Goce Delcev University —Stip
Faculty of Agriculture

GROUND WATER POLLUTION IN ALLUVIAL AND PROLLUVIAL REGION OF THE STRUMICA VALLEY, REPUBLIC OF MACEDONIA

Biljana Kovacevik[1], Blazo Boev[2], Ilija Karov[1] and Sasa Mitrev[1]

[1] *Faculty of Agriculture, Goce Delcev University of Stip, KrsteMisirkov bb, 2000 Stip, Republic of Macedonia*
[2] *Faculty of Natural and Technical Sciences, Goce Delcev University of Stip, KrsteMisirkov bb, 2000 Stip, Republic of Macedonia*

Abstract

The quality of groundwater is investigate for possible agriculture pollution in the traditional agriculture region of Strumica. Almost 200 samples are investigate for a total content of Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, HCO_3^-, SO_4^{2-}, NO_3^-, NO_2^-, NH_4^+, and PO_4^{3-}. The results showed that groundwater in the study area are generally neutral to slightly alkaline. The abundance of the major ions is $Mg^{2+}>Ca^{2+}>K^+>Na^+$ for cations and $HCO_3^->Cl^->SO_4^{2-}$ for anions. Concentrations range is between 1,40 - 36,71mg/l, 0,50 - 354,44 mg/l, 7,43 – 411,18 mg/l, 1,07- 96,14 mg/l and 0,25 – 55,89 mg/l for Na^+, K^+, Ca^{2+} Mg^{2+} and NH_4^+, respectively. Regarding anions Cl^-, HCO_3^-, SO_4^{2-}, NO_3^-, NO_2^-, and PO_4^{3-} concentration range is 4,19 – 614,31mg/l, 0,25 – 1116,38 mg/l, 0,25 – 300,45 mg/l, 0,14 – 284,44 mg/l, 0,25 – 35,85 mg/l and 0,25 – 7,80 mg/l, respectively. A multivariate statistical analysis is performed to evaluate the possible interrelationship within the set of variables. Statistical and hydrochemical analysis suggest that the quality of groundwater is mainly affected by the geological composition of the area. Factor analysis (FA) revealed five significant factors of 15 variables and account for 69,38 % of the total variance. Although nitrates are considered as significant source of widespread groundwater contamination when it comes to agriculture areas, the investigation didn't show any severe contamination with the exception of the periphery of the valley which is considered to be related with the thickness of the basal lithozone (20-50 m) represented mostly by sandstones and the shallow aquifers.

Key words: irrigation quality parameters, hydrochemical analysis, agriculture pollution.

Introduction

Groundwater is a significant water supply source in many developed and rural area. One of the most recognized pollutant of groundwater worldwide is agriculture and it is considered as one of the most serious environmental problem. Since 1980's the concern over the groundwater agriculture pollutants in Europe has been growing. Agriculture has been cited as a leading non-point source, causer of groundwater pollution in many area of the world (FAO, 1996; Ignazi, 1993). The most important agriculture pollutant of groundwater is nitrate (US EPA, 1994). High concentration of nitrate in drinking water is a possible health threating. Nitrate concentrations in groundwater can reach high levels leaching or runoff from agricultural land or contamination from human and animal wastes as a consequence of the oxidation of ammonia. Nitrate pollution in groundwater has been announced in many agriculture develop areas of Europe like Austria, Czech Republic, France, Germany, Romania and Slovak Republic (EEA, 1999). Slovenia published that in almost 25% of sampled wells, concentrations of nitrates in groundwater exceeded 25mg/L. In the Republic of Moldova this value exceeded MCL of 50 mg/L, while in Northern Europe (Iceland, Finland, Norway and Sweden) nitrate concentrations in groundwater are relatively low (Jamie B et al., 1996).

The aim of this study was to investigate the quality of the ground water for the possible non pointed pollution in the region of Strumica and determine the agriculture pollution impact relative to the other types of pollutants, using multivariate statistics analysis. The investigated region is a vulnerable zone because of the fifty year traditional vegetable production, thus it is important to have insight the possible threat of groundwater in this area from the agriculture pollutants. This is a first study about the quality of groundwater in the region of Strumica.

Materials and methods

Groundwater samples are collected from 216 sampling boreholes in fourteen different areas of the Strumica region, Republic of Macedonia. The areas include villages: Borievo, Kuklish, Monospitovo, Prosenikovo, Dabile, Sachevo, Ednokukjevo, Ilovica, Banica, Robovo, Piperevo, Dobrejtci, Bansko and the town of Strumica (Fig.1). Samples are collected during May and June, 2013 according to the EPA guidelines (2007). Each sample has been collected from a single borehole. Latitude and longitude are determined using a Global Positioning System (Garmin Ltd., UK). Specific well information such as the depth of the well is obtained from the owner. Samples are collected after 10 minutes flushing, and transferred in to a sterile glass bottles. All samples are acidified with the addition of sulfuric acid (Fluka). No acidified fractions are used for measurements of anions such as Cl– and alkalinity. Samples are kept at 4°C until analysis.

Groundwater samples collected from the field are analyzed for the major cations (Mg^{2+}, Na^+, K^+, Ca^{2+}) and anions (HCO_3^-, CO_3^{2-}, SO_4^{2-}, PO_4^{3-} and Cl^-). Cl^-, CO_3^{2-} and HCO_3^- are analyzed by volumetric methods. SO_4^{2-}, NO_3^-, NO_2^- and NH_4^+ are determined by spectrophotometer JENWAY 6715 UV Vis. Mg^{2+}, Na^+, K^+, Ca^{2+} and P^{5+} are analyzed by inductively coupled plasma-mass spectrometry (ICP-MS), (Agilent 7500 CX). $PO_4^{3-}$is calculate from P^{5+}. pH is measured by pH meter HANNA HI 2211-01 and conductivity by conductometer JENWAY 4520. Hydrochemical variables are used to characterize the chemical evolution of the groundwater and identify the possible controlling factor. Ion exchange between groundwater and its host environment is performed from the chloro -alkaline indices (CAI) suggested by Schoeller (1977). The origin of chloride ion in the groundwater is determined compared with the relationship to the total cations. R square graphical analysis between mol ratio of chloride and cations is used to detect the dissolution of chloride salt. Statistical analysis are performed using the program Statistica, version 10 (StatSoft. 2011). Descriptive statistics analysis is used to perform analysis of data, including maximum and minimums, means and medians. Factor analysis is are used to detect the general relationship between variables and to find the main process that control a spatial variation of groundwater quality (Wang 2013; Ujevic et al., 2012). Important indicators like: permeability index (PI), residual sodium carbonate (RSC), sodium adsorption ratio (SAR), percentage of sodium (Na%) and magnesium ratio (MR) are used for the investigation of groundwater quality for irrigation purposes (Aastri 1994; Subramani et al., 2005; Eaton 1950).

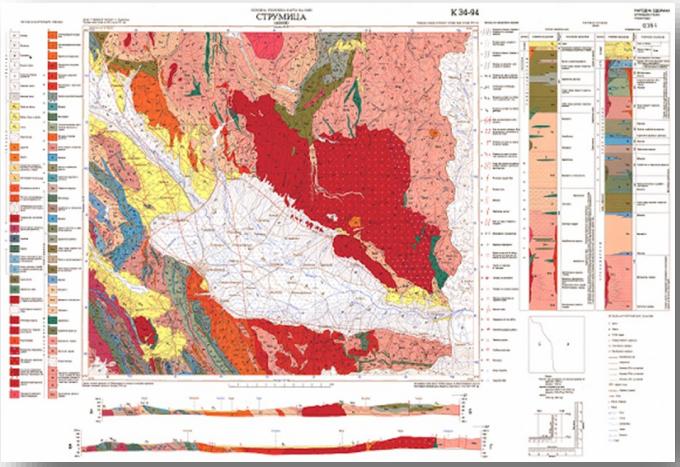

Fig. 1 The region of Strumica.

Results and disscution

Considering the fact that almost entire study area is vulnerable regarding the presence of the septic tanks, fertilizer application and plant debris, it is surprisingly that groundwater nitrate pollution was detected in villages suited at the periphery of the valley. The most affected were villages are Ilovica, Kulklish and Banica (mean values 125,46 mg/l , 266,42 mg/l, 83,94 mg/l, respectively). The geological composition of land in this part of the valley is presented with the prolluvial type of land with high porosity, very slim upper organic layer and shallow aqufers which decrease the time of possible interactions. The permeability index (PI) (Raju et al.,2009) shows that only 4,6% of all investigated samples located in the village of Kulkish and Monospitovoof belong to class III not suitable for irrigation.. The majority of samples (54%)belong in the class II and the rest 41,4% belong in class I suitable for irrigation.

Residual sodium carbonate (RSC) (Eaton F.M., 1950) and Sodium Adsorption ratio (SAR) (Karanth, 1987) revealed that all samples belong to the excellent category with good quality for irrigation purposes. Percentage of sodium (Na%) (Willox, 1955) 70% of samples belong to the excellent category, 23% in good category and the rest 7% are classified in permissible. Magnesium ratio (MR) (Paliwal, 1972) showed that 7% are unsuitable for irrigation mostly located in the village of Dobrejci.

Tab .1 Descriptive statistical analysis of results

	Mean	Geometric (Mean)	Median	Min	Max	Percentile (10,00)	Percentile (90,00)	Std.Dev.	Coef.Var
Depth (m)	40,32	28,45	21,00	4,50	130,00	13,00	95,00	34,59	85,80
pH	7,79	7,78	7,73	6,84	8,67	7,18	8,43	0,47	6,02
ECw (µS/cm)	4,79	4,25	4,65	0,79	17,49	2,36	7,39	2,42	50,61
Mg^{2+} (mg/l)	13,20	9,43	9,41	1,07	96,14	3,54	29,94	12,44	94,25
Na^+ (mg/l)	7,03	5,92	5,99	1,40	36,71	2,71	11,22	4,87	69,25
K^+ (mg/l)	11,75	6,02	5,44	0,50	354,44	2,36	16,45	34,32	292,17
Ca^{2+} (mg/l)	49,60	40,72	38,86	7,43	411,18	20,04	95,42	38,29	77,18
$CaCO_3$ (mg/l)	220,01	132,85	201,95	0,03	915,07	79,97	372,30	134,75	61,25
HCO_3^- (mg/l)	272,52	162,79	268,30	0,04	1116,38	91,47	456,99	165,39	60,69
Cl^- (mg/l)	38,55	25,27	24,39	4,19	614,31	8,74	73,31	53,50	138,79
NO_3^- (mg/l)	22,29	4,54	2,86	0,14	284,44	0,61	65,73	44,63	200,19
NH_4^+ (mg/l)	1,00	0,12	0,09	0,03	55,89	0,03	1,93	4,71	469,09
NO_2^- (mg/l)	0,58	0,04	0,03	0,01	35,85	0,03	0,04	3,22	559,94
SO_4^{2-} (mg/l)	24,07	12,04	16,97	0,50	300,45	2,50	48,73	35,94	149,28
PO_4^{3-} (mg/l)	0,52	0,20	0,18	0,00	7,80	0,04	1,07	1,06	202,88

Tab. 2 Percent contribution of each factor

	F 1	F 2	F 3	F 4	F 5	Comm.
d	-0,37	-0,02	0,07	**-0,76**	0,00	0,39
pH	-0,11	**0,83**	-0,21	0,01	-0,01	0,57
ECw	0,36	**0,59**	0,19	0,16	0,43	0,61
Mg	**0,76**	0,25	0,06	0,24	-0,10	0,80
Na	0,09	0,14	**-0,34**	**-0,45**	**0,56**	0,28
K	0,12	0,14	0,00	0,18	**0,76**	0,57
Ca	**0,87**	0,21	0,01	-0,01	0,08	0,92
HCO3	0,32	**0,86**	0,26	0,04	0,03	0,88
Cl	**0,89**	-0,01	-0,04	0,08	0,08	0,89
NO3	0,44	-0,35	0,13	0,02	**0,47**	0,58
NH4+	-0,03	0,13	**0,85**	-0,06	-0,01	0,33
NO2	0,07	-0,13	0,06	**-0,74**	-0,13	0,17
SO4	**0,67**	-0,01	-0,22	0,05	0,28	0,65
PO4	-0,23	-0,25	0,42	-0,12	**0,48**	0,23
Eigenvalue	3,92	1,86	1,58	1,25	1,12	9,73
Total variance %	27,98	13,26	11,26	8,90	7,98	69,38

Conclusion

The groundwater quality in the Strumica region has been evaluated for their chemical composition and suitability for agriculture uses. Agriculture producers heavily depend on groundwater as an irrigation source because of its low economical consumption and the suitable location of the borehole which is usually very close to the area of irrigation.

Chemical analysis shows that 35% of the groundwater in the region of Strumica belongs in very hard category, 25% in hard category, 28% in moderately hard category. Only 12% are soft waters. Waters are generally neutral to slightly alkaline. The aboundance of the major ions is in the following order $Mg^{2+}>Ca^{2+}>K^+>Na^+$ and $HCO_3^->Cl^->SO_4^{2-}$. Hydrochemical analysis show that chloride salt dissolution is the major source of the cations and chloride in groundwater. More than half of the samples are effected by the ion exchange Na^+ and K^+ from the groundwater with Mg^{2+} and Ca^{2+} from the rock formation in the area. According to the classification of water based on SAR, RSC and %Na the majority of samples are suitable for irrigation. Regarding PI and MR only 23 of investigated 216 samples are not suitable for irrigation located mostly in the villages Kuklish and Dobrejtci.

Although the study area have more than forty years tradition in agriculture production it was not found severe contamination from fertilizers except in the villages located in the periphery of the valley associated with the porosity of prolluvial type of land and relatively thin surface layer of the soil which decrease the time of exposure of the sorption processes of the pollutants especially the nitrates from fertilizers. The regions located in the valley where the alluvial type of land is present nitrate pollution is not detected. We assumed that geological composition in the valley has a major role in preventing of fertilizers leaching from agriculture land.

References

1.Aastri J.C.V. 1994. Groundwater chemical quality in river basins, hydrogeochemical facies and hydrogeochemical modeling. Bharathidasan University, Thiruchirapalli, Tamil Nadu, India.
2. Eaton F.M. 1950. Significance of carbonate in irrigation water. Soil Science. 69(2):123-133.
3. EEA (1999). Groundwater quality and quantity in Europe. Authors: A. Scheidleder, J. Grath, G. Winkler, U. Stärk, C. Koreimann and C. Gmeiner, Austrian Working Group on Water S. Nixon and J. Casillas, Water Research Centre; P. Gravesen, Geological Survey of Denmark and Greenland; J. Leonard, International Office for Water; M. Elvira, Centro de Estudios y Experimentación de Obras Públicas Final editing: S. Nixon ETC-IW Leader: T. J. Lack This report was prepared under the supervision of Niels Thyssen, Project manager, European Environment Agency. Copenhagen, 1999.
4. FAO. 1993a. An overview of pollution of water by agriculture. J.A. Sagardoy. In: Prevention of Water Pollution by Agriculture and Related Activities, Proceedings of the FAO Expert Consultation, Santiago, Chile, 20-23 Oct. 1992. Water Report 1. FAO, Rome. pp. 19-26.
5. Ignazi, J.C. 1993. Improving nitrogen management in irrigated, intensely cultivated areas: the approach in France. In: Prevention of Water Pollution by Agriculture and Related Activities. Proceedings of the FAO Expert Consultation, Santiago, Chile, 20-23 Oct. 1992. Water Report 1. FAO, Rome. pp 247-261.
6. Karanth K.R. 1987. Groundwater assessment, development and management. Tata McGraw Hill, New Delhi, 720.
7. Raju, N.J., Ram, P. and Dey, S. 2009. Groundwater quality in the lower lishing. Publishing Co., Calcutta, 160.
8. Shoeller H. 1977. Geochemistry of groundwater. In: Groundwater studies-An International guide for Reseaerh and Practice. UNESCO, Paris, 1-18.
9. Subramani T., Elango L., Damodarasamy S.R. 2005. Groundwater quality and its suitability for drinking and agricultural use in Chithar River Basin, Tamil Nadu, India. Environmental Geology, 47: 1099-1110.
10. Ujevic B. M. Capak K., Jazbec A., et al., 2012. Hydrochemical Characterization of Arsenic Contaminated Alluvial Aquifers in Eastern Croatia Using Multivariate Statistical techniques and Arsenic risk Assessment. Science of the total Environment 420: 100-110.
11. Wilox L.W. 1955. Classification and use of Irrigation Waters. U.S. Dept. of Agriculture, Circular No. 696. Washington D.C., 19.
12. Wang Y., Wang P., BaiY. et al. 2013. Assessment of Surface water quality via Multivariate statistical Techniques: A case study of the Songhua River Harbin Region, China. Journal of Hydro-Environmental Research 7(1):30-40.