concentration: an average of 1.68 µg g⁻¹ and a medial of 0.29 µg g⁻¹ (0.03–6.50 µg g⁻¹ range) which accounts for 0.4 to 6.7% from the total arsenic, the sum of As(III) and As(V). The rapidity of the microwave extraction and the relative stability of the extracts are expected to minimize the redox interconversion of inorganic arsenic species [10]. However, oxidation reactions cannot be totally excluded and the reported values for i-As(III) should be considered to be minimum. Higher i-As(III) to i-As(V) ratios have been reported in heavily polluted soils in another region of metallurgical activity in Bulgaria [13], indicating that the oxidation rates for arsenite in soil could be a slower process than anticipated from thermodynamic data only. The percentage of i-As(III) with respect to the total As, %As(III), shows statistically a significant correlation with concentrations of copper ($R^2 = 0.43$, $p = 0.01$) and especially of zinc ($R^2 = 0.51$, $p = 0.01$) in soils. Emissions of arsenic from the smelters are mainly in the form of As(III) and the above-mentioned correlations are an indication of similar sources and environmental distribution of arsenic, zinc and copper. No such correlation could be revealed between concentrations of As(III) and pseudo-total Pb contents that could be attributed to different distribution and pathways of these two pollutants, or otherwise, an additional contribution of Pb sources such as prolonged utilization of leaded gasoline. No correlation could be noticed between %As(III) and the total As contents in soils, either. MMA and DMA were not been detected (<0.02 µg g⁻¹ As) in examined soil samples.

There is a good correlation between the concentration of pseudo-total As extracted with 6 mol l⁻¹ HNO₃ (y) and the total i-As, As(III)+As(V), extracted with 0.3 mol l⁻¹ H₃PO₄ (x):

$$y = (0.94 \pm 0.12)x - (8.0 \pm 11.1); R^2 = 0.96.$$

Conclusions

Soils near the copper smelter in Pirdop (Bulgaria) are polluted with arsenic, which is present in the form of only two species: inorganic As(V) as a prevailing form, while the levels of inorganic As(III) are not negligible, especially in samples polluted with copper and zinc. Pollution seems localized near the smelter being a source of As(III). It is necessary to have a more rigorous monitoring program of soils, water and plants in order to assess the risk for arsenic-born diseases in the region.

References

1. I. Ahumada, P. Escudero, L. Ascar, J. Mendoza, P. Richter, *Commun. Soil Sci. Plant Anal.* 35 (2004) 1615.
2. D. L. Tsalev, Z. K. Zaprianov, in *Atomic Absorption Spectrometry in Occupational and Environmental Health Practice*, Vol. 1, Analytical Aspects and Health Significance, CRC Press, Boca Raton, Florida, 1983, p. 87.
3. D. L. Tsalev, in *Atomic Absorption Spectrometry in Occupational and Environmental Health Practice*, Vol. 2, Determination of Individual Elements, CRC Press, Boca Raton, Florida, 1984, p. 13.
4. D. L. Tsalev, in *Atomic Absorption Spectrometry in Occupational and Environmental Health Practice*, Vol. 3, Progress in Analytical Methodology, CRC Press, Boca Raton, Florida, 1995, p. 19.
5. L. J. Spokes, T. D. Jickells, in A. M. Ure, C. M. Davidson (Eds), *Chemical Speciation in the Environment*, Blackie Academic & Professional, London, 1995.
6. A. Kabata-Pendias, H. Pendias, *Trace Elements in Soils and Plants*, Ch. 10, CRC Press, Boca Raton, Florida, 1984.
7. Y. Bohari, G. Lobos, H. Pinochet, F. Pannier, A. Astruc, M. Potin-Gutier, *J. Environ. Monit.* 4 (2002) 596.
8. C. Reinmann, P. de Caritat, *Chemical Elements in the Environment. Factsheets for the Geochemist and Environmental Scientist*, Springer, Berlin, 1998, p. 42.
9. Y. Bohari, A. Astruc, M. Astruc, J. Cloud, *J. Anal. Atom. Spectrom.* 16 (2001) 774.

10. M. Montperrus, Y. Bohari, M. Bueno, A. Astruc, M. Astruc, *Appl. Organomet. Chem.* 16 (2002) 347.
11. M. V. Callardo, Y. Bohari, A. Astruc, M. Potin-Gautier, M. Astruc, *Anal. Chim. Acta* 441 (2001) 257.
12. P. Petrov, D. L. Tsalev, I. Liotchev, *Higiena i Zdraveopazvane (Hygiene and Protection of Health)* 22 (1979) 574 (in Bulgarian).
13. D. L. Tsalev, I. I. Petrov, *C. R. Acad. Sci. Bulg.* 35 (1981) 1413.
14. S. Patel, K. Shrivastava, R. Brandt, N. Jakubowski, W. Corns, P. Hoffmann, *Environ. Geochem. Health* 27 (2005) 131.
15. Regulation No. 3 of the Committee for Environmental Protection, *Official Gazette* No. 36 (1979), p. 330 (in Bulgarian).

Bulgarian Chemistry and Industry

The journal issues original research, new theoretical concepts and application, and critical reviews in the science or industrial practice of all aspects of chemistry, chemical engineering, applied chemistry, environmental protection and improved and emerging technologies.

The journal puts out Review articles, Articles, Notes, and Letters.

The language of the journal is exclusively English.

Chemistry

Analytical, Inorganic, Organic and bioorganic, Physical, Electrochemistry, Catalysis, Electrochemical power sources, Corrosion, Galvanochemistry

Chemical technology

Inorganic, Organic and bioorganic, Polymers and plastics, Fine chemicals and pharmaceuticals, Coal, gas and oil processing, Petrochemistry, Ceramics and glasses, Nanomaterials

Environmental protection

Air, water and soil: Chemical and biochemical methods

Analytical instrumentation and chemical equipment

Subscription rates: EUR 200 (Europe), EUR 220 (all other countries).

Payments only by bank transfer should be directed to:

Union of Chemists in Bulgaria
UniCredit Bulbank
1 Ivan Vazov St., 1000 Sofia, Bulgaria
SWIFT BIC: UNCRBGSF
IBAN: BG95UNCR96603110024610
VAT number: BG121462139

BULGARIAN CHEMISTRY AND INDUSTRY

CONTENTS

Volume 78, Numbers 1–4, January-December 2007

Atmospheric air pollution by the gas emissions of coal-fired thermal power plants II. Ambient air pollution of Stara Zagora region from Maritsa East power complex	A. Lenchev, J. Ninov, I. Grancharov	1
High-temperature thermodynamic investigation of nanodispersed oxides obtained in thermal plasma	K. Zaharieva, G. Vissokov, L. Brakalov	6
Arsenic speciation in soils in the vicinity of a copper smelter in Pirdop, Bulgaria	Y. Bohari, T. Stoichev, D. L. Tsalev, A. Bosev	9
Application of inductively coupled plasma atomic emission spectrometry to the determination of trace elements in surface water samples in Parangalitsa preserve, Blagoevgrad region (Bulgaria)	M. K. Milanova, Iv. I. Boevski, A. Georgiev, N. N. Daskalova	13
Chemisorptive and infrared spectroscopic behaviour of bimetallic palladium-lead and platinum-lead catalysts	Ch. Bonev	18
Corrosion protection properties of nano-composite hybrid coatings with zirconia and ceria	V. Kozhukharov, G. Tsaneva, S. Kozhukharov, J. Gerwann, M. Schem, T. Schmidt, M. Veith	23
European fundamental lead-free soldering research	G. P. Vassilev	30
Catalyst preparation methods	L. A. Petrov	34
Instructions to authors		43