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Arsenic in Air and Soil in the Vicinity of the Central Gas Station Molve, Croatia

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Abstract Spatial and temporal distribution of arsenic levels in soil during the 9 year monitoring period was investigated on four different soil types in the area of the gas borehole system Podravina in Croatia. Arsenic levels in the PM_{10} particle fraction were measured periodically at the same locations for 3 years. Arsenic levels in soil significantly depended on soil types. Elevated levels were found on gleysol vertic, at two sampling sites, with values exceeding 30 mg/kg of arsenic in soil. Arsenic levels in air were low and they were not significantly different between sampling sites, suggesting that gas borehole activities have no influence on arsenic levels in the environment.

Keywords PM_{10} particle fraction · Gas borehole system · Pannonian Plain

Arsenic is a metalloid widely distributed in the environment. It is of special concern to public health associations and scientific community because of its toxicity and serious impact on human health. Arsenic can occur naturally in soils through weathering of the parent material or it can accumulate due to industrial and agricultural practices (metallurgic industrial waste, melting and mining operations, use of pesticides and herbicides) (WHO 2001). Anthropogenic release of arsenic into the atmosphere is mainly caused by combustion of fuels in stationary sources (coal, oil), smelting of metals, cement production and other sources (Pacyna et al. 2007).

The Pannonian Plain is well known as an area with elevated levels of arsenic in groundwater. Values much higher than 10 μg/L, recommended by WHO, have been reported in Hungary, Romania and Croatia (Smedley and Kinniburgh 2002; Varsányi and Kovács 2006; Ćavar et al. 2005; Habuda-Stanić et al. 2007) and arsenic is often associated with geological sources. However, there is only little information about arsenic levels in soil. Terrestrial plants can accumulate arsenic from soil and introduce this metal into the food chain. Therefore, Croatian legislation defines the maximal acceptable content (MAC) of arsenic in soil. Agricultural soil is considered to be polluted if arsenic levels are higher than 20 mg/kg in light soil and 30 mg/kg in heavy soil.

The Central Gas Station (CGS) of the gas borehole system Podravina is located in the western part of the Pannonian Plain, near the village Molve, in Croatia. CGS is the main plant for gas production from the surrounding boreholes and 70% of total gas produced in Croatia is produced here. Natural gas is here collected, treated, purified and then distributed to consumers. Over the last 20 years, scientists of a multidisciplinary research team have monitored its influence on air, water, soil, plant, wild and domestic animals and on humans. This paper presents the results of monitoring arsenic levels in air and soil on four different locations in the area of CGS.

Materials and Methods

The Central Gas Station (CGS) of the gas borehole system Podravina is located near the village Molve in north-eastern Croatia, in the Pannonian Plain (Fig. 1). Samples of air

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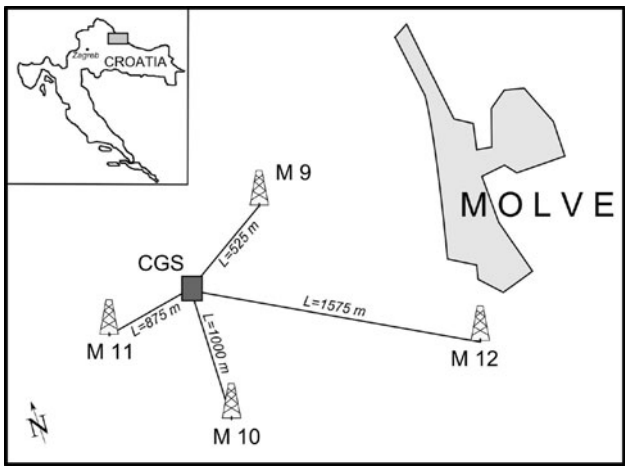

Fig. 1 Locations of sampling sites in the area of the Central Gas Station Molve

and soil were collected at four locations in the surroundings of boreholes Molve 9 (M 9), Molve 10 (M 10), Molve 11 (M 11) and Molve 12 (M 12). Geographical locations of sampling sites are summarized in Table 1.

Measurements of arsenic in particulate matter with an aerodynamic diameter less than 10 μm (PM_{10} particle fraction) were conducted periodically, twice a year, from 2006 to 2008, over 30 consecutive days. Sampling periods were March 31–April 29 and June 26–July 26 in 2006, February 19–March 21 and June 11–July 11 in 2007 and April 14–May 14 and June 23–July 23 in 2008. Samples were collected on cellulose membrane filters (Sartorius Stedim, diameter 90 mm, pore size 3 μm) from approximately 100 m^3 of air over 24 h. Samples of particulate matter were digested with nitric acid, and arsenic was analyzed using atomic absorption spectrometry with electrothermal atomization and Zeeman background correction (PerkinElmer AAnalyst 600). The method detection limit was 0.03 ng/m^3 (calculated according to the standard method HRN EN 14902/AC:2007) and the accuracy of the method was determined by adding known amounts of As standard solution onto membrane filters. The recoveries ranged from 98% to 103%.

Soil samples were collected twice a year, in spring and in autumn. Surface (0–3 cm) and subsurface samples (3–8 cm) were taken with a Holland probe and knife according to the method ISO 10381:2002, 1–8. In the borehole M 9 area, soil samples were collected on two different types of soil: gleysol vertic dystric and regosol acric on Aeolian sand. Samples from Molve 10 were collected on stagnosol luvic, from Molve 11 on gleysols clayic and from Molve 12 on gleysol vertic. Soil types were determined according to the "World reference base for soil resources 2006" (FAO 2006). Air dried soil was crumbled, sieved (<2 mm) and homogenized according to the HRN ISO 11464:2004 protocol, extracted in aqua regia at 95°C for 2 h (HRN ISO 11466:2004), and arsenic was analyzed using different methods: hydride generation atomic absorption spectrometry and inductively coupled plasma mass spectrometry. Internal and external QC procedures were integrated. Internal QC involved checking the accuracy and repeatability of measurements by analyzing the reference material and doing a minimum of three consecutive measurements. Accuracy was controlled using the reference material ISE, Wepal, and recovery was >97%. Repeatability was also controlled and RSD was less than 3%. External QC involved annual participation of a relevant laboratory in proficiency testing programs in soil related fields.

Results and Discussion

Average mass concentrations of arsenic in the PM_{10} particle fraction for each measuring period are presented in Fig. 2, while descriptive statistics of these measurements are given in Table 2.

The results show that arsenic levels in air were low at all sampling sites during the tree-year periodical monitoring. The highest 24 h concentration was 3.38 ng/m^3 measured at borehole M 11 in April 2006. Values measured during the winter period in 2007 were 2–3 times higher than those for the summer period of 2007. In contrast, average values measured at all four locations during the summer period of

Table 1 Geographic locations of sampling sites in the area of CGS Molve

Sampling site	Geographic coordinate system (GPSmap 60C, Garmin, 2006)		Gauss-Krüger coordinate system (zone 5 for Croatia; software ILWIS Academic 3.2)		Above sea level/m
	Latitude	Longitude	Y	X	
Molve 9	N 46°6.643′	E 17°0.627’	6,423,516.29	5,107,838.73	120
Hill near Molve 9	N 46°6.722′	E 17°0.547′	6,423,415.06	5,107,986.34	122
Molve 10	N 46°6.085′	E 17°0.134′	6,422,868.24	5,106,813.17	118
Molve 11	N 46°6.541′	E 16°59.496′	6,499,350.73	5,107,173.84	115
Molve 12	N 46°6.047′	E 17°1.142′	6,424,166.08	5,106,726.63	125

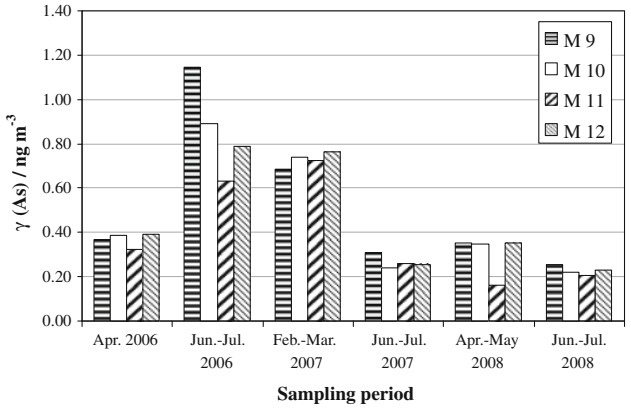

Fig. 2 Average mass concentrations of arsenic in the PM_{10} particle fraction (ng/m^3) measured at Molve 9 (M 9), Molve 10 (M 10), Molve 11 (M 11) and Molve 12 (M 12)

Table 2 Descriptive statistics of arsenic mass concentrations in the PM_{10} particle fraction in the vicinity of CGS (ng/m^3)

Measurement period	Sampling site	N	$C_{avg} \pm SD$	C_{50}	Range
Apr. 2006	M 9	29	0.36 ± 0.41	0.29	0.03–1.84
	M 10	30	0.39 ± 0.37	0.30	0.05–1.77
	M 11	30	0.33 ± 0.63	0.16	n.d.–3.38
	M 12	30	0.39 ± 0.35	0.30	0.05–1.52
Jun–Jul. 2006	M 9	31	1.14 ± 0.68	1.04	0.12–2.69
	M 10	30	0.89 ± 0.49	0.89	0.11–1.89
	M 11	29	0.63 ± 0.45	0.57	0.11–1.83
	M 12	30	0.79 ± 0.43	0.69	0.10–1.95
Feb–Mar. 2007	M 9	31	0.69 ± 0.57	0.59	n.d.–1.81
	M 10	31	0.74 ± 0.58	0.67	n.d.–1.98
	M 11	31	0.73 ± 0.57	0.67	n.d.–2.02
	M 12	31	0.76 ± 0.63	0.66	n.d.–2.05
Jun–Jul. 2007	M 9	31	0.31 ± 0.16	0.26	0.06–0.68
	M 10	31	0.24 ± 0.12	0.21	0.07–0.62
	M 11	29	0.26 ± 0.13	0.23	0.05–0.58
	M 12	31	0.25 ± 0.13	0.24	0.06–0.55
Apr–May 2008	M 9	31	0.35 ± 0.26	0.28	n.d.–1.23
	M 10	31	0.35 ± 0.25	0.32	n.d.–1.21
	M 11	31	0.16 ± 0.11	0.13	n.d.–0.46
	M 12	31	0.35 ± 0.24	0.30	n.d.–1.16
Jun.–Jul. 2008	M 9	31	0.26 ± 0.16	0.21	0.06–0.73
	M 10	31	0.22 ± 0.14	0.20	0.08–0.71
	M 11	31	0.21 ± 0.15	0.16	0.06–0.72
	M 12	31	0.23 ± 0.16	0.20	0.07–0.75

N Number of samples, $C_{avg} \pm SD$ average ± standard deviation, C_{50} median, *Range* Minimum–Maximum; *n.d.* not detectable

2006 were 2–3 times higher than those for the same periods in 2007 and 2008 as well as for April 2006 and April–May 2008. One-way analysis of variance (ANOVA) showed no

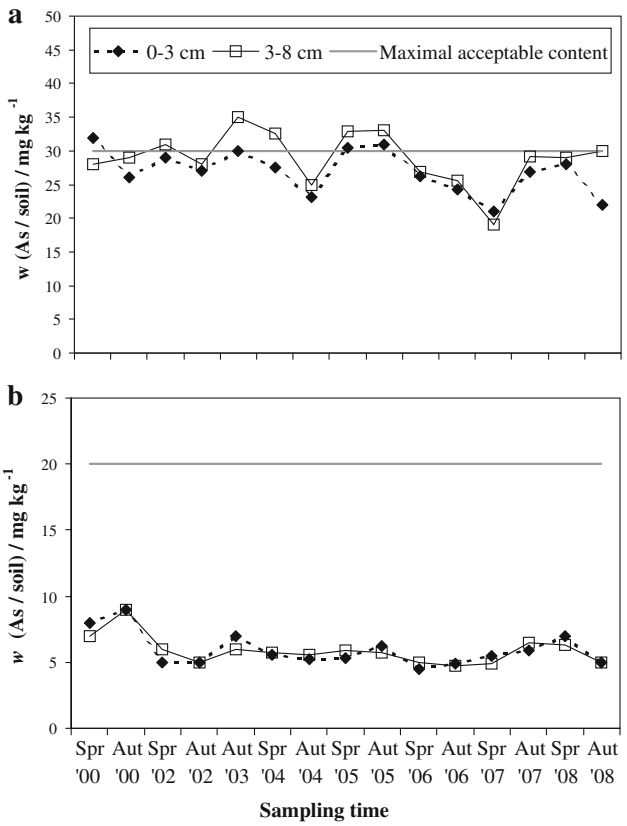

Fig. 3 Mass fraction of arsenic in soil (mg/kg) in surface and subsurface soil layers at Molve 9 on **a** gleysol vertic dystric (*heavy soil*) and **b** regosol acric (*light soil*)

significant difference between the sampling sites, so the spatial distribution of arsenic in air was homogeneous over the studied area. Exceptions were the sampling period June–July of 2006 when arsenic concentrations in the PM_{10} fraction differed between all sampling sites ($p < 0.01$) and the sampling period April–May of 2008 with lower values at the sampling site M 11.

Mass fractions of arsenic in soil on locations in the surroundings of M 9, M 10, M 11 and M 12 are presented in Figs. 3 and 4, respectively. Values measured in surface and subsurface soil layers were not significantly different at any sampling site. No marked trend was observed at M 9, M 10 and M 12 and a slightly decreasing trend was recorded at M 11. The results show that arsenic levels in soil strongly depend on soil type. Elevated values were determined on gleysol vertic at M 9 and M 12, with mass fractions of arsenic often above the maximal acceptable content (MAC) of 30 mg/kg for heavy soil. The highest concentration, 42 mg/kg, was found in the surface soil layer at location M 12 in the autumn of 2006. The most interesting results were obtained in the surroundings of M 9 where samples were taken at two locations with different soil types, gleysol vertic dystric, classified as heavy soil,

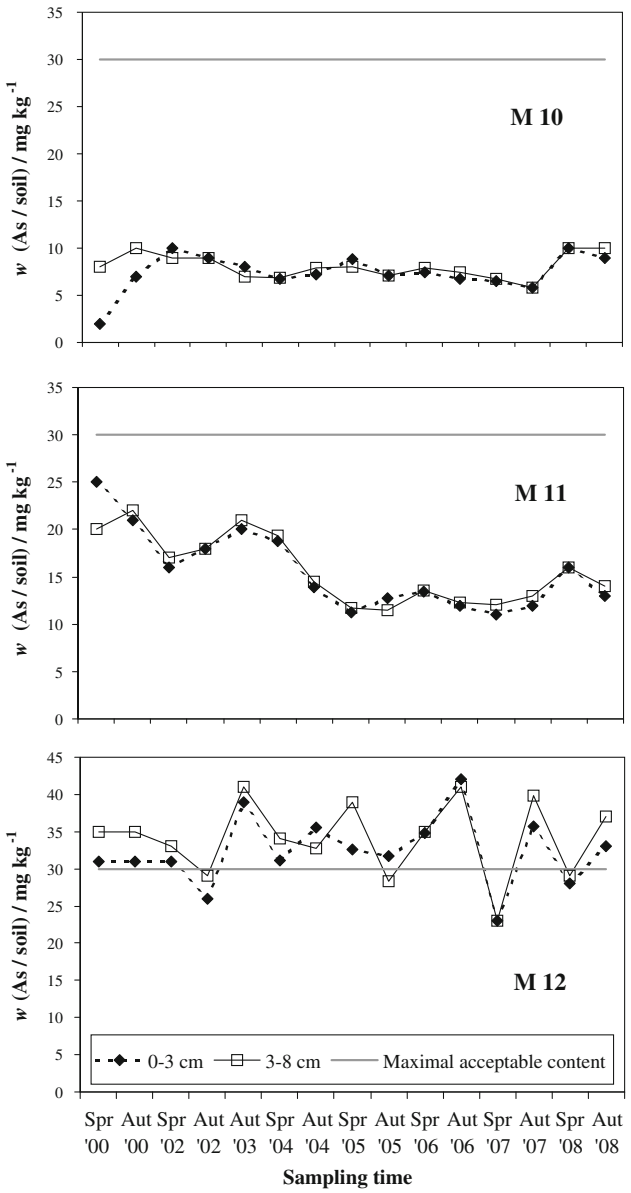

Fig. 4 Mass fraction of arsenic in soil (mg/kg) in surface and subsurface soil layers at Molve 10 (M 10) on stagnosol luvic, Molve 11 (M 11) on gleysol clayic and Molve 12 (M 12) on gleysol vertic

and regosol acric which is classified as light soil. Arsenic levels in gleysol vertic dystric ranged from 19 to 35 mg/kg and were 4 to 6 times higher than in regosol acric. Stagnosol luvic (at M 10) and gleysol clayic (at M 11) are also heavy soils but the results obtained there were below MAC.

Comparison of our results for arsenic in PM_{10} particles with some other studies shows that they are at rural or background levels that are not affected by industrial sources. European estimation is 0.2–1.5 ng/m^3 in rural, 0.5–3 ng/m^3 in urban and 50 ng/m^3 in industrial areas (Mandal and Suzuki 2002). In rural and urban areas in Greece, Vassilakos et al. (2007) measured arsenic in PM_{10} in summer and in winter periods of 2003. During the summer period, arsenic levels were below the detection limit (0.02 ng/m^3) at both sampling sites while during winter they found 4.62 ± 2.79 ng/m^3 in the rural area and 14.7 ± 7.3 ng/m^3 in the urban area.

Sánchez-Rodas et al. (2007) investigated the potential influence of copper smelting on arsenic emissions in Huelva, Spain, and during the campaign in 2001 they found 7.7 ng/m^3 (1.6–29.4 ng/m^3) of arsenic in PM_{10} samples and 9.9 ng/m^3 (1.3–79.8 ng/m^3) in 2002.

Gidhagen et al. (2002) measured arsenic in PM_{10} particles, topsoil (0–5 cm depth) and subsoil samples (approximately 50 cm depth) at seven locations in central and northern Chile throughout a year. The aim of the study was to assess the influence of industry and arsenic emissions from copper and gold smelters on air quality in rural areas. Arsenic levels in air ranged from 2.4 to 30.7 ng/m^3 but the levels did not exceed 5 ng/m^3 at locations faraway from industry. Arsenic levels in soil at four locations were higher than 50 mg/kg, with the maximum measured value of 291 mg/kg. In areas with high arsenic concentrations in soil, atmospheric levels were low while in areas with high atmospheric levels the soil levels were below 20 mg/kg; thus, the authors did not find a relation between arsenic levels in soil and in the atmosphere.

Coskun et al. (2006) measured heavy metal pollution of surface soil in Turkey and found arsenic in the range 1.9–51 mg/kg with the median value 7 mg/kg. They also compared these results with Dutch maximum allowable values of 29 mg/kg and the world median of 6 mg/kg Ahsan et al. (2009)found 33.15 and 6.10 mg/kg arsenic in agricultural soil in Bangladesh with higher values on soil which was irrigated with as contaminated groundwater.

Since our air monitoring results show that there is no influence of the CGS plant on arsenic levels in air, high arsenic values on gleysol vertic cannot be attributed to this source of emission. The explanation could probably be found in pedogenesis or soil forming processes and factors. Arsenic on gleysol vertic is above the Croatian MAC, Dutch maximum allowable concentration and the world median and is comparable to contaminated soil in Bangladesh and Chile. As the soil in the surroundings of CGS is used for agriculture and crop production, permanent soil monitoring is recommended. Further studies are also needed to estimate the influence of arsenic contaminated soil on metal uptake by plants growing in that area.

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