

ONE FACTORIAL ANOVA IN ASSESSMENT OF GROUNDWATER QUALITY IN VULNERABLE AREA OF AGRICULTURE POLLUTION

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Abstract

Arsenic polluted groundwater was found in the Strumica region located in the south-east part of the Republic of Macedonia where an intensive agriculture production is concentrated on the area of around 1000 km². Out of 185 samples collected from boreholes, 64 samples have arsenic in concentrations greater than 10 µg/L, from which 30 samples have a concentration greater than 50 µg/L with a maximum concentration of 176.56 µg/L. Pollution mostly occurs in the groundwater located in the central part of the valley characterized by alluvial plains and young aquifer. Around 57% of the polluted samples have origin from deep groundwater with a depth greater than 40 m. Reductive environment, high Fe, Mn, HCO₃⁻ concentrations as well as low SO₄²⁻ and NO₃⁻ content in polluted samples suggests that reductive dissolution is a major mechanism by which arsenic is released into the groundwater. Highly polluted samples are characterized by high concentrations of Mn and Fe. Other investigated ions are present in low concentrations. Single factorial ANOVA showed significant differences between As concentrations in shallow and deep groundwater. Multivariate factor analysis was performed to identify the covariance structure between the investigated variables. Arsenic was positively correlated to HCO₃⁻ and Mn in shallow groundwater and with HCO₃⁻, Ca, and Mn in deep groundwater suggesting that arsenic is mobilized in groundwater by reductive dissolution of Mn oxides from the bedrock.

Key words: *arsenic, shallow groundwater, deep groundwater, reductive dissolution.*

INTRODUCTION

Groundwater is a major source of 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 contribute to the accumulation of this toxic element in the topsoil or subsoil and after some time render the soil unfit for agriculture production (Bhattacharya et al., 2002). According to Jiang and Singh (1994), agricultural inputs like pesticides and fertilizers may also increase the concentration of arsenic in the soil. Environmental and climate conditions may contribute to leaching it into the groundwater. Some amount can be taken up by plants from the soil or the contaminated irrigation water. The quantity depends on plant variety and the contamination level. Arsenic is a phytotoxic element and may cause chlorosis, yield decrease, and stunt of the plant growth. Plants usually accumulate arsenic in roots and shoots, but some plants like rice, lettuce, carrot, and potatoes are capable to accumulate As in the edible parts of the plant making it unsuitable for human consumption or other intended use (Kabata-Pendias A. and Mukherjee B. A., 2007). The pollution of groundwater with arsenic has become a global concern problem. Polluted groundwater has 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 (Rosas et al., 1999; Smedley et al., 2002), or in large alluvial deltaic plains (Berg et al., 2001; Smedley et al., 2005; Polya et al., 2005). 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. Arsenic pollution of groundwater which is related to mineralization and mining activities are localized in recognized regions and have been reported worldwide like the USA (Twarakawi N.K.C. and Kaluarachchi J.J., 2006) Canada (Bernard D.W., 1983; Grantham D.A. and Jones J.F., 1977), Africa (Smedley et al., 2007), Greece (Komnitsas K. et al., 1995), India (Chakraborti D. et al., 1999; Pandey P.K. et al., 2002), Mexico (Armienta M.A. et al., 2005), Thailand (Williams M., 1996), England (Thornton I., 1994), etc. Arsenic polluted groundwater associated with geothermal fluids has been reported in the USA (Wilkie J.A. and Hering J.G., 1998; Welch A.H. et al., 2000), Japan (Swedlund P.J. and Webster J.G., 1998), and New Zealand (Robinson B. et al., 1995). Data related to arsenic contamination of groundwater associated with pesticide applications are limited and until now have been reported only in the United States (Bednar A.J., 2002; Cai Y. et al., 2002 and Wiegand G.E., 1999). In the Republic of Macedonia arsenic polluted groundwater has been found in Pelagonia valley the region of Prilep (max. 75 µg/L) (Mirčovski V. et al., 2014), and the region of Strumica (max. 117.8 µg/L) (Ivanova Š. and Ambarkova V., 2015). According to Ravenscroft et al. (2009), there are four mobilization mechanisms of arsenic in nature: reductive dissolution (RD), alkali desorption (AD), sulfide oxidation (SO), and geothermal (GT). The purpose of this study was to make an assessment of arsenic pollution of groundwater which is used for irrigation and situated under intensive agriculture activities using chemometric methods like single factorial analysis of variance and multivariate factor analysis.

MATERIAL AND METHODS

Investigated area

The investigation was conducted in the Strumica valley, located in the south-eastern part of North Macedonia, approximately 15 km to the west of the border with Bulgaria. The groundwater of the investigated area belongs to the transboundary Petrich valley aquifer shared by the Republic of North Macedonia and Bulgaria and it is hydraulically linked with the surface water of the Struma/Strymonas river basin (Fig.1). The Aquifer is made up of Pliocene, predominantly, and Quaternary lake sediments, alluvial sands, gravels, clays, and sandy clays (UNECE 2011). The Strumica river is a transboundary tributary to the Struma/Strymonas river which source is in western Bulgaria (Vitoshka Mountain, south of Sofia) and ends in the Aegean Sea (Strymonikos Gulf – Greece) (Fig. 1). The discovered thickness of the basal lithozone ranges from 20-50 m (Rakicevik et al., 1973). The region is characterized by an intensive agriculture production since the 1950's when cotton was the main cultivated crop for the existence of domestic growers. The construction of the irrigation systems Turia and Vodocha in 1979, contribute to the replacement of cotton production with early vegetable production which contributes to the development of the food cane industry. The region is reached in hydro geothermal water which according to Gorgieva et al. (2000) belongs in the hydrothermal systems in the fractured granites of Paleozoic or Mesozoic age. Springs and boreholes with different temperatures are present within small distances in the village of Bansko. The maximum measured temperature is 73°C and the predicted maximum temperature is 120°C (Gorgieva, 1989). The reservoir in the granites lies under thick Tertiary sediments. An abundant mine with copper and gold deposits is present in the village of Illovitca located in a northwest-southeast striking Tertiary magmatic arc, that covers large areas of Macedonia, Serbia, Central Romania, Southern Bulgaria, Northern Greece, and Eastern Turkey (Carter S., 2008).

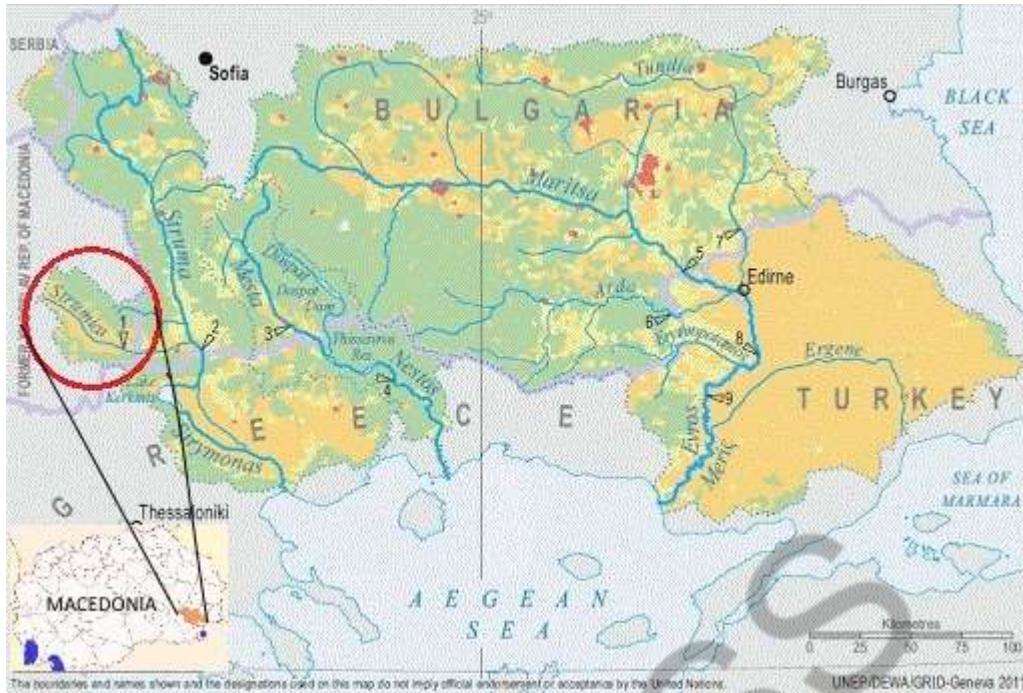


Figure 1. Geographic location of the investigated region, the Strumica valley.

Chemical analysis

Each sample was collected from a borehole located in the field of agricultural production, according to EPA guidelines (Johnston, 2007) 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. Sulfate (SO_4^{2-}), nitrate (NO_3^-), nitrite (NO_2^-), and ammonia (NH_4^+) were determined by the 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*. The 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). The equipment was linearly calibrated from 1 to 100 $\mu\text{g/L}$, using a certified standard solution (Sigma ICP Multielement Standard Solution). Linearity was checked after every 10 samples. Accuracy has been tested by analyzing a certified reference material, NIST SRM 1643 c "Trace elements in water." Bias ranged from 2 to 7%. Precision expressed as intermediate precision was better than 10% for all analyzed elements.

Statistical analysis

Descriptive statistics analysis was used to perform analysis of data, including mean, median, maximum and minimums, standard deviation, and variance. One factorial ANOVA in excel was performed to see if there are significant differences of As concentrations in shallow and deep groundwater. Groundwater composition was subject to a factor analysis to understand the covariance structure between As and other variables. Varimax normalized type of rotation and multiple R – square methods were used for the extraction of the loadings. Descriptive and factor analysis are performed in the statistical program Statistica version 10 (StatSoft Inc., 2011).

RESULTS AND DISCUSSION

Chemical and physical characteristics of groundwater

A total number of 185 groundwater samples have been analyzed for their quality and heavy metal content (Tab. 1). The depth of the investigated boreholes ranged between 4.5

and 130 m with a median of 21 m. The analytical results show that the pH values of groundwater samples varied between 6.84 and 8.67 with a 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°C with a median value of 4.74 dS/m. According to Sawyer N.G and Mc Cartly D.L. (1967), the total hardness expressed as mass of CaCO₃ ranged between 0.03 – 915.07 mg/L. Around 32% of groundwater samples belong in the very hard category, 25% in the hard category, 28% belong in the moderately hard category and 25% were characterized in soft category. All heavy metals and trace elements except As, Mn, and Fe are found below the national MCL (Maximum Concentration Limits).

Almost 35% of investigated samples have total arsenic content greater than 10 µg/l, from which 16% have concentrations greater than 50 µg/L with a maximum concentration of 176.56 µg/L. The most polluted were samples from the village of Robovo (eight out of nine investigated samples) with a concentration range from 65.23 – 176.56 µg/L, then 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 were polluted (11.54 – 80.42 µg/L) with a concentration greater than 10 µg/l. Arsenic polluted groundwater was sampled mostly from the boreholes located in the central part of the valley characterized by alluvial plains and young aquifer.

Table 1. Statistic summary of concentrations of chemical variables resulting from the 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
HCO₃⁻ (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
NO₃⁻ (mg/L)	0.14	284.44	23.30	2.98	45.50	195.27
NO₂⁻ (mg/L)	<LOD	35.85	0.73	0.025	3.99	546.69
NH₄⁺ (mg/L)	<LOD	55.89	1.12	0.09	5.01	448.86
SO₄²⁻ (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
PO₄³⁻ (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

Most of the arsenic polluted samples (42 samples) have depth between 21-100 m. Only fifteen samples have depth not greater than 20 m and 7 samples have a depth between 100 - 125 m. The contaminated groundwater is mostly alkaline (pH between 7.5 – 8.53), with a high concentration of bicarbonate (HCO₃⁻ 177.06 – 511.87) and moderate conductivity (ECw 2.48 – 7.2) (Tab. 2). Arsenic bearing rocks like calcite forms of limestone, iron oxide minerals,

and sodium feldspars are common for the investigated region (Rakicevik and Pendzerkoski 1973). Groundwater from the boreholes in the village of Bansko, an area rich in geothermal springs, shows no significant content of arsenic in groundwater. The most important geothermal spring in this region has an arsenic concentration of 22.52 µg/L, suggesting that arsenic presence in groundwater in the region have no geothermal origin. Reducing environment present in the groundwater of the investigated area, high Fe, Mg, HCO₃ as well as low SO₄ and NO₃ content suggests that reductive dissolution is a major mechanism by which arsenic is released into the groundwater.

Table 2. Statistic summary of concentrations of chemical variables resulting from the descriptive analysis of arsenic polluted samples

	Min	Max	Mean	Median	SD	CV
d (m)	17.00	125.0	64.77	76.50	38.38	59.26
pH	7.50	8.53	8.02	8.035	0.34	4.22
EC_w (dS/m)	2.48	7.20	4.95	4.98	1.17	23.65
HCO₃⁻ (mg/L)	177.06	511.87	359.23	385.45	92.34	25.70
Cl⁻ (mg/L)	6.28	49.53	15.89	11.09	11.67	73.45
NO₃⁻ (mg/L)	0.65	19.81	3.77	1.60	5.33	141.27
NO₂⁻ (mg/L)	< LOD	0.120	0.03	0.03	0.02	63.23
NH₄⁺ (mg/L)	< LOD	17.930	1.51	0.39	3.39	224.34
SO₄²⁻ (mg/L)	0.77	25.760	7.06	2.50	7.91	112.01
Na⁺ (mg/L)	1.66	18.350	8.39	7.45	3.61	42.98
PO₄³⁻ (mg/L)	< LOD	7.80	1.09	0.23	1.87	172.32
K (mg/L)	1.23	10.26	4.83	4.84	2.59	53.59
Ca (mg/L)	12.71	70.97	41.40	37.44	16.22	39.18
Mg (mg/L)	3.39	42.33	9.30	6.51	9.26	99.63
As (µg/L)	50.04	176.56	101.93	90.60	38.61	37.88
Mn (µg/L)	68.42	2175.17	692.13	592.86	498.72	72.06
Fe (µg/L)	28.01	1048.61	258.33	112.52	270.58	104.74
Ni (µg/L)	0.54	8.99	2.64	1.70	2.49	94.17
Cu (µg/L)	< LOD	4.25	0.86	0.38	1.00	115.7
Zn (µg/L)	2.90	88.73	21.73	12.1	22.04	101.43
Pb (µg/L)	< LOD	16.35	1.16	0.25	3.04	261.92
Co (µg/L)	< LOD	0.70	0.30	0.25	0.12	40.24

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 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 than in unpolluted samples.

Statistical analysis

One factorial ANOVA

Single-factor ANOVA was performed to investigate if there are significant differences between As concentrations in shallow groundwater with depth up to 40 m and deep groundwater with a depth greater than 40 m. For that purpose, the obtained values for As concentrations were previously normalized using Box-Cox transformation. The analysis showed that F (37.97) is higher than F critical (3.89) and p-value (4.17 E⁻⁹) is much lower than 0.05 which indicates that there is a significant difference between shallow groundwater and

deep groundwater regarding As concentration. The mean values of As concentrations 15.86 ppm and 34.05 ppm for shallow and deep groundwater respectively, indicate that higher concentrations are present in deep groundwater suggesting its natural origin.

Table 3. Single factor ANOVA for As concentrations in shallow and deep groundwater

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	93.83	1	93.83	37.97	4.17E-09	3.89
Within Groups	472	191	2.47			
Total	565.83	192				

Factor analysis

Factor analysis performed for all groundwater samples revealed two factors with eigenvalues greater than one which explains only 29.96% of the total variance and 44.35% of communalities leaving too many residuals (unexplained sums of squares) (Table 4). Due to the information from this analysis, it was not possible to give a logical explanation of the association of variables. It is assumed that this outcome due to different chemical processes dominated in shallow and deep groundwater. The composition of shallow groundwater is more prone to the processes of sorption and desorption as a result of clay and organic matter content in the topsoil and subsoil. The composition of deeper groundwater is more prone to the processes related with the aquifer composition. To lower the percent of residuals, and to obtain more clear associations, factor analysis was performed separately for shallow and deep groundwater. Factor analysis for shallow groundwater revealed four factors with eigenvalues greater than one which explain 43.64% of the total variance and 50.19% of communalities (Table 5). The analysis positively associates As with HCO₃⁻ and Mn suggesting that arsenic is mobilized in groundwater by reductive dissolution of Mn oxides from the bedrock. Factor analysis for deep groundwater revealed five factors with eigenvalues greater than one. Arsenic was positively associated with HCO₃⁻, Ca, and Mn in the third factor which explains 10% of the total variance (Table 6). The obtained result is in accordance with the association obtained from the analysis of shallow groundwater, which is difficult to conclude based on the analysis when shallow and deep groundwater were statistically processed together.

Table 4. Factor analysis for all investigated samples

	F1	F2	Comm
HCO ₃ ⁻	-0.15	0.76	70.34
Cl ⁻	0.68	0.55	85.64
NO ₃ ⁻	0.56	-0.01	47.48
SO ₄ ²⁻	0.67	0.27	64.97
Na	0.11	0.04	29.39
PO ₄ ³⁻	-0.16	-0.06	17.88
K	0.29	0.10	45.74
Ca	0.61	0.65	88.76
Mg	0.45	0.50	67.71
As	-0.49	0.30	36.04
Mn	-0.16	0.60	44.44
Fe	-0.30	0.12	15.59
Ni	0.23	0.32	37.36
Cu	0.19	0.02	18.74
Zn	0.01	0.10	16.67
Pb	0.06	-0.00	10.53
Co	0.43	0.55	56.67
E-value	3.69	1.41	44.35%
Total variance %	21.68	8.28	

Table 5. Factor analysis of investigated variables for shallow groundwater of the Strumica region

	F1	F2	F3	F4	Comm
HCO ₃ ⁻	0.38	0.67	0.04	0.01	71.03
Cl ⁻	0.87	-0.01	-0.07	0.14	86.85
NO ₃ ⁻	0.23	-0.27	0.07	0.66	55.16
SO ₄ ²⁻	0.69	-0.21	0.03	0.15	67.04
Na	0.15	0.05	-0.27	0.28	29.28
PO ₄ ³⁻	-0.22	-0.05	0.05	0.54	31.44
K	0.18	0.01	-0.21	0.47	53.15
Ca	0.84	0.11	0.18	0.24	90.28
Mg	0.71	0.04	-0.12	-0.12	65.83
As	-0.18	0.65	-0.04	0.02	43.37
Mn	0.28	0.58	0.07	-0.09	54.30
Fe	-0.09	0.34	-0.00	-0.05	13.41
Ni	0.24	0.24	0.36	0.35	39.22
Cu	0.09	-0.08	0.59	-0.03	35.09
Zn	0.13	0.02	0.61	-0.11	37.46
Pb	-0.06	0.03	0.25	0.04	13.36
Co	0.74	0.12	0.12	0.05	66.92
E-value	3.71	1.63	1.09	1.01	50.19%
Total variance %	21.85	9.58	6.40	5.95	

Table 6. Factor analysis for investigated variables for deep groundwater of the Strumica region

	F1	F2	F3	F4	F5	Comm
HCO ₃ ⁻	-0.12	0.24	0.86	-0.01	-0.13	86.33
Cl ⁻	0.84	0.15	-0.06	0.19	0.12	84.43
NO ₃ ⁻	0.58	-0.32	-0.11	0.13	-0.26	71.20
SO ₄ ²⁻	0.41	0.10	0.06	0.05	0.71	69.35
Na	0.13	0.06	0.09	0.09	0.77	79.76
PO ₄ ³⁻	-0.04	0.05	0.09	-0.75	-0.07	57.72
K	0.84	0.04	0.05	-0.07	0.31	84.14
Ca	0.40	-0.01	0.80	0.15	0.12	85.21
Mg	0.22	0.14	0.16	-0.03	-0.45	54.66
As	-0.23	0.14	0.59	-0.07	0.03	53.85
Mn	-0.04	-0.39	0.50	-0.14	-0.21	63.87
Fe	-0.07	0.01	-0.05	-0.65	-0.08	48.10
Ni	0.21	-0.79	-0.00	0.11	-0.09	74.67
Cu	0.36	-0.37	-0.19	0.23	-0.01	60.74
Zn	-0.04	-0.14	0.07	0.09	-0.09	32.65
Pb	-0.10	-0.63	-0.25	-0.03	0.13	68.88
Co	-0.06	-0.75	-0.05	0.00	0.03	65.85
E-value	3.00	2.56	1.83	1.44	1.24	67.14%
Total variance %	16.66	14.22	10.19	7.98	6.91	

CONCLUDING REMARKS

The assessment of arsenic pollution of groundwater situated under the intensive agriculture activities was investigated in this study. The investigation was performed on the Macedonian part of the Perich valley aquifer, located in the central part of the Strumica valley. Although, the region has potential for agrochemical, industrial and geothermal pollution, the investigation shows that groundwater is naturally contaminated from arsenic rich geological formations. The mechanism of reductive-dissolution from iron oxides are recognized as the main process that contributes to groundwater pollution. The obtained concentration levels of

pollution 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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ЕДНО ФАКТОРИЈАЛНА АНОВА ВО ПРОЦЕНКА НА КВАЛИТЕТОТ НА ПОДЗЕМНИТЕ ВОДИ ВО КРИТИЧНИ ОБЛАСТИ НА ЗАГАДУВАЊЕ КОЕ ПОТЕКНУВА ОД ЗЕМЈОДЕЛСКИ АКТИВНОСТИ

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Резиме

Зголемени концентрации на арсен се детектирани во подземните води на Струмичкиот регион, лоциран во југоисточниот дел на Македонија каде интензивно земјоделско производство е концентрирано на површина од околу 1000 km². Од вкупно 185 примероци на подземна вода собрани од различни бушотини, 64 покажаа концентрации повисоки од 10 µg/l. Од нив, 30 примероци имаа концентрации повисоки од 50 µg/L со максимална концентрација од 176.56 µg/L. Ваквите зголемени концентрации на арсен се забележани кај примероците од подземна вода собрани од бушотини лоцирани главно во централниот дел на Струмичката котлина кој се карактеризира со алувијални почви и млади подземни базени. Околу 57% од загадените примероци се собрани од бушотини со длабочина поголема од 40 m. Редуцирачката средина, високите вредности за Fe, Mn, HCO₃⁻ како ииските вредности добиени за SO₄²⁻ and NO₃⁻ сугерираат дека редуктивната дисолуција е главниот механизам на ослободување на арсенот во подземните води. Примероците каде беа забележани повисоки концентрации на As се карактеризираат со високи концентрации на Mn и Fe. Другите испитувани јони беа присутни во ниски концентрации. Анализата со едно факторијалната АНОВА покажа значителна разлика помеѓу концентрациите на As во плитките (< 40 m) и длабоките (> 40 m) примероци на подземна вода. Мултиваријатната факторна анализа покажа позитивна корелација помеѓу As, HCO₃⁻ и Mn во плитките примероци и As, HCO₃⁻, Ca, и Mn во длабоките примероци на подземна вода. Ваквиот резултат оди во прилог на заклучокот дека As е ослободен во подземните води со редуктивна дисолуција на оксидите на Mn кои влегуваат во составот на карпите од подземните базени.

Клучни зборови: *арсен, плитка подземна вода, длабока подземна вода, редуктивна дисолуција.*