ASSESMENT OF ARSENIC POLLUTED GROUNDWATER IN THE STRUMICA REGION, AN INTENSIVE AGRICUTURE PRODUCTION AREA

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Abstract

Arsenic polluted groundwater was found in the south-east part of the Republic of Macedonia where an intensive agriculture production is concentrate on the area of 963 km^2. Out of 185 samples collected from boreholes, 64 samples have arsenic in concentrations greater than 10 µg/L, from which 30 samples have concentration greater than 50 µg/L with maximum concentration of 176.56 µg/L. The affected aquifers are mostly concentrated in the central part of the valley characterized with alluvial plains and young aquifers. Polluted samples are collected from boreholes with different depths: 15 samples are shallow (4,5 - 20 m), 42 samples are deep (21-100 m) and 7 samples have depth greater than 100 m. The contaminated groundwater is slightly acidic to neutral (pH between 7.5 – 8.53), with high alkalinity (HCO_3^- 177.06 – 511.87) and moderate conductivity (ECw 2.48 – 7.2). Highly affected samples are characterized with high concentrations of Mn and Fe. Other investigated ions such as Mg, Na, K, Ca, P, Cu, Ni, Co, Zn and Pb are present in low concentrations. Factor analysis revealed high positive correlation between arsenic, iron and manganese which suggest the natural origin of arsenic in groundwater. Reducing environment, high iron, high manganese and bicarbonate content, as well as low sulfate and nitrate content, show that reductive dissolution is one of the mechanisms by which arsenic is released into the groundwater.[1]

Key words: agriculture, boreholes, irrigation, geochemical composition, factor analysis.

Introduction

Groundwater is a major source for irrigation in the world. If arsenic polluted groundwater is used for irrigation, serious problems may occur in agriculture production. Permanent irrigation of soil with arsenic polluted water may accumulate this toxic element in the topsoil and after a period of years render the soil unfit for agriculture production.[2] Agricultural inputs like pesticides and fertilizers can also increase the concentration of arsenic in the topsoil.[3] Environmental and climate conditions may contribute in leaching it in to the groundwater. Some plants can take it up from soil or contaminated irrigation water. The quantity depends on plant variety and the contamination level. Arsenic is phytotoxic element and may cause chlorosis, yield decrease and stunt of the plant growth. Although arsenic is usually concentrate in roots and shoots, some plants like rice, lettuce, carrot and potatoes can accumulate it in the edible parts of the plant making it unsuitable for human consumption or other intended use.[4] The pollution of groundwater with arsenic have become a global concern problem. Polluted groundwater have been found in many parts of the world in different hydrogeological and geochemical conditions. Literature data show that majority of the arsenic polluted groundwater provinces are in young unconsolidated sediments, usually from Quaternary or Holocene age in arid or semiarid settings [5,6], or in large alluvial deltaic plains [7,8,9] This, heavy metalloid and oxyanion-forming element can reach the groundwater from natural sources like mineralization and geothermal activity or human activities like mining, industry and the use of arsenical pesticides in agriculture and forest preservation. The aim of this study was to determine arsenic polluted groundwater and find its possible origin in the valley of Strumica, since limited investigations and not enough data is available for this the most important agriculture region in the country.

Materials and methods

Investigated area The Strumica valley is located in the south-eastern part of Macedonia, approximately 15 km to the west of the border with Bulgaria. Boreholes located in the town of Strumica and villages Borievo, Kuklish, Monospitovo, Prosenikovo, Dabile, Sachevo, Ednokukjevo, Ilovica, Banica, Robovo, Piperevo, Dobrejtci and Bansko are included in this investigation. According to the lithological composition of the Strumica basin, the age of the lithozonata is determined that belonging to Upper-Eocene. The discovered thickness of the basal lithozone ranges from 20-50 m.[10] The region is characterized with an intensive agriculture production since 1950's when cotton was the main cultivated crop for existence of domestic growers. The most intensive cotton production was present in the villages of Bosilevo, Ednokukjevo, Robovo, Murtino and Monospitovo. The construction of the irrigation systems Turia and Vodocha in 1979, contribute to the replacement of cotton production with early vegetable production which contribute in development of food cane industry.

Analysis Each sample was collected from a single borehole located in the field of agricultural production, according to EPA guidelines[11] and analyzed for the quantity of major cations, anions, heavy metals and trace elements. Anions like chlorine, carbonate and bicarbonate were analyzed by volumetric methods. Sulphate (SO_4^{2-}), nitrate (NO_3^-), nitrite (NO_2^-) and ammonia (NH_4^+) were determined by colorimetric method using spectrophotometer type JENWAY 6715, UV Vis (EPA 375.4; EPA 352.1; EPA 354.1; EPA 350.2). pH is measured by pH meter HANNA HI 2211-01 and electrical conductivity is measured with conductometer JENWAY 4520, in situ. Total oxidation state of arsenic (As), magnesium (Mg), sodium (Na), potassium (K), calcium (Ca), phosphorus (P), manganese (Mn), copper (Cu), nickel (Ni), cobalt (Co), iron (Fe), zinc (Zn) and lead (Pb) were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS), (Agilent 7500 CX). Chemical composition of groundwater was subjected to correlation and factor analysis to understand the covariance structure between the variables. Factor analysis are used to detect the relationship between As and other investigated ions using statistical program Statistica, version 10 (StatSoft. Inc., 2011).

Table 2. Multivariate factor analysis scores for the investigated samples

	F 1	F2	F3	F4	F5	Comm.
d	-0.33	-0.17	**-0.59**	-0.17	0.28	0.51
pH	-0.16	**0.81**	0.19	-0.21	-0.05	0.67
ECw	0.39	**0.71**	0.03	0.21	0.01	0.71
HCO_3^-	0.31	**0.80**	-0.12	-0.16	-0.16	0.92
Cl^-	**0.89**	-0.03	0.08	0.09	-0.01	0.95
NO_3^-	0.28	-0.04	0.0	**0.82**	0.18	0.79
NO_2^-	-0.04	-0.25	-0.26	-0.06	**0.58**	0.30
NH_4^+	-0.08	0.03	-0.47	0.13	-0.28	0.29
SO_4^{2-}	**0.74**	0.04	0.1	0.13	0.07	0.82
Na^+	0.27	-0.16	**-0.51**	0.08	-0.12	0.36
PO_4^{3-}	-0.19	-0.12	-0.44	**0.63**	-0.09	0.46
K	0.03	-0.07	0.11	**0.89**	-0.05	0.76
Ca	**0.84**	0.28	0.01	0.18	0.10	0.96
Mg	**0.71**	0.16	0.25	-0.11	-0.13	0.89
As	-0.19	0.40	**-0.58**	-0.13	-0.11	0.51
Mn	0.34	0.44	-0.29	-0.19	0.09	0.55
Fe	-0.14	-0.10	**-0.69**	-0.08	0.02	0.45
Ni	0.22	**0.54**	0.01	0.39	**0.52**	0.66
Cu	0.17	-0.18	0.10	0.07	**0.7**	0.34
Zn	0.00	0.26	0.097	-0.03	0.42	0.24
Pb	-0.11	0.17	0.14	0.06	0.264	0.226
Co	**0.75**	0.06	-0.06	-0.06	0.194	0.604

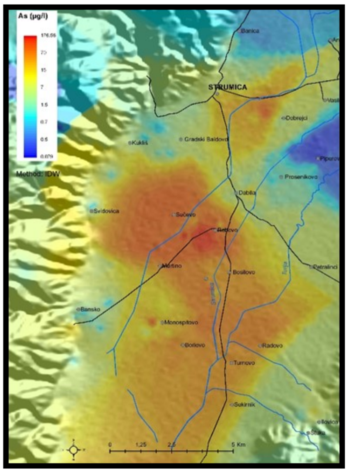
Results and discussion

A total number of 185 groundwater samples have been analyzed for their quality and heavy metal content (Tab. 1). Well depth of the investigated boreholes ranged between 4.5 and 130 m with the median of 21 m. The analytical results show that pH values of groundwater samples varied between 6.84 and 8.67 with the median of 7.83, which indicates that waters are generally slightly alkaline. The electrical conductivity of groundwater varies between 1.22 and 17,49 dS/m at 25 with the median value of 4,74 dS/m. Around 32% of groundwater samples belong in very hard category, 25% in hard category, 28% belong in moderately hard category and the remain samples fall in soft category. All heavy metals and trace elements except As, Mn and Fe are found below the national MCL (Maximum Concentration Limits) (Tab.1). Out of 185 investigated samples, 64 have total arsenic content greater than 10 µg/l, from which 30 samples have concentration greater than 50 µg/L with maximum concentration of 176.56 µg/L.

Table 1. Statistic summary of concentrations of chemical variables resulting from descriptive analysis of investigated samples

	Min	Max	Mean	Median	SD	CV
d (*m*)	4.50	130	40.2	21.00	34.32	85.36
pH	6.84	8.67	7.85	7.83	0.45	5.67
ECw (*dS/m*)	1.22	17.49	4.88	4.74	2.46	50.41
HCO_3^-(*mg/L*)	0.04	750.97	269.65	265.25	156.61	58.08
Cl (*mg/L*)	4.19	614.31	39.59	25.13	55.77	140.88
NO_3^- (*mg/L*)	0.14	284.44	23.30	2.98	45.50	195.27
NO_2^- (*mg/L*)	<LOD	35.85	0.73	0.025	3.99	546.69
NH_4^+ (*mg/L*)	<LOD	55.89	1.12	0.09	5.01	448.86
SO_4^{2-} (*mg/L*)	<LOD	300.45	24.97	17.57	37.73	151.06
Na (*mg/L*)	1.4	36.71	7.06	5.95	5.07	71.84
PO_4^{3-} (*mg/L*)	<LOD	7.8	0.54	0.19	1.1	202.62
K (*µg/L*)	1.15	354.44	12.06	5.38	2.35	16.58
Ca (*mg/L*)	7.43	411.18	51.10	39.84	39.61	77.52
Mg (*mg/L*)	1.07	96.14	13.55	9.77	12.51	92.33
As (*µg/L*)	0.08	176.56	21.58	2.60	38.51	178.45
Mn (*µg/L*)	<LOD	3328.88	465.10	288.55	606.78	130.46
Fe (*µg/L*)	<LOD	3165.71	212.29	71.69	386.89	182.25
Ni (*µg/L*)	0.32	21.58	3.36	2.59	2.67	79.49
Cu (*µg/L*)	<LOD	21.55	1.35	1.04	1.74	128.66
Zn (*µg/L*)	2.34	1371.41	49.79	14.22	160.16	321.67
Pb (*µg/L*)	0.06	16.35	0.92	0.47	1.66	181.78
Co (*µg/L*)	0.25	2.1	0.39	0.25	0.36	91.62

Fig. 2 GIS map of arsenic distribution in the investigated area.



The most polluted are samples in the village of Robovo (eight out of nine investigated samples) with concentration range from 65.23 – 176.56 µg/L, than samples from the village of Sachevo where seventeen out of nineteen investigated boreholes exceeded the level of 10 µg/l, with the concentration range from 23.31 to 172.42 µg/L. In the village of Ednokukjevo thirteen out of eighteen samples (range 10.37 – 109.46 µg/L) and in the village of Borievo eleven out of twelve investigated samples where polluted (11.54 – 80.42 µg/L) with concentration greater than 10 µg/l. Arsenic polluted aquifers are mostly concentrated in the central part of the valley characterized with alluvial plains and young aquifers (Fig.2).Most of the polluted samples (42 samples) have depth between 21-100 m. Only fifteen samples have depth not greater than 20 m and 7 samples have depth between 100 - 125 m. The contaminated groundwater are mostly alkaline (pH between 7.5 – 8.53), with high concentration of bicarbonate (HCO_3^- 177.06 – 511.87) and moderate conductivity (ECw 2.48 – 7.2). Highly polluted samples with arsenic concentration greater than 50 µg/L are characterized with low content of sulphate (0.77 – 25.76 µg/L), phosphate (0.025 – 7.8 µg/L), potassium (1.23 – 10.48 µg/L), calcium (12.71 – 75.48 µg/L), magnesium (3.39 – 42.33 µg/L), nickel (0.54 – 8.99 µg/L), cuprum (0.25 – 4.25 samples. µg/L), zinc (2.91 – 88.73 µg/L), lead (0.25 – 16.35 µg/L) and cobalt (0.25 – 0.7 µg/L). Concentrations of iron (28.01 – 3165.71 µg/L) and manganese (68.42 – 2175.17 µg/L) showed higher values

Factor analysis Factor analysis revealed five factors and show around 59% of the total variance including 19 variables from observed 22 variables. High positive loadings for pH, ECw and HCO_3^- indicates that chemical processes in the investigated groundwater are mostly affected by the presence of these ions. F(3) show high negative loadings for depth, sodium, arsenic and iron. This factor indicates the origin of the As in the groundwater of the region. F(4) has high positive loadings for nitrates, phosphates and potassium.which associate to fertilizer leaching from the surface in this region, which are used usually as potassium nitrate or potassium phosphate. F (5) has high positive loadings for nitrites, nickel and copper in range between 0.518 – 0.718. This factor indicate the mine deposits in the region (Tab. 2 and Table 3). No significant correlation between arsenic, nitrate, phosphate and potassium suggest that arsenic is not derived in groundwater by surface leaching. In contrary, the correlation between arsenic, iron, depth and sodium, suggest the natural rather than anthropogenic origin of the arsenic in groundwater and associate the presence of arsenic with the iron oxides and sodium feldspats from sedimentary rock formations in the region. According to the geological composition calcite forms of limestone, iron minerals, as well as sodium feldspats are common for the investigated area.[10,12] Reducing environment, high iron, high manganese and bicarbonate content as well as low sulphate and nitrate content show that reductive – dissolution is probably the main mechanism of arsenic mobilization in the investigated area.

Table 3. Varimax scores of the performed factor analysis

	Eigen values	Contribution %	Elements with high loadings
1	4.787	21.759	Cl, SO_4^{2-}, Ca, Mg, Co
2	2.742	12.463	pH, ECw, HCO_3^-, Ni
3	2.136	9.710	d, Na, As, Fe
4	1.746	7.935	NO_3^-, PO_4^{3-}, K
5	1.589	7.222	NO_2^-, Ni, Cu
Total	23,48	59,089	94,64

Conclusion

The study points out that arsenic polluted groundwater is present in the southeast part of the Republic of Macedonia, located in the central part of the Strumica valley. Although, the region has potential for agrochemical and geothermal pollution, the investigation shows that groundwater is naturally contaminated from arsenic reach geological formations. The mechanism of reductive-dissolution from iron oxides are recognized as the main process that contribute to groundwater pollution. Once again, principal component analysis has been proven as useful method in determination of correlation between the elements in the environment. The obtained concentration levels show that groundwater from these sources could be hazardous for humans and animals and should not be considered as a potential source for drinking water. Regarding the agricultural production no significant symptoms of plant toxicity are observed in the field (unpublished data). Even though, there is a possible threat for agriculture production in the future. The investigation of soil pollution in critical points should be priority in order to determine the impact of polluted irrigation water in the region.

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