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Reports from the Field

Arsenic occurrence in drinking water supply systems in ten municipalities in Vojvodina Region, Serbia ☆

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ABSTRACT

Vojvodina, a northern region of Serbia, belongs to the Pannonian Basin, whose aquifers contain high concentrations of arsenic. This study represents arsenic levels in drinking water in ten municipalities in Serbia. Around 63% of all water samples exceeded Serbian and European standards for arsenic in drinking water. Large variations in arsenic were observed among supply systems. Arsenic concentrations in public water supply systems in Vojvodina were much higher than in other countries in the Pannonian Basin.

1. Introduction

The Ministry of Health of the Republic of Serbia has implemented a national plan entitled "Monitoring Programme of Drinking Water Quality from Public Water Supply Systems" in 1978. It obliged public water supply systems and public health institutes to perform routine monitoring over the quality of drinking water in Serbia. One of its goals was to estimate inorganic arsenic levels in groundwater sources used for public water supply.

Vojvodina is a northern region of Serbia, geographically belonging to the southern part of the Pannonian Basin, together with Hungary, Romania, Slovakia and Slavonia in Croatia. The Pannonian Basin and the greater part of the Balkan Peninsula in south-east Europe belong to the Danube River Basin, which is geologically and geochemically complex (Dangic, 2007). Quaternary sedimentary aquifers within the Pannonian Basin contain high concentrations of naturally occurring arsenic (Varsanyi and Kovacs, 2006). In the water-sediment system, arsenic is specially enriched in clay fraction of the soil; tertiary magmatic rocks contain 3.1 mg As/kg, whereas soils contain 10 mg As/kg (Dangic, 2007). On the other side, arsenic concentrations are lower in the Danube River water and shallow riparian groundwaters (0.1–8 μg/L) (Dangic, 2007).

Other sources of arsenic include foodstuffs (primarily fish and marine organisms), air and soil, and some human activities, such as the use of arsenical pesticides, burning of fossil fuels and disposal of industrial wastes (Mandal and Suzuki, 2002). Exposure to inorganic arsenic as arsenite (As(III)) or arsenate (As(V)) occurs from water and dust particles, whereas fish and seafood predominantly contain organic arsenic compounds (Francesconi and Kuehnelt, 2002). Arsenic concentrations in different types of soil in urban areas in Serbia range from 6 to 10 mg/kg (Ministry of Environment and Spatial Planning of Serbia, 2009). Average annual emission of arsenic in atmospheric total suspended particles in several urban zones in Serbia ranges from 2 to 18.6 ng/m^3 (Institute of Public Health of Serbia, 2009).

The European Food Safety Authority Panel on Contaminants in the Food Chain (CONTAM) has in 2009 estimated national inorganic arsenic exposures from food and water across 19 European countries. Based on their report, this exposure ranged from 0.13 to 0.56 μg/kg of body weight per day for average consumers and from 0.37 to 1.22 μg/kg of body weight per day for 95th percentile consumers (EFSA Panel, 2009).

Although arsenic is a known water pollutant in Vojvodina for many decades, public water supply systems lack technical and financial resources for its removal. Since arsenic does not change water color, odor or taste, exposed populations may continue to use the contaminated water for drinking, cooking and soil/garden/plants watering all their lives, thus ingesting large amounts of

Abbreviations: As, arsenic; CONTAM, the European Food Safety Authority Panel on Contaminants in the Food Chain; SRPS ISO, Serbian Standardization Organization and International Standardization Organization

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arsenic. Knowing that arsenic causes skin, bladder, and internal cancers (Abernathy et al., 1999), its presence in water represents a major public health topic. In the nearest future, Serbia will implement many European Union Directives regarding water quality and will have to find means to treat this problem. The aim of this study was to report current distribution of arsenic in drinking water from public water supply systems in ten municipalities in Vojvodina Region, Serbia.

2. Materials and methods

Vojvodina Region administratively consists of 45 municipalities. National Monitoring Programme of Drinking Water Quality in Serbia shows that public water supply systems in 20 municipalities (44.4% of all municipalities in Vojvodina) contain high amounts of arsenic. Regional authorities in these 20 municipalities were invited to participate in the study by collecting and analyzing arsenic in their water supply systems in 2008. Those who failed to respond were invited again in 2009. The response rate was 50%, i.e. 10 municipalities provided all data on time. Other municipalities were excluded from the study because of their refusal or lack of financial resources to analyze arsenic (7 municipalities), or because of inadequate sampling or analysis procedures (3 municipalities).

Total arsenic concentrations were measured in water samples from public water supply systems during 2008 and 2009. No statistical difference was observed between the samples taken in various years and therefore the most recent data were included in the analysis. Water samples from individual wells or bottled water were not taken into consideration.

Sampling and analyses of drinking water were performed at the following laboratories: at the Institute of Public Health of Vojvodina (in Novi Sad), the Institute of Public Health in Subotica, the Institute of Public Health in Zrenjanin and at the Institute of Public Health of Serbia in Belgrade. All laboratories were accredited and authorized according to SRPS ISO/IEC 17025 and SRPS ISO 9001 standards. Laboratory procedures for sample management, analytical methods and quality control measures (accuracy, precision and detection limits) were standardized by Serbian law (Book of Regulations on the Hygienic Correctness of Drinking Water 98/42, 1998). Current Serbian regulations limit arsenic levels at 10 μg/L (Book of Regulations on the Hygienic Correctness of Drinking Water 98/42, 1998).

Total arsenic water was determined using the HG-AAS technique (Perkin-Elmer 1100 atomic absorption spectrometer equipped with a MHS-20 hydride generation system, Perkin-Elmer Corp., Norwalk, CT, USA). Reagents of analytical grade or higher quality were used. Hydride generation was performed using a 3% (w/v) $NaBH_4$ in 1% NaOH (both Merck suprapur; E. Merck, Darmstadt, Germany) solution. The radiation source was a hollow cathode lamp of arsenic (Perkin-Elmer) used at a wavelength of 193.7 nm and a spectral slit width of 0.7 nm. Hydride generation (HG) was performed with 0.6% $NaBH_4$ dissolved in 0.5% NaOH and 5 mol/dm^3 HCl. The hydrids were then transported to a heated quartz cell and the atomic absorption of the analyte was measured. With this method a limit of detection of 0.5 μ/L and limit of quantification of 2 μ/L were obtained by analyzing 4 series of 10 repeated analyses of blank samples and calculating the three standard deviations of these responses. Recovery of standards was 80–120%.

Descriptive statistic was presented as median values, 10th and 90th percentiles for numeric variables and percents for categorical variables. Differences between several samples were analyzed using Kruskal Wallis test for non-parametric data. STATISTICA software was used for all data analyses (Version 6, StatSoft Inc., Tulsa, OK, USA).

3. Results

In total, 577 water samples from public water supply systems from ten municipalities in Vojvodina were analyzed for arsenic. As shown in Table 1, almost 63% of all samples exceeded the current standard. Srbobran and Subotica municipalities (in the north-west of Vojvodina) had the lowest number of samples that exceeded the arsenic levels. Arsenic was detected in all water samples from Senta and Kanjiza (north-east of Vojvodina), and in 94% of samples in Zrenjanin (eastern part of Vojvodina) (Table 1).

Geographical distribution of arsenic in the study area and in the whole region of Vojvodina is shown in Fig. 1. High levels of arsenic are present in ten investigated municipalities (red circles) and are known to be present in ten more municipalities (yellow squares), but more precise data were unavailable at the present.

The distribution of total arsenic in drinking water by public water supply systems in the investigated municipalities is shown in Table 2.

Table 1
Number of analyzed samples, number and percent of samples with exceeded arsenic levels in public water supply systems in Vojvodina Region, according to Serbian maximum allowed value.[a]

Municipality	No. of analyzed samples	No. of samples with exceeded[a] As levels	% of samples with exceeded[a] As levels
Zrenjanin	144	135	93.8
Bačka Palanka	174	126	72.4
Bački Petrovac	60	24	40.0
Bač	8	3	37.5
Srbobran	42	3	7.1
Titel	18	16	88.9
Temerin	55	27	49.1
Subotica	52	5	9.6
Kanjiza	12	12	100.0
Senta	12	12	100.0
Total	577	363	62.9

As—arsenic.

[a] Over 10 μg/L.

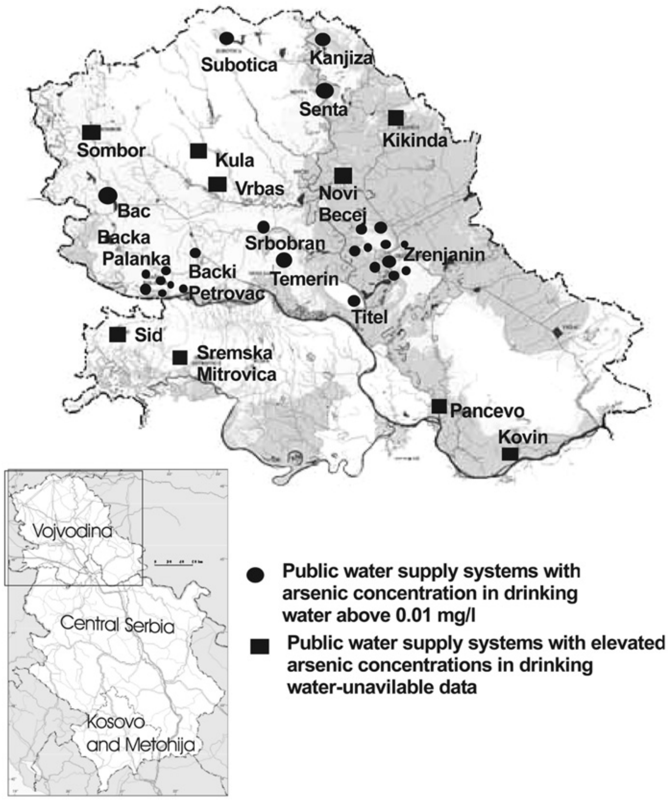

Fig. 1. Geographical distribution of municipalities in Vojvodina according to arsenic levels. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

Large variations in arsenic concentration were observed among water supply systems (median ranged from 2 to 250 μg/L; maximum value ranged from 5 to 349 μg/L). The highest concentrations were reported in the city of Zrenjanin and most of its villages (eastern part of Vojvodina), in municipalities Temerin (central to north-east), Subotica (north) and village Čelarevo (west).

Fig. 2 represents the distribution of mean arsenic concentrations in water supply systems. In total, only 11% of all water supply

Table 2
Total inorganic arsenic concentrations (μg/L) in water samples from public water supply systems in Vojvodina Region by municipalities and villages.

Municipality/ village	Median As level	10th percentile of As level	90th percentile of As level	Maximum As level
Zrenjanin	77.0	61.6	99.0	200.0
Melenci	232.5	73.0	346.3	349.0
Taras	250.0	76.0	336.8	344.0
Jankov Most	60.0	41.6	83.0	85.0
Mihajlovo	82.5	60.0	95.5	110.0
Elemir	112.5	35.4	209.8	224.0
Klek	70.0	51.0	89.2	96.0
Aradac	90.0	42.4	130.0	155.0
Perlez	2.0	2.0	4.7	5.0
Farkadzin	13.0	10.0	29.0	30.0
Lazarevo	5.0	4.1	8.0	8.0
Bačka Palanka	32.0	15.0	49.0	98.0
Despotovo	21.5	11.0	30.7	53.0
Obrovac	43.0	34.0	63.9	98.0
Čelarevo	87.0	86.0	87.0	88.0
Silbas	6.0	2.0	11.0	11.0
Pivnice	2.0	1.0	12.0	15.0
Tovariševo	20.0	16.0	33.8	36.0
Mladenovo	38.0	31.0	52.0	70.0
Bački Petrovac	14.5	11.0	17.5	18.0
Bač	15.0	12.0	45.0	52.0
Srbobran	13.0	12.0	15.0	15.0
Titel	14.0	11.0	23.0	25.0
Temerin	46.0	23.2	230.2	420
Subotica	46.0	16.0	69.0	71.0
Kanjiža	17.0	16.0	20.0	20.0
Senta	38.5	25.0	52.0	52.0

As—arsenic.

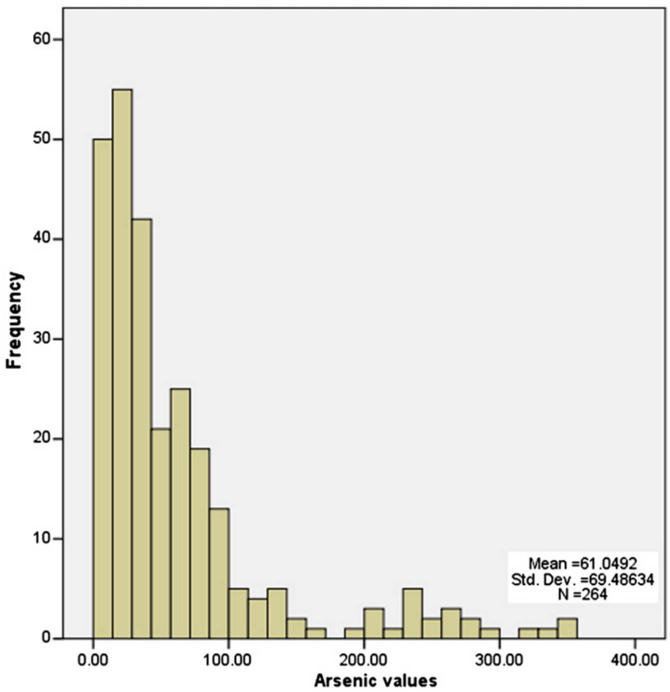

Fig. 2. Distribution of mean arsenic concentrations in water supply systems in ten investigated municipalities in Vojvodina.

systems in Vojvodina had arsenic concentrations below the limit (10 μg/L). About a half (50.4%) of them reported arsenic concentrations ranging from 11 to 50 μg/L and further 38.6% systems had mean arsenic levels over 50 μg/L. The differences among the investigated municipalities were highly statistically significant (Kruskal Wallis test: $\chi^2 = 137.039$; $p < 0.001$).

4. Discussion

This is a first study on the distribution of arsenic in public water supply systems in Vojvodina and Serbia. It shows a large variation in arsenic levels in the region. Mean arsenic levels were much higher than those reported in other countries in the Pannonian Basin. The lowest arsenic concentrations in water were found in Slovakia (median values 0.69–0.95 μg/L; maximum 37–39 μg/L), followed by Romania (median 0.48–0.70 μg/L; maximum 24–95 μg/L) and Hungary (median 7.7–28 μg/L; maximum 31–88 μg/L) (Lindberg et al., 2006). Other Hungarian researchers reported arsenic levels from 0 to 300 μg/L (mean 51 μg/L) (Varsanyi and Kovacs, 2006). The arsenic content in drinking water in some parts of Vojvodina (primarily Zrenjanin) is higher than in other geologically independent parts of the world, such as Spain (ranging from 1 to 118 μg/L) (Medrano et al., 2009) or Mexico (ranging from 10 to over 40 ppb) (Meza et al., 2004).

Our study has shown that almost two-thirds of water samples in ten municipalities in Vojvodina have exceeded both Serbian and European drinking water standards regarding arsenic levels. On the contrary, only 8% of the samples exceeded the standards in Slovakia (Lindberg et al., 2006). Our situation might be similar to the one in Bangladesh, where more than 50% of groundwater wells contain arsenic over 10 μg/L and further 28% of wells contain arsenic over 50 μg/L (Yu et al., 2003).

The main objective for the future research will be to estimate individual exposure to arsenic. According to national census, the population size in the study area is 470,233 people, i.e. 23.8% of the population in Vojvodina or 6.4% of the total Serbian population (Statistical Office of the Republic of Serbia, 2009). Studies show that individual exposure and risk assessment may be based on arsenic levels in drinking water (Ayotte et al., 2006). At the same time, other exposure pathways, such as the use of bottled water or water from individual wells, must be taken into consideration, because they could increase the size of the exposed population (Thundiyil et al., 2007). Considering predominant agricultural activity in Vojvodina, arsenic exposure from pesticides and occupational exposure will be assessed as further important risk factors (Ayotte et al., 2006).

5. Conclusion

This pilot study has reported very high concentrations of arsenic in public water supply systems across ten municipalities in Vojvodina Region, Serbia. Elevated levels of arsenic should initiate social, economical and technological actions in order to reduce it to acceptable limits. Furthermore, this should raise public health concern and produce further studies on arsenic exposure and risk assessment in Serbian population.

References

Abernathy, C.O., Liu, Y.-P., Longfellow, D., Aposhian, H.V., Beck, B., Fowler, B., Goyer, R., Menzer, R., Rossman, T., Thompson, C., Waalkes, M., 1999. Arsenic: health effects, mechanisms of actions, and research issues. Environ. Health. Perspect. 107, 593–597.

Ayotte, J.D., Nolan, B.T., Nuckols, J.R., Cantor, K.P., Robinson, G.R., Baris, D., Hayes, L., Karagas, M., Bress, W., Silverman, D.T., Lubin, J.H., 2006. Modeling the probability of arsenic in groundwater in New England as a tool for exposure assessment. Environ. Sci. Technol. 40, 3578–3585.

Book of Regulations on the Hygienic Correctness of Drinking Water, 1998. Službeni list SRJ 42/98, Belgrade (In Serbian).

Dangic, A., 2007. Arsenic in surface- and groundwater in central parts of the Balkan Peninsula (SE Europe). In: Bhattacharya, P., Mukherjee, A.B.B., Bundschuh, J., Zevenhoven, R., Loeppert, R.H. (Eds.), Arsenic in Soil and Groundwater Environment—Biogeochemical Interactions, Health Effects and Remediation. Trace Metals and other Contaminants in the Environment, vol. 9, pp. 207–236.

EFSA Panel on Contaminants in the Food Chain (CONTAM), 2009. Scientific opinion on arsenic in food. EFSA. Journal. 7, 1351. Available at: 〈www.efsa.europa.eu/en/scdocs/scdoc/1351.htm〉.

Francesconi, K.A., Kuehnelt, D., 2002. Arsenic compounds in the environment. In: Frankerberger Jr., W.T. (Ed.), Environmental Chemistry of Arsenic. Marcel Dekker, New York, pp. 51–94.

ISO/IEC 17025:2005. General Requirements for the Competence of Testing and Calibration Laboratories. International Organization for Standardization, Geneva.

ISO 9001:2000. Quality Management System—Requirements. International Organization for Standardization, Geneva.

Institute of Public Health of Serbia, 2009. Indicators of Environmental Quality in Republic of Serbia in 2008. Institute of Public Health of Serbia, Belgrade (In Serbian) Available at: 〈www.batut.org.rs〉.

Lindberg, A.L., Goessler, W., Gurzau, E., Koppova, K., Rudnai, P., Kumar, R., Fletcher, T., Leonardi, G., Slotova, K., Gheorghiu, E., Vahter, M., 2006. Arsenic exposure in Hungary, Romania and Slovakia. J. Environ. Monit. 8, 203–208.

Mandal, B.K., Suzuki, K.T., 2002. Arsenic round the world: a review. Talanta 58, 201–235.

Medrano, M.J., Boix, R., Pastor-Barriuso, R., Palua, M., Damian, J., Ramis, R., Del Barrio, J.L., Navas-Acien, A., 2009. Arsenic in public water supplies and cardiovascular mortality in Spain. Environ. Res.. doi:10.1016/j.envres.2009.10.002.

Meza, M.M., Kopplin, M.J., Burgess, J.L., Gandolfi, A.J., 2004. Arsenic drinking water exposure and urinary excretion among adults in the Yaqui Valley, Sonora, Mexico. Environ. Res. 96, 119–126.

Ministry of Environment and Spatial Planning of Serbia, 2009. Report o environmental quality in Republic of Serbia in 2008. Republic of Serbia, Ministry of Environment and Spatial Planning, Environmental Protection Agency, Belgrade (In Serbian).

Statistical Office of the Republic of Serbia, 2009. Statistical Yearbook of Serbia. Statistical Office of the Republic of Serbia, Belgrade. (In Serbian) Available at: 〈http://webrzs.stat.gov.rs/axd/en/god.htm〉.

Thundiyil, J.G., Yuan, Y., Smith, A.H., Steinmaus, C., 2007. Seasonal variation of arsenic concentration in wells in Nevada. Environ. Res. 104, 367–373.

Varsanyi, I., Kovacs, L.O., 2006. Arsenic, iron and organic matter in sediments and groundwater in the Pannonian Basin, Hungary. Appl. Geochem. 21, 949–963.

Yu, W.H., Harvey, C.M., Harvey, C.F., 2003. Arsenic in groundwater in Bangladesh: a geostatistical and epidemiological framework for evaluating health effects and potential remedies. Water. Resour. Res. 39, 1146.