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Groundwater quality as a source for irrigation in Strumica valley, Republic of Macedonia

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Abstract. *The quality of groundwater was investigated for possible agriculture pollution in the traditional agriculture region of Strumica, situated in the southeast part of the Republic of Macedonia. Almost 200 samples of water from boreholes in 14 different points were collected and analyzed by relevant standard methods for a total content of* Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+, Cl^-, HCO_3^-, SO_4^{2-}, NO_3^-, NO_2^-, *and* PO_4^{3-}. *The results showed that groundwater in the studied area is generally neutral to slightly alkaline. The abundance of the major ions is* $Mg^{2+}>Ca^{2+}>K^+>Na^+$ *and* $HCO_3^->Cl^->PO_4^{3-}>SO_4^{2-}$. *Concentration range of the main cations* Na^+, K^+, Ca^{2+} Mg^{2+} *and* NH_4^+ *is 1.40 – 36.71mg/L, 0.68 – 354.44 mg/L, 7.43 – 411.18 mg/L, 1.07 – 96.14 mg/L and < LOQ (limit of quantification) – 55.89 mg/L, 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, 0.04 – 750.97 mg/L, < LOQ – 300.45 mg/L 0.14 – 284.44 mg/L, < LOQ – 35.85 mg/L and < LOQ – 7.80 mg/L, respectively. A multivariate statistical analysis is performed to evaluate the possible interrelationship within a 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 14 variables and account for 71.54 % of the total variance. Although nitrates are considered a significant source of widespread groundwater contamination, when it comes to agricultural areas the result didn't show any severe contamination except in the periphery of the valley which is considered to be related to the thickness of the basal lithozone represented by sandstones and the shallow aquifers.*

Keywords: irrigation quality parameters, hydrochemical analysis, multivariate statistical analysis, agricultural pollution.

Introduction

Groundwater is a significant water supply in many developed and rural area. It often occurs in association with geological formations thus containing higher concentrations of dissolved salts compared to surface waters. Naturally groundwater contains dissolved solids in concentrations ranging from few mg/l to several hundred mg/l. Major dissolved components of groundwater include the anions bicarbonate, chloride and sulphate and the cations sodium, calcium, magnesium and potassium (Karanth, 1987). The type and concentrations of major ions depend on the geological composition of the unsaturated zone and the aquifer. The concentrations of these major ions in the groundwater may increase due to the impact of the anthropogenic factor and make it unsuitable for domestic or agriculture use. The most recognized pollutants are industry, agriculture and sewages. The pollution of groundwater is recognized as one of the most serious environmental problems in many areas, worldwide. Since the 1980s the concern over groundwater agricultural pollutants in Europe has been growing. Agriculture has been cited as a leading non-point source of groundwater pollution in many areas of the world (FAO, 1996; Ignazi, 1993; EEA, 2012). The European Community responded with the groundwater Europe legislation focused on controlling groundwater pollution from industrial and urban sources – Directive 80/68/EEC (EC, 1979) and the Directive 91/676/EEC (EC, 1991) regarding protection of waters against pollution by nitrates from agricultural sources. In accordance with Directive 2000/60/EC (EC, 2000), the EU member states are obliged to prevent and control the pollution of the groundwater and to established criteria for assessing its good chemical status.

The most important agricultural pollutant of groundwater is nitrate. High concentration of nitrate in drinking water is a possible health threat. Its concentrations in groundwater can reach high levels of leaching or runoff from agricultural land or contamination from human and animal wastes as a consequence of the oxidation of ammonia (US EPA, 1994). Nitrate pollution in groundwater has been announced in many agriculture developed areas of Europe such as Austria, the Czech Republic, France, Germany, Romania and the Slovak Republic (EEA, 1999). Slovenia published that in almost 25% of sampled wells, concentrations of nitrates in groundwater exceeded 25 mg/L. In Moldova this value exceeded MCL of 50 mg/L. In Northern Europe (Iceland, Finland, Norway and Sweden) nitrate concentrations in groundwater are relatively low (EEA, 2012). In Bulgaria, in a region with high anthropogenic impact from industry and agriculture Georgieva et al. (2011) established in groundwater from drilled wells levels of NO_3^- up to 140 mg/l, NO_2^- up to 0.352 mg/l and NH_4^+ up to 0.260 mg/l. The results of PCA for NO_3^-, NO_2^- and NH_4^+ showed that two rotated principal components (varifactors), with eigenvalues higher than 1, were extracted (they described about 70.3% of the overall variance). The correlation matrices revealed positive mutual relationships between NO_3^- and NO_2^-, and between NO_2^- and NH_4^+ contents. In the same region Kostadinova (2014) has investigated the presence of nitrates during a period of one year and found out that the concentrations are higher in the low underground water period, from October till December with maximum concentration of 94.6 mg/L. No data is available for the nitrate concentrations in groundwater in the Republic of Macedonia until now.

The aim of this study was to investigate the quality of groundwater for the possible non pointed pollution in the region of Strumica and determine the agricultural pollution impact relative to the other types of pollutants using a multivariate statistics analysis. The investigated region is a vulnerable zone because of the 50 years of traditional vegetable production, thus it is important to have an

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insight into the possible threat of groundwater in this area from the agricultural pollutants. This is a first study about the quality of groundwater in the region of Strumica.

Materials and methods

Area of investigation

Strumica and its municipality are located in the southeast end of the Republic of Macedonia, below the borders with Greece and Bulgaria at 22°35' North latitude, 23°45' East longitude and 256 m altitude with the average rainfalls of 70.50 mm. The municipality has a total area of 963 km^2 and about 95000 inhabitants. Alluvial soil type and the Mediterranean climate are the main reasons for becoming the most important region for early vegetable production in the country in the last 50 years. Since the 1980s the main source for irrigation are groundwater aquifers which agricultural producers explore mostly through the boreholes. Agriculture and food industry are the main activities in the region and possible source of groundwater pollution. Wastewater from the industry, agriculture and sewage goes into the canals which seep into the Struma river, passing through the villages of Dobrejtsi, Piperovo, Prosenikovo, Dabilje, Robovo, Bosilovo and Ednokukjevo. Although geologically unexplored, it is considered that the region is rich in gold, radioactive substances and quartz as well as non-metallic minerals such as feldspars and calcium carbonate (Rakicevic et al., 1973).

Sampling

Groundwater samples are collected from boreholes in 14 different areas in the Strumica region, Republic of Macedonia. The investigated area includes the villages of Borievo, Kuklish, Monospitovo, Prosenikovo, Dabile, Sachevo, Ednokukjevo, Ilovica, Banica, Robovo, Piperevo, Dobrejtci, Bansko and the town of Strumica (Figure 1). Samples were collected in May and June, 2013. Each sample was 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 were collected after 10 minutes' flushing, transferred into a sterile dark glass bottles and transported in a refrigerated bag to the laboratory. Samples were acidified with the addition of sulfuric acid (Fluka). No acidified fractions were used for measurements of anions such as Cl^-, SO_4^{2-} and alkalinity. Samples were kept at 4°C and analyzed in the maximum period of three days (Johnston, 2007).

Analysis

Groundwater samples collected from the field are analyzed for the quantity of major cations (Mg^{2+}, Na^+, K^+, Ca^{2+} and NH_4^+) and anions (HCO_3^-, CO_3^{2-}, SO_4^{2-}, PO_4^{3-} and Cl^-). Anions like Cl^-, CO_3^{2-} and HCO_3^- are analyzed by volumetric methods. Sulphates (SO_4^{2-}), nitrates (NO_3^-), nitrites (NO_2^-) and ammonia (NH_4^+) are determined by colorimetric method using spectrophotometer type JENWAY 6715, UV Vis (EPA 375.4; EPA 352.1; EPA 354.1; EPA 350.2). Magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), calcium (Ca^{2+}) and phosphorus (P^{5+}) are analyzed by inductively coupled plasma-mass spectrometry (ICP-MS), (Agilent 7500 CX). pH is measured by pH meter HANNA HI 2211-01. Electrical conductivity is measured with 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 other cations and anions. R square graphical analysis between mol ratio of chloride and cations is used to detect the dissolution of chloride salt. Statistical analysis is performed using the program Statistica, version 10. Descriptive statistics analysis is used to perform analysis of data, including maximum and minimums, means and medians, percentiles, variance and standard deviation. Factor analysis is used to detect the general relationship between variables and to find the main process that controls the pollution of groundwater quality (Wang, 2013; Ujevic et al., 2012). Important indicators like: permeability index (PI) (Doneen, 1964), residual sodium carbonate (RSC) (Eaton, 1950), sodium adsorption ratio (SAR) (Karanth, 1987), percentage of sodium (Na%) (Willox, 1955) and magnesium ratio (MR) (Paliwal, 1972) are used for the investigation and assessment of groundwater quality for irrigation purposes.

Results and discussion

A total number of 216 groundwater samples have been analyzed for their physicochemical parameters. The summary of descriptive statistical analysis is given in Table 1. The majority of the investigated boreholes, around 69.5% are shallow (0 – 50 m), while 26.8% are with depth between 51 – 100 m. Other 3.7% have more than 100 m depth and are located mostly in the village of Borievo. Waters are generally neutral to slightly alkaline. Considerable spatial variation is observed for the distribution of major cations with the dominance of $Mg^{2+}>Ca^{2+}>K^+>Na^+$ and anions with the dominance of $HCO_3^->Cl^->PO_4^{3-}>SO_4^{2-}$. Bicarbonate is the major anion in the groundwater of the study area and responsible for the slight alkalinity of the water. According to Sawyer and Mc Cartly (1967), around 32% of groundwater samples belong to a very hard category, 25% to hard category, 28% belong to moderately hard category and the remaining samples fall in the soft category. The research shows that 34.45% of the investigated samples exceeded the national MCL for drinking water quality of 10 mg/L for nitrate. Considering the fact that almost the entire study area is vulnerable regarding the presence of septic tanks, fertilizer application and plant debris, it is surprising that nitrate pollution is not spatially present in the study area. The most affected are the villages Ilovica, Kulklish, Banica and Bansko situated at the periphery of the valley. It is assumed that higher nitrate concentration in groundwater at the periphery of the valley is associated with the thickness of the basal lithozone represented by sandstones, which ranges from 20 – 50 m depth (Figure 1) (Rakicevic et al., 1973). Boreholes in these villages are shallow with the median of 12 m.

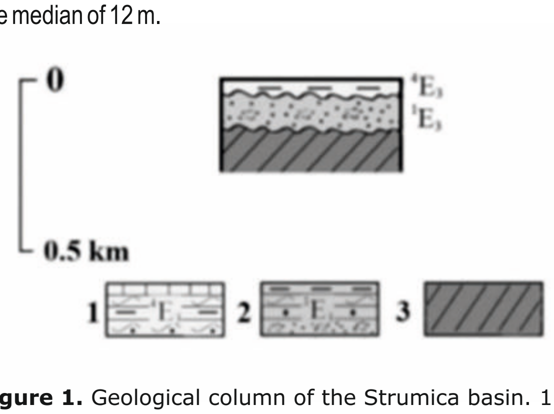

Figure 1. Geological column of the Strumica basin. 1 – basal lithozone, 2 – upper flysch lithozone, 3 – paleorelief

Table 1. Descriptive analysis of groundwater quality data in the study area

Parameters	Median	Mode	Minimum	Maximum	Std.Dev.	Coef.Var.	Percentile 10	Percentile 90
d (m)	21	18.00	4.5	130	34.31	85.36	13	94.5
pH	7.81	8.20	6.84	8.67	0.44	5.61	7.27	8.43
ECw	4.72	6.26	1.22	17.49	2.42	50.38	2.26	7.35
HCO_3^- (dS/m)	257.53	Multiple	0.04	750.97	156.19	58.22	91.47	454.2
Cl^- (mg/L)	24.76	11.09	4.19	614.31	54.20	139.93	8.74	73.31
NO_3^- (mg/L)	2.98	.69	0.14	284.44	44.29	196.47	0.61	65.73
NO_2^- (mg/L)	0.03	.025	< LOQ	35.85	3.85	565.55	0.025	0.025
Nh_4^+ (mg/L)	0.08	.025	< LOQ	55.89	4.84	459.59	0.025	1.96
SO_4^{2-} (mg/L)	17.69	2.50	< LOQ	300.45	36.57	149.78	2.5	48.73
Na^+ (mg/L)	6.03	Multiple	1.4	36.71	4.97	69.95	2.69	11.28
PO_4^{3-} (mg/L)	0.18	.025	< LOQ	7.8	1.07	204.45	0.025	1.07
K^+ (mg/L)	5.43	Multiple	0.68	354.44	35.05	298.18	2.35	16.45
Ca^+ (mg/L)	39.51	28.50	7.43	411.18	38.98	77.75	19.99	95.42
Mg^+(mg/L)	9.72	Multiple	1.07	96.14	12.69	94.87	3.45	29.94

Once the nitrate is found in anaerobic conditions it may degrade to much more toxic nitrite. According to WHO (2011) nitrite concentration in drinking water should not exceed the value of 3.3 mg/L. The Macedonian standard is stricter as permitted content of nitrate in drinking water is up to 0.01 mg/L (Government of the RM, 1999). In this study NO_2^- was found in detectable concentrations only in the villages of Monospitovo and Borievo in 24% and 15.4% of all samples collected, respectively. Considering the fact that canning industry is also developed in the region, we investigate the NO_3^-/NO_2^- and Na^+/NO_2^- mol ratio of the samples collected from the village of Monospitovo and Borievo in order to find out if NO_2^- originates from sodium nitrite, high water soluble substance used as a food preservative. Samples from the village of Monospitovo show different NO_3^-/NO_2^- mol ratio from the samples collected in the village of Borievo indicating that nitrite is associated with different sources of pollution. Samples from the village of Monospitovo show a molar ratio of NO_3/NO_2 in the range from 1.3 – 1.34 very close to the mol ratio of 1:1 in the reaction of nitrate degradation which means that the origin of nitrite is related to the nitrogen cycle in anaerobic conditions. The molar ratio of Na^+/NO_2^- of the samples collected from the village of Borievo show values between 0.41 and 0.56, very close to the mass ratio of sodium nitrite (0.50). Considering the fact that food canning industry is located near this village, it is assumed that the pollution of nitrite in these samples comes from the canning industry. The presence of deep boreholes in this village contributes to the formation of anaerobic conditions which results in reduced oxidation processes.

Ammonia was found under the instrument detection limit in 65.3% of the samples. Natural levels of ammonia in groundwater are usually below 0.2 mg/L. Anaerobic groundwater may contains up to 3 mg/L (Walton et al., 2012). It is considered that ammonia in water is an indicator for possible bacterial, sewage and animal waste pollution. No significant contamination of ammonia was found in the investigated period which means that ammonia couldn't contribute to the increase of nitrate concentration as a result of oxidation. The concentration of chloride in groundwater can be a useful indicator for the anthropogenic contamination. Usually concentration below 100 mg/L is considered normal for groundwater (Walton et al. 2012). Investigation for chloride pollution in the study area shows that only 3.4% of the investigated samples had concentration greater than 100 mg/L, 21.2% had concentration between 50 – 100 mg/L and the majority of the samples (75.4%) had concentration lower than 50 mg/L. The most affected where the villages of Borievo, Prosenikovo and the samples from the town of Strumica. Chloride may reach groundwater in agriculture land leaching from fertilizers usually in the form of KCl. But it can also have a natural origin dissolved in water from halit minerals such as NaCl or other less common salts such as MgCl and $CaCl_2$. The Cl/HCO_3 mol ratio ranges from 0.03 to 1 suggesting that the aquifers are not saline and there is no introduction of saline water in the investigated aquifers. The plot of Ca^{2+} against Cl_2 concentration suggests that most of the samples have input of Cl^- from $CaCl_2$ (Figure 3).

Gypsum ($CaSO_4.2H_2O$) or its anhydrite are used as inorganic fertilizers and source of sulphate and calcium to improve soil quality. The investigation shows that sulphate in the study area is present in very low concentrations. Around 35% of investigated samples have concentration of sulphate below the limit of instrument detection. Only seven samples exceed the value of 100 mg/L and one sample exceeds the value of 250 mg/L. The Ca^{2+}/SO_4^{2-} mol ratio of this sample is very close to the unity suggesting a common source of these ions. Since the depth of the borehole is 5.5 m and the location of the borehole is in the field it is assumed that the pollution originates from the fertilizer usage.

The molar ratio of Ca^{2+} versus Mg^{2+} ranges between 0.18 and 30.31 indicating the excess of Ca^{2+} over Mg^{2+} in 95% of the samples. CAI is performed to access the ion exchange between the groundwater during its travel in the sub-surface according to Schoeller (1977). In this study 56.7% of the samples have positive values for both equations which means that in these groundwater aquifers there is an ion exchange between Na^+ and K^+ from the groundwater with Mg^{2+} and Ca^{2+} from the rock formation in the area. Other 43.3% have negative values for both indices and therefore a reverse exchange is present in the investigated period in these samples. The presence of phosphate ion is not a cause for concern because most of the samples have concentration lower than 1 μg/L (Table 1).

Factor analysis

Factor analysis revealed five factors (Table 2). The first factor

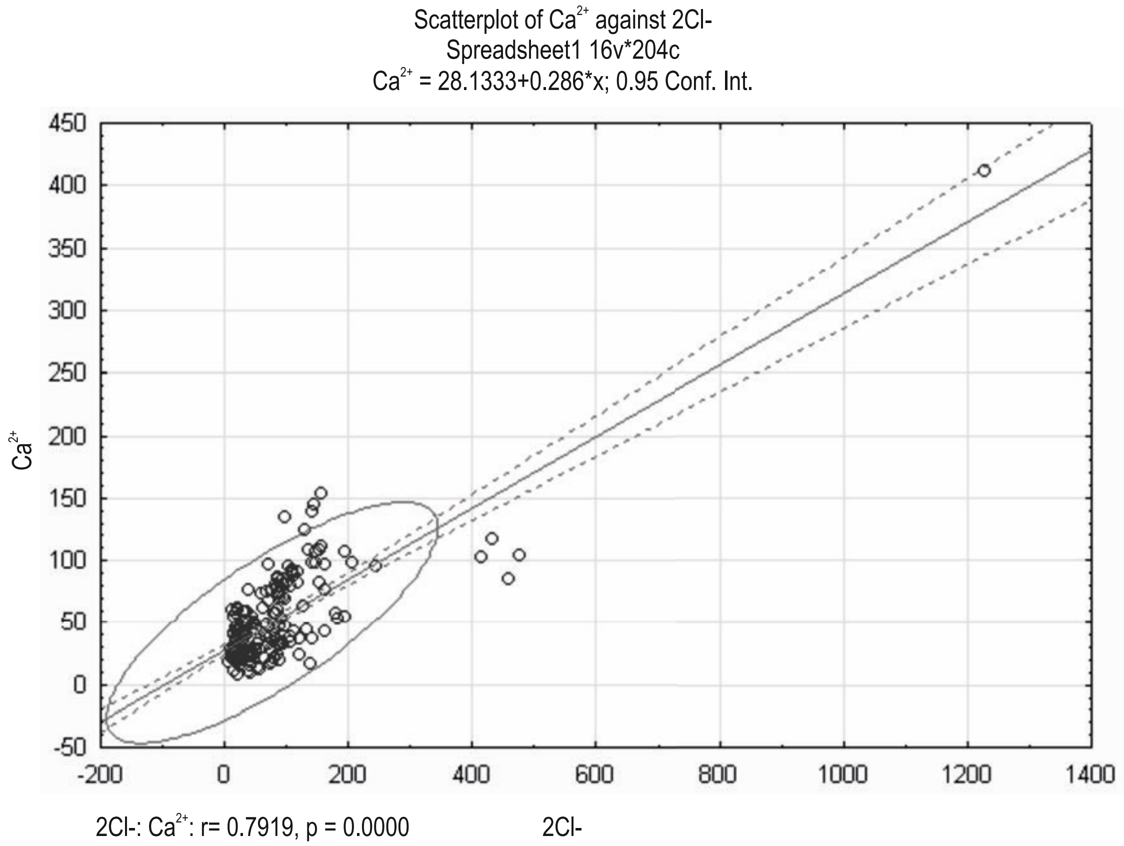

Figure 2. R square graphical analysis between mol ratio of chloride and calcium

(F1) shows significant relationship between chloride, sulphate, calcium and magnesium indicating that the presence of these ions in the investigated samples originates from the geological composition of the rock formations. The second factor (F2) shows the relationship between nitrates, sodium, phosphate and potassium. This factor indicates the role of fertilizers in groundwater pollution. The third factor (F3) is for the dissociation of carbonates and their influence to the acidity and hardness of the groundwater. Factor four (F4) shows significant relationship between nitrite and depth of the borehole with factor loadings of 0.73 and 0.73, respectively. But the loading of nathrium (0.54) should not be underestimated in this factor. Therefore, this factor is related to the causes of groundwater pollution with nitrite in the same way as anaerobic conditions are related to the depth of the borehole and the canning industry.

Irrigation water quality

Permeability index (PI). Calculated values for PI range from 4.33% to 152.25%. The result shows that only 4.6% of all investigated samples belong to class III (< 25%) which according to Raju et al. (2009) are not suitable for irrigation. All of these samples are located in the village of Kulkish except two which are located in the village of Monospitovo. Around 54% of the samples belong to class II (27% – 75%) and the rest 41.4% belong to class I (>75%) which indicates that they are suitable for irrigation.

Residual sodium carbonate (RSC). RSC values for all investigated samples do not exceed MCL of 1.25 meq/L, which means that there is no hazardous effect of carbonate and bicarbonate from the irrigation water in the investigated samples.

Sodium Adsorption ratio (SAR). This indicator characterizes the relationship between infiltration capacity of the soil and water salinity. Infiltration rates increase as water salinity increases (Ayers and Westcot, 1985). In the investigated samples SAR ranged between 0.023 and 1.34. According to Richards (1954) all samples belong to the excellent category and there is no negative sodicity effect from the investigated water samples in this period.

Table 2. Factor analysis: Percent contribution of each factor

Parameters	F1	F2	F3	F4	F5	Comm.
d	-0.38	-0.09	-0.1	0.73	0.13	0.38
pH	-0.16	-0.13	0.77	-0.17	-0.26	0.54
ECw	0.4	0.41	0.63	-0.11	0.22	0.74
HCO_3^-	0.33	0.07	0.84	0.01	0.27	0.89
Cl^-	0.9	0.07	0.00	-0.04	-0.06	0.89
NO_3^-	0.42	0.55	-0.34	0.00	0.02	0.58
NO_2^-	0.03	-0.05	-0.2	0.73	-0.01	0.2
NH_4^+	-0.03	-0.01	0.1	0.02	0.93	0.34
SO_4^{2-}	0.74	0.18	0.03	-0.12	-0.08	0.73
Na^+	0.13	0.47	0.25	0.54	-0.18	0.28
PO_4^{3-}	-0.22	0.57	-0.33	0.07	0.36	0.29
K^+	0.12	0.79	0.2	-0.08	-0.08	0.63
Ca^{2+}	0.87	0.07	0.2	0.04	0.02	0.93
Mg^{2+}	0.76	-0.07	0.24	-0.18	0.02	0.81
Eigenvalue	4.11	1.98	1.6	1.2	1.12	10.01
Total variance	29.39	14.13	11.43	8.55	8.04	71.54

Percentage of sodium (Na%). Another indicator for the sodium hazard in irrigation water is the percentage of sodium. High concentration of sodium in irrigation water results in poor internal draining of soil. The computed %Na for the study area ranged from 2.23% to 67.3%. Around 70% of the samples belong to the excellent category (<20%), 23% to the good category (20 –40%) and the rest 7% are classified as permissible.

Magnesium ratio (MR). The effect of Mg^{2+} in irrigated water is expressed by the magnesium ratio. The computed MR values in the study area range from 3.2 % to 85.74%. Around 7% are unsuitable for irrigation mostly located in the village of Dobrejci.

Conclusion

The groundwater quality in the Strumica region has been evaluated for its chemical composition and suitability for agriculture uses. Agriculture producers in this region 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 to the very hard category, 25% to the hard category, 28% to the moderately hard category. Only 12% are soft waters. Waters are generally neutral to slightly alkaline. The abundance of the major ions is in the following order Mg^{2+} >Ca^{2+}> K^{+}>Na^{+} and HCO_3^{-}>Cl^{-}>SO_4^{2-}. Hydrochemical analysis shows that chloride salt dissolution is the major source of the cations and chloride in groundwater. More than half of the samples are affected 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 all samples are suitable for irrigation. Regarding PI and MR only 23 of the investigated 216 samples are not suitable for irrigation located mostly in the villages of Kuklish and Dobrejtci.

Although the study area has more than forty years' tradition in agriculture production, severe contamination from fertilizers has not been found except in the villages located in the periphery of the valley associated with the thickness of the basal lithozone represented by sandstones. The conducted analysis indicates that the geological composition of the area has a major role in preventing the leaching of fertilizers from the agriculture land.

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Instruction for authors

Preparation of papers

Papers shall be submitted at the editorial office typed on standard typing pages (A4, 30 lines per page, 62 characters per line). The editors recommend up to 15 pages for full research paper (including abstract references, tables, figures and other appendices)

The manuscript should be structured as follows: Title, Names of authors and affiliation address, Abstract, List of keywords, Introduction, Material and methods,Results, Discussion, Conclusion, Acknowledgements (if any), References, Tables, Figures.

The title needs to be as concise and informative about the nature of research. It should be written with small letter /bold, 14/ without any abbreviations.

Names and affiliation of authors The names of the authors should be presented from the initials of first names followed by the family names. The complete address and name of the institution should be stated next. The affiliation of authors are designated by different signs. For the author who is going to be corresponding by the editorial board and readers, an E-mail address and telephone number should be presented as footnote on the first page. Corresponding author is indicated with *.

Abstract should be not more than 350 words. It should be clearly stated what new findings have been made in the course of research. Abbreviations and references to authors are inadmissible in the summary. It should be understandable without having read the paper and should be in one paragraph.

Keywords: Up to maximum of 5 keywords should be selected not repeating the title but giving the essence of study.

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Material and methods: The objects of research, organization of experiments, chemical analyses, statistical and other methods and conditions applied for the experiments should be described in detail. A criterion of sufficient information is to be possible for others to repeat the experiment in order to verify results.

Results are presented in understandable tables and figures, accompanied by the statistical parameters needed for the evaluation. Data from tables and figures should not be repeated in the text.

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Discussion: The objective of this section is to indicate the scientific significance of the study. By comparing the results and conclusions of other scientists the contribution of the study for expanding or modifying existing knowledge is pointed out clearly and convincingly to the reader.

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