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

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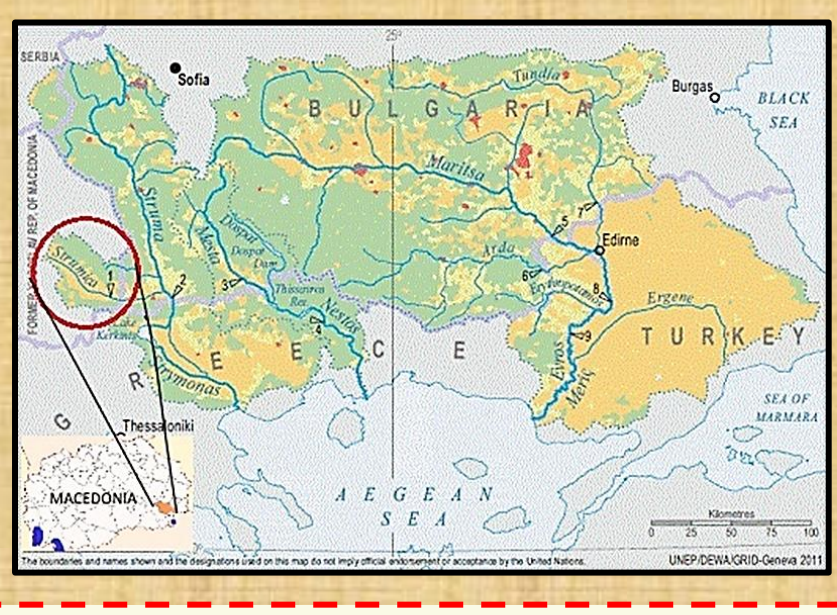
Abstract

Arsenic polluted groundwater was found in the Strumica region located in the south-east part of the Republic of North Macedonia where an intensive agriculture production is concentrated. 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 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 groundwater with depth lower than 40 m and with HCO3-, Ca, and Mn in groundwater with depth greater than 40 m suggesting that arsenic is mobilized in groundwater by reductive dissolution of Mn oxides from the bedrock.



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 .

Table 1. 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
ECw (*dS/m*)	2.48	7.20	4.95	4.98	1.17	23.65
HCO_3^- (*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
NO_3^- (*mg/L*)	0.65	19.81	3.77	1.60	5.33	141.27
NO_2^- (*mg/L*)	< LOD	0.120	0.03	0.03	0.02	63.23
NH_4^+ (*mg/L*)	< LOD	17.930	1.51	0.39	3.39	224.34
SO_4^{2-} (*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
PO_4^{3-} (*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

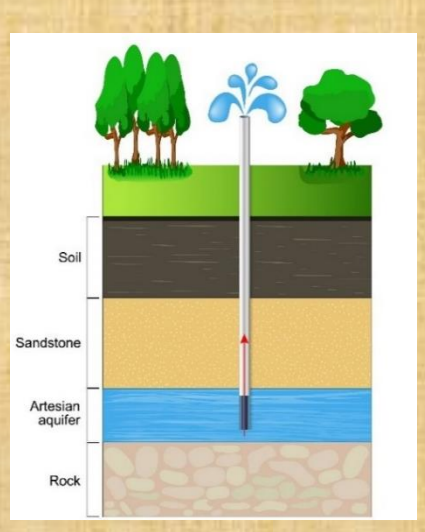


Table 2. Single factor ANOVA for As concentrations in shallow and deep groundwater

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				

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.

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.

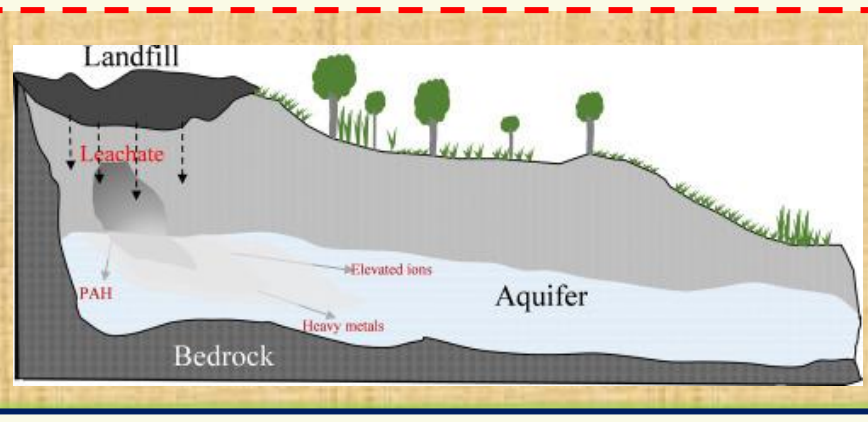


Table 3. Factor analysis of investigated variables for shallow groundwater of the Strumica region

	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%**
TV %	21.85	9.58	6.40	5.95	

Table 4. Factor analysis of 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%**
TV %	16.66	14.22	10.19	7.98	6.91	

CONCLUSION

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 reach geological formations. The mechanism of reductive-dissolution from Mn 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.