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GEOCHEMICAL ASSESSMENT OF SOME NATURAL WATERS FROM EASTERN AND SOUTH-EASTERN MACEDONIA

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Abstract: The paper deals with short review and determination of macro-, micro-, trace and ultratrace elements in some natural waters from eastern and couth-eastern Macedonia. In our study were investigated 16 samples of natural waters from the villages Trabotivište near the city of Delčevo, Istibanja near Kočani, Neokazi near Probištip, Plačkovica, Karaorman, Gorni Balvan and Lakavica near Štip, Jargulica near Radoviš, Murtino, Robovo, Gabrovo and Smolare near Strumica. Obtained results showed that most of the analyzed elements in all selected water samples were below the Macedonian maximum allowable levels and WHO water standards. Increased concentrations of some elements indicate anthropogenic pollution of the water from the fertilization of arable land, livestock farms. There is a strong positive correlation between Ca → SO_4, Na, Mg; Ti → Ca, Mg, Na, K, B; U → Mo, Rb, Cs, As; B → Ca, Ti, Ge, Cl, HCO_3; Li → Mg, Na, K, B, Sr, Rb; Ge → Ca, Mg, Na, B, Ti, Li, Cl, Pb; Cl → Mg, Na, K, B, Sr, Li, Pb; HCO_3 → Ca, Mg, Na, K, B, Ti, Sr, Li, Pb, Co, Se, Ge; NO_3 → Na, Sr, Li, Pb, Cs, Se; SO_4 → Na; TDS → EC. According to the obtained values for total hardness, investigated waters are hard, moderately hard and very hard. High values for total hardnes sare mainly due to solubility of carbonate rocks. Positive CAI values noted in Neokazi (samples 1 and 2), Jargulica (samples 1 and 2), Novo Selo, Murtino, Robovo, Gabrovo and Smolare suggest that sodium and potassium from water are exchanged with magnesium and calcium in rock following base exchange reactions (chloro-alkaline equilibrium), whereas negative CAI values noted at Trabotivište, Istibanja, Karaorman Plačkovica, Lakavica (samples 1 and 2) suggest that magnesium and calcium from water are exchanged with sodium and potassium in rocks favouring cation-anion exchange reactions (chloro-alkaline disequilibrium). After Piper diagram the type of water in the study area is mainly calcium/magnesium bicarbonate and are most likely result of the composition of the geological environment through which the water flows where this natural water circulates. Knowing the natural water quality of the research area is of particular importance because these waters are used by the residents of this region as drinking water and for irrigation.

Key words: natural water; trace elements; pH; TDS

INTRODUCTION

Water is important source of intake of trace elements in humans and an essential component for life. The chemical constituents of natural water are derived from water–rock interactions such as dissolution and mineral–water equilibria. Thus, the geochemistry of a natural water sample reflects a some times complex history of its flow path through various rock types under varying physiochemical conditions, temperature and pressure.

All waters contain both natural contaminants, particularly inorganic contaminants that arise from the geological formations through which the water flows and to a varying extent, anthropogenic pollution by microorganisms and chemicals. In natural waters, trace elements, especially metals, may be present in different physico-chemical forms varying in size, charge and density. Trace elements in natural water comprehensively covers the microchemical processes occurring in the water phase. Trace elements can be categorized into those essential to human life, such as Fe, Cu, Mn, Cr, Co, Mo, Se, Zn and those potentially toxic like Ag, As, Cd, Pb and Ni. Certain essential trace elements such as Cr, Fe, Co, Mn and Se can be toxic when concentrations are raised above specific levels.

Trace elements concentrations in the natural waters vary widely depending on the geochemistry of rocks in the immediate environment. Interactions of water with rocks and soils developed from them, dictate our intake of these elements. They are mostly associated with igneous and metamorphic rocks and in particular, with ore bodies (Edwards et al., 2000).

Trace elements needed in very minute quantities (Selinus, et al., 2005) may have biotoxic effects in human biochemistry and are of great concern.

Knowledge of rock types and mineralization in a particular area can help to find out potential health problem with concentration of particular elements and the type of trace elements contaminates varies with the mineralization of the area (Pyenson, 2002, Williamson and Rimstidt, 1994).

In our study were investigated samples of natural waters from the villages: Trabotivište near the city of Delčevo, Istibanja near Kočani, Neokazi near Probištip, Plačkovica, Karaorman, Gorni Balvan and Lakavica near Štip, Jargulica near Radoviš, Murtino, Robovo, Gabrovo and Smolare near Strumica. Localities where samples are taken are shown in Figure 1.

Fig. 1. Localities where samples are taken

RESULTS AND DISCUSSION

According to quantity, elements in natural waters are devided on:

– macro (majority) elements: >100 mg/kg (ppm) = 0.01% Na, K, Mg, Ca, Cl, P,

– micro (minority) elements: 10 – 100 mg/kg Fe, Zn,

– trace elements: < 10 mg/kg Al, As, B, Cd, Co, Cr, Cu, F, Hg, I, Mn, Mo, Ni, Pb, Se, Sn,

– ultratrace elements: <1 μg/kg (ppb).

There are several factors that control how much of a certain trace element will be present in natural waters: amount of the element in the rock through which the water flows; solubility of that element under the conditions that exist in the aquifer; flow rate of the water and hence the contact time between the water and the rock (Hem, J. D., 1989).

The presence of macro-, micro-, trace and ultra-trace elements in investigated water samples have been depicted in tables 1, 2, 3, 4, respectively.

Table 1

Concentration of Ca, Mg, Na, K, Fe, Mn, Al, B, Mo and Ti

	Ca	Mg	Na	K	Fe	Mn	Al	B	Mo	Ti
Trabotivište (Delčevo)	59	16.61	13.80	3.4	33.20	0.397	0.099	24	0.75	73
Istibanja (Kočani)	29	18.65	26.98	14.3	31.52	0.091	0.091	46	0.74	35
Neokazi – sample 1 (Probištip)	60	35.10	51.80	5.4	19.13	0.080	0.053	88	5.12	84
Neokazi – sample 2 (Probištip)	56	29.82	52.10	11.4	23.90	0.082	0.037	100	5.59	79
Gorni Balvan (Štip)	36	26.70	69.60	3.8	18.51	0.064	0.050	63	11.90	51
Plačkovica (Štip)	13	3.19	5.11	1.5	16.14	0.061	0.044	3	0.07	16
Karaorman (Štip)	26	102.60	114.50	19.6	28.55	0.079	0.448	173	0.83	39
Lakavica – sample 1 (Štip)	117	119.10	69.30	7.6	19.57	0.076	0.048	73	1.95	171
Lakavica – sample 2 (Štip)	124	106.80	104.30	5.4	21.99	0.115	0.197	385	0.64	181
Jargulica – sample 1 (Radoviš)	30	13.33	12.22	3.2	20.28	0.091	0.084	24	0.30	39
Jargulica – sample 2 (Radoviš)	35	14.84	17.02	4.0	23.24	0.085	0.088	55	0.34	47
Novo Selo (Strumica)	19	4.90	7.25	2.3	23.46	0.068	0.057	5	0.54	22
Murtino (Strumica)	21	8.98	10.00	1.6	26.44	0.719	0.051	43	0.68	24
Robovo (Strumica)	24	10.66	10.00	1.2	26.60	0.188	0.050	38	2.05	28
Gabrovo (Strumica)	25	3.65	6.73	1.7	25.69	0.087	0.149	2	11.66	29
Smolare (Strumica)	16	5.45	4.23	4.4	25.72	0.283	0.068	2	1.71	18

Table 2

Concentration of Sr, Ba, Rb, Li, Cs, Be, Zn, Pb, Cd, Cu and Ni

	Sr	Ba	Rb	Li	Cs	Be	Zn	Pb	Cd	Cu	Ni
Trabotivište (Delčevo)	234	0.19	0.99	3.4	0.077	0.002	34.21	0.117	0.032	3.72	1.23
Istibanja (Kočani)	262	9	1.18	6.6	0.046	0.004	8.12	0.240	0.010	2.55	0.61
Neokazi – sample 1 (Probištip)	2228	9	14.70	27.3	7.274	0.021	7.19	0.689	0.028	1.03	1.03
Neokazi – sample 2 (Probištip)	2758	34	15.75	31.0	12.31	0.009	6.59	0.529	0.018	1.16	1.04
Gorni Balvan (Štip)	311	6	0.83	21.6	0.042	0.016	5.18	0.398	0.023	1.14	0.62
Plačkovica (Štip)	63	6	0.29	2.4	0.059	0.008	49.39	0.074	0.011	0.58	1.42
Karaorman (Štip)	639	3	1.54	32.9	0.094	0.013	10.24	0.536	0.011	1.61	0.63
Lakavica – sample 1 (Štip)	814	30	0.85	9.4	0.052	0.023	18.03	0.579	0.012	1.11	2.26
Lakavica – sample 2 (Štip)	992	6	0.41	17.8	0.023	0.015	18.04	0.798	0.017	1.75	2.51
Jargulica – sample 1 (Radoviš)	660	5	0.11	1.5	0.074	0.009	3.46	0.246	0.009	1.37	0.62
Jargulica – sample 2 (Radoviš)	192	27	0.26	2.7	0.076	0.007	2.24	0.187	0.008	0.56	0.74
Novo Selo (Strumica)	60	3	0.19	5.2	0.072	0.003	24.41	0.075	0.011	1.27	0.51
Murtino (Strumica)	302	35	0.27	1.2	0.058	0.002	1.04	0.108	0.009	0.95	0.33
Robovo (Strumica)	356	36	0.18	1.8	0.049	0.003	2.42	0.178	0.015	0.83	0.34
Gabrovo (Strumica)	24	1	0.45	1.4	0.076	0.003	6.54	0.058	0.026	0.66	0.43
Smolare (Strumica)	48	2	0.18	2.6	0.073	0.005	10.60	0.047	0.025	1.37	1.24

Calcium and magnesium

The contents of Ca^{2+} and Mg^{2+} determine the hardness of the water, which is an important parameter for reducing the toxic effects of some of the elements. Concentration of calcium in studied waters is in range of 13–124 ppm.

Source of magnesium includes ferromagnesium minerals in igneous and metamorphic rocks and magnesium carbonate in limestone and dolomite. Magnesium salts are more soluble than calcium, but they are less abundant in geological formations. Concentration of magnesium in studied waters varies from 3.19 to 119.10 ppm.

Sodium

The major source of sodium in natural waters is from weathering of feldspars, evaporates, and clay. Sodium salts are very soluble and remain in solution. Concentration of sodium in studied waters varyies from 5.11 to 114.50 ppm. Typical sodium concentrations in natural waters range between 5 and 50 mg/l. The most common sources of elevated sodium levels in natural water are: erosion of salt deposits and sodium bearing rock minerals, naturally occurring brackish water of some aquifers, infiltration of surface water contaminated by road salt, irrigation and precipitation leaching through soils high in sodium, natural water pollution by sewage effluent, infiltration of leachate from landfills or industrial sites.

Potassium

Potassium is less abundant than sodium in natural waters. Its concentration rarely exceeds 10 mg/l in natural waters. The range of specific levels of sodium is minimum 1.2 ppm in Robovo to maximum 19.6 ppm in Karaorman. In all tested waters, the sodium content is lower than the WHO standard.

Iron

Iron in the ferric form is nearly insoluble in normal water, but in the ferrous form 10 ppm or more may be present. In natural waters, iron may be present as ferrous bicarbonate ($Fe(HCO_3)_2$), ferrous hydroxide, ferrous sulfate ($FeSO_4$), and organic (chelated) iron. Concentration of iron in studied waters varies from 16.14 to 33.20 ppb.

Manganese

Manganese is rarer in water than iron in range from 0.043 to 0.0868 ppb except in Novo Lagovo where the value of the Mn is equal to 5.623 ppb. Manganese may be brought into solution by activity of microorganisms.

Aluminium

Aluminum is nearly insoluble in water in the pH range from 5 to 9. Concentration of aluminium in studied waters varies from 0.037 to 0.197 ppb.

Boron

Concentrations of boron in natural water throughout the world range widely, from 0.3 to 100 mg/l. Boron is a component of some very stable minerals and in trace concentrations is widespread in soils and waters.

The main minerals of B are borax (sodium tetraborate, $Na_2B_4O_7{\cdot}10H_2O$) and kernite ($Na_2B_4O_7{\cdot}4H_2O$). Borax and kernite are fairly soluble in water: the solubility of those minerals in 20°C water reaches 25 g/kg (Крайнов et al., 2004).

$$Na_2B_4O_7 + 7H_2O = 4H_3BO_3 + 2NaOH.$$

It is known that in neutral water (pH 7) even 99% of boron is in the form of B-acid. In slightly alkaline water, certain anions of B acid happen. For example, at pH 8 water may contain 6% of H_2BO^{3-}.

The concentration of boron in natural water is regulated by two factors:

1) availability of this trace element in water-bearing rocks and soils;

2) geochemical conditions inside the aquifers.

WHO has recommended a limit of 0.3 mg/l^{-1} boron. In studied waters the concentration of boron is in range between 2 and 385 ppb. Strong positive correlation as between B and Ca, Ti, Ge, Cl, HCO_3 were determined.

Lithium

Lithium is probably common in amounts less than 1 ppm in water. The lithium Li^{+1} ion oxidation state is generally soluble and mobile in natural water (Reimann and Birke, 2010). Lithium in groundwater may have multiple geogenic sources. It occurs in the minerals spodumene ($LiAlSi_2O_6$) and lepidolite ($K_2Li_3Al_4Si_7O_{21}(OH, F)_3$), but also in many other minerals. Pegmatite and brines especially are strongly enriched in Li (Kesler, et al,. 2012). In a European study, a median value of 2.6 µg/l Li (min. <0.2 µg/l and max. 75 µg/l) (Reimann and Birke, 2010). Concentrations of Li in studied waters are in range of 1.2–32.9 ppb.

Strontium

Strontium is very similar in chemical behavior to calcium and minor amounts probably occur in many waters (Reimann and Birke, 2010). Concentration of Sr in studied waters is in range of 24–2758 ppb.

Zinc

The maximum allowable concentration and permissible concentration of zinc in drinking water are 15 ppm and 5 ppm, respectively. According to WHO, the average values of zinc in all the water samples are below the permissible limit. The concentration of zinc in all water samples is 2.24–49.39 ppb. Hence all the samples collected from all sources are below from maximum permissible limit for zinc.

Nickel

The permissible concentration of nickel in ground water is 0.02 ppm. Concentrations of nickel in studied waters are in range of 0.33–2.26 ppb. All studied samples are within the permissible limit.

Beryllium and barium

Nothing is known of the distribution of beryllium in natural water. Barium has a highly insoluble sulfate and only traces of barium can be expected in waters where sulfate is present. Concentrations of Ba in studied waters is in range of 0.19–36 ppb.

Rubidium and cesium

Very little information is available about rubidium and cesium in natural water. Concentrations of Rb and Cs in studied waters vary from 0.11 to 15.75 and from 0.023 to 12.31 ppb, respectively.

Chromium

The maximum permissible limit of chromium in drinking water according to WHO is 0.05 ppm. The obtained data show that chromium content in investigated waters is within between 0.19 to 1.61 ppb.

Arsenic and selenium

Arsenic and selenium probably occur as anions and are of interest because of their toxic character, but rarely do unpolluted waters that are otherwise potable contain harmful amounts. Concentration of As is in range between 0.27 and 870.4 ppb, while the concentration of Se is 0.33–3.65 ppb.

Table 3

Concentration of Co, Cr, V, As, Se, Sb, Tl, Bi, Ga, Ge and Pd

	Co	Cr	V	As	Se	Sb	Tl	Bi	Ga	Ge	Pd
Trabotivište (Delčevo)	0.280	0.27	0.29	0.41	0.61	0.212	0.088	0.723	1.97	0.08	0.272
Istibanja (Kočani)	0.150	0.43	0.66	0.55	0.58	0.164	0.070	0.029	1.70	0.11	0.142
Neokazi – sample 1 (Probištip)	0.458	0.42	3.21	2.46	3.65	0.545	0.122	0.018	1.73	0.17	0.104
Neokazi – sample 2 (Probištip)	0.353	0.50	0.61	0.80	4.60	0.768	0.134	0.042	2.54	0.17	0.330
Gorni Balvan (Štip)	0.234	0.33	7.54	7.93	1.34	0.518	0.115	0.012	1.08	0.20	0.070
Plačkovica (Štip)	0.083	0.19	0.05	0.52	0.33	0.187	0.148	0.010	1.38	0.03	0.079
Karaorman (Štip)	0.195	2.22	0.78	0.35	1.59	0.056	0.090	0.014	0.48	0.25	0.100
Lakavica – sample 1 (Štip)	0.832	0.53	2.01	2.99	1.14	0.116	0.112	0.016	0.84	0.44	0.069
Lakavica – sample 2 (Štip)	0.849	0.64	2.38	2.31	1.64	0.081	0.108	0.015	0.99	0.45	0.122
Jargulica – sample 1 (Radoviš)	0.179	1.61	0.70	0.45	0.67	0.020	0.112	0.009	1.10	0.05	0.241
Jargulica – sample 2 (Radoviš)	0.186	0.44	0.35	0.34	2.93	0.042	0.086	0.010	2.36	0.06	0.056
Novo Selo (Strumica)	0.084	0.69	1.37	0.46	0.50	0.014	0.101	0.009	0.60	0.04	0.044
Murtino (Strumica)	0.118	0.28	0.06	117.8	0.41	0.063	0.081	0.009	2.91	0.10	0.072
Robovo (Strumica)	0.095	0.27	0.03	45.55	0.43	0.069	0.075	0.012	2.93	0.10	0.055
Gabrovo (Strumica)	0.107	0.26	0.39	0.37	0.41	0.080	0.084	0.023	0.24	0.04	0.057
Smolare (Strumica)	0.073	0.14	0.29	2.19	0.93	0.185	0.081	0.025	0.48	0.05	0.018

Table 4

Concentration of Ag,Sn,U, $CaCO_3$, $SO4^{2-}$ and Cl

	Ag	Sn	U	$CaCO_3$	$SO4^{2-}$	Cl
Trabotivište (Delčevo)	0.187	0.143	1.781	360.5	45.78	13.93
Istibanja (Kočani)	0.012	0.018	2.051	228	83.90	32.14
Neokazi – sample 1 (Probištip)	0.025	0.041	8.377	345	218.4	64.3
Neokazi – sample 2 (Probištip)	2.112	0.044	9.468	336	131.3	105
Gorni Balvan (Štip)	0.038	0.015	0.297	285	101.17	40.71
Plačkovica (Štip)	0.006	0.021	0.001	58	13.71	7.5
Karaorman (Štip)	0.034	0.035	0.319	656	219.87	114.6
Lakavica – sample 1 (Štip)	0.014	0.031	4.995	592	449.3	60
Lakavica – sample 2 (Štip)	0.019	0.026	2.940	698	440.0	83.57
Jargulica – sample 1 (Radoviš)	0.039	0.022	0.123	142	30.16	32.14
Jargulica – sample 2 (Radoviš)	0.027	0.028	0.054	175	50.58	31.07
Novo Selo (Strumica)	0.007	0.028	0.301	105	6.04	16.43
Murtino (Strumica)	0.017	0.024	0.015	215	1.58	17.14
Robovo (Strumica)	0.004	0.032	0.022	235	26.32	25.71
Gabrovo (Strumica)	0.004	0.074	61.85	166	14.53	12.86
Smolare (Strumica)	0.004	0.014	0.065	75	33.31	18.21

Sulfate

Sulfate is the form in which sulfur usually occurs in water. Weathering of sulfide bearing rocks or direct solution of evaporate deposits may be important sources of sulfate. The maximum value of sulfate in drinking water is 400 mg/liter (WHO, 2011).

Sulphate concentration in investigated waters is varies from 1.58. to 449.3 mg/l and these values are within permissible limits prescribed by WHO. The high concentration of sulfate in water from Lakavica might indicate the sulfate mineral in the aquifer of the system.

Chloride

Some chloride are dissolved from rocks and some may be associated with connate and juvenile water. Chloride in natural waters is derived from chloride-rich sedimentary rocks.

Chloride concentration varies from 7.5 to 114.6 mg/l which is lower than the WHO standards.

Uranium

Traces of uranium are common in natural waters. Uranium concentration in the study waters varies from 0.001 to 110.8 ppb.

Concentrations of NO_3, NO_2, $PO4^{3-}$, NH_4, F, HCO_3 and pH are given in Table 5.

Nitrate

Maximum concetnrations of nitrate were detected in waters from Neokazi (sample 2, 93.28 mg/l) and Karaorman (143.3 mg/l) and these values are higher from the limits (50 mg/l) prescribed by WHO. Nitrate may be added to water by organic pollution or leaching of fertilized soils. In some waters the presence of nitrate is not easily explained.

Fluoride

The main minerals of F are fluorspar (CaF_2), fluorapatite ($3Ca_3(PO_4)\cdot CaF_2$) and cryolite (Na_3AlF_6). Fluorspar and fluorapatite are only slightly soluble in water: at 20°C water dissolves only 14.7–22 mg/l of CaF_2 (Крайнов et al., 2004). Even such a poor solubility of these minerals depends upon the reaction of water-fluorspar is better soluble in alkaline water, although it is also slightly more soluble in acid water:

$$CaF_2 + OH^- = CaOH^+ + 2F^-,$$

$$CaF_2 + 2H^+ = Ca_2^+ + 2HF.$$

These minerals are also even less soluble in water rich in Ca.

Fluoride concentrations in water are normally very low. According to WHO 1984, the maximum permissible limit of fluoride in drinking water is 1.5 ppm and the highest desirable limit is 1.0 ppm. Fluoride concentrations above 1.5 ppm in drinking water cause dental fluorosis and much higher concentration skeletal fluorosis. Low concentration (approximately 0.5 ppm) provides protection against dental caries. Concentration of fluoride in the study area is in the range of acceptable limit 0.081–1.17 mg/l of WHO guidelines for drinking water quality (WHO, 2011).

Table 5

Concentration of NO_3, NO_2, PO_4^{3-}, NH_4, F, HCO_3 and pH

	NO_3	F	PO_4^{3-}	NO_2	NH_4	HCO_3	CO_3	pH
Trabotivište (Delčevo)	3.566	0.555	0.016	0.0083	0.098	278	301	7.09
Istibanja (Kočani)	11.95	0.455	0.030	0.0101	0.005	187	219	7.19
Neokazi – sample 1 (Probištip)	45.05	0.780	0.012	0.0006	0.005	261	285	7.71
Neokazi – sample 2 (Probištip)	93.28	0.928	0.012	0.0006	0.005	258	280	7.66
Gorni Balvan (Štip)	35.47	0.564	0.012	0.0006	0.005	235	249	8.2
Plačkovica (Štip)	0.147	0.081	0.017	0.0006	0.005	398	45	8.04
Karaorman (Štip)	143.3	0.872	0.012	0.0006	0.005	620	630	7.63
Lakavica – sample 1 (Štip)	1.864	0.472	0.012	0.0006	0.005	428	475	7.95
Lakavica – sample 2 (Štip)	21.65	0.266	0.015	0.0006	0.005	524	574	7.94
Jargulica - sample 1 (Radoviš)	34.38	0.136	0.013	0.0006	0.005	100	112	8.09
Jargulica – sample 2 (Radoviš)	12.72	0.154	0.013	0.0006	0.005	26	140	8.27
Novo Selo (Strumica)	1.86	0.374	0.067	0.0053	0.005	78	86	7.99
Murtino (Strumica)	0.813	0.373	0.083	0.0074	1.616	185	194	7.29
Robovo (Strumica)	0.536	0.254	0.019	0.0088	0.379	201	219	6.99
Gabrovo (Strumica)	0.416	1.17	0.011	0.0052	0.005	131	141	8.04
Smolare (Strumica)	0.715	0.317	0.012	0.0006	0.005	52	59	7.75

Ammonium ions

Maximum concetnrations of ammonium ions were detected in waters from Murtino (1.616 mg/l) and Gabrovo (0.379 mg/l) and these values are higher from limits prescribed by WHO.

Phosphate

Phosphate may be contributed by organic pollution and may be introduced in the treatment of public supplies, but is rarely present in amounts over 1 ppm. Concentration of phosphate in the study waters is in range of 0.012 – 0.315 ppm.

Bicarbonate is the major constituent of natural water. It comes from the action of water containing carbon dioxide on limestone, marble, chalk, calcite, dolomite, and other minerals containing calcium and magnesium carbonate. The carbonate-bicarbonate system in natural waters controls the pH and the natural buffer system. pH is an important environmental factor which provides information on many types of geochemical balances (Shyamala et al., 2008). pH values of the study area are neutral to alkaline type in the range of acceptable limit of 6.99–8.28, and they are in the desirable ranges, after WHO guidelines for drinking water quality (WHO, 2011).

According to the obtained values for total hardness, investigated waters are hard, moderately hard and very hard. High values for total hardness are mainly due to solubility of carbonate rocks.

The values for TH, TDS and EC are given in Table 6.

Table 6

Concentration of TH, TDS and EC

	Hardness concentracion $CaCO_3$ (mg/l) *(TH)*	Classification	TDS	EC (μS/cm)
Trabotivište (Delčevo)	216	very hard	770	1203
Istibanja (Kočani)	149	hard	656	1025
Neokazi – sample 1 (Probištip)	294	very hard	1046	1634
Neokazi – sample 2 (Probištip)	262	very hard	1041	1627
Gorni Balvan (Štip)	199	very hard	817	1277
Plačkovica (Štip)	45.6	soft	503	786
Karaorman (Štip)	486	very hard	2021	3158
Lakavica – sample 1 (Štip)	781	very hard	1747	2730
Lakavica – sample 2 (Štip)	748	very hard	2006	3134
Jargulica – sample 1 (Radoviš)	130	hard	388	606
Jargulica – sample 2 (Radoviš)	148	hard	450	703
Novo Selo (Strumica)	67.6	moderately hard	246	384
Murtino (Strumica)	89.3	moderately hard	469	733
Robovo (Strumica)	104	moderately hard	538	841
Gabrovo (Strumica)	77.5	moderately hard	364	569
Smolare (Strumica)	62.3	moderately hard	220	344

TDS

TDS is used for estimation of total dissolved salts in water (Purandara et al., 2003), which may have an impact on the taste and suitability for use of water for various purposes. The measured values for TDS varies from 220 to 2021 ppm (avg. 830 ppm). On comparison with the WHO water standards (1000 ppm) was observed that 5 analyzed samples (Neokazi – samples 1 and 2, Karaorman, Lakavica – samples 1 and 2) have TDS concentrations greater than the prescribed limits.

EC

The electrical conductivity is a measure of the capacity of water to conduct electrical current, it is directly related to the concentration of salts dissolved in water, and therefore to the Total Dissolved Solids (TDS). Salts dissolve into positively charged ions and negatively charged ions, which conduct electricity. Never the less, when the salt concentration reaches a certain level, electrical conductivity is no longer directly related to salts concentration. This is because ion pairs are formed. Ion pairs weaken each other's charge, so that above this level, higher TDS will not result in equally higher electrical conductivity.

CAI

Chloro-alkaline indices, CAI 1 = Cl^{-} (Na + K) / Cl and CAI 2 = Cl – (Na + K) / SO_4 + HCO_3 + CO_3 + NO_3 (Schoeller, 1977), were calculated to study the process of ion exchange between the natural water and its host environment during rock-water interaction. Positive CAI values noted in Neokazi (samples 1 and 2), Jargulica (samples 1 and 2), Novo Selo, Murtino, Robovo, Gabrovo and Smolare suggest that sodium and potassium from water are exchanged with calcium and magnesium in rock following base exchange reactions (chloro-alkaline equilibrium), where as negative CAI values noted at Trabotivište, Istibanja, Karaorman Plačkovica, Lakavica (samples 1 and 2), suggest that magnesium and calcium from water are exchanged with sodium and potassium in rock favouring cation-anion exchange reactions (chloro-alkaline disequilibrium).

$$\text{a) natural water } \underset{Ca^{2-},\, Mg^{2-}}{\overset{Na^{''},\, K^{+}}{\rightleftarrows}} \text{ country rock}$$

$$\text{b) natural water } \underset{Na^{+},\, K^{+}}{\overset{Ca^{2+''},\, Mg^{2+}}{\rightleftarrows}} \text{ country rock}$$

One method of comparing the results of chemical analyses of natural water is with at rilinear diagram (Piper, 1953) (Fig. 2). This diagram consists of two lower triangles that show the percentage distribution, on the milli equivalent basis, of the major cations (Mg^{++}, Ca^{++} and $Na^+ + K^+$) and the major anions (Cl^-, SO_4^{2-} and $CO_3^{2-} + HCO_3^-$) and a diamond-shaped part above that summarizes the dominant cations and anions to indicate the final water type. This classification system shows the anion and cation facies in terms of major-ion percentages. The water types are designated according to the area in which they occur on the diagram segments.

The cation distribution indicates that the samples range in composition from calcium / magnesium to predominantly mixed cation. In the anion triangle, there is a tendency toward bicarbonate type water.

The high concentration of calcium and magnesium might because for hard water in some of the investigated samples.

The correlation matrix using the raw data analysis shows a strong positive correlation between Ca → SO_4, Na, Mg; Ti → Ca, Mg, Na, K, B; U → Mo, Rb, Cs, As; B → Ca, Ti, Ge, Cl, HCO_3; Li → Mg, Na, K, B, Sr, Rb; Ge → Ca, Mg, Na, B, Ti, Li, Cl, Pb; Cl → Mg, Na, K, B, Sr, Li, Pb; HCO_3 → Ca, Mg, Na, K, B, Ti, Sr, Li, Pb, Co, Se, Ge; NO_3 → Na, Sr, Li, Pb, Cs, Se. Also significant positive correlation between SO_4–Na, TDS – EC. The rest of other correlations between ions are not significant.

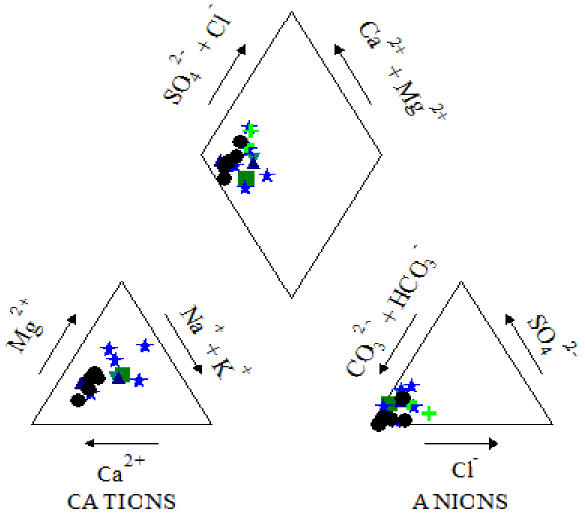

Fig. 2. Piper diagram of investigated waters

CONCLUSION

This study showed that most of the analyzed elements in all selected water samples were below the Macedonian maximum allowable levels and WHO water standards. In creased concentrations of some elements indicate anthropogenic pollution of the water from the fertilization of arable land, livestock farms. There is a strong positive correlation between Ca → SO_4, Na, Mg; Ti → Ca, Mg, Na, K, B; U → Mo, Rb, Cs, As; B → Ca, Ti, Ge, Cl, HCO_3; Li → Mg, Na, K, B, Sr, Rb; Ge → Ca, Mg, Na, B, Ti, Li, Cl, Pb; Cl → Mg, Na, K, B, Sr, Li, Pb; HCO_3 → Ca, Mg, Na, K, B, Ti, Sr, Li, Pb, Co, Se, Ge; NO_3 → Na, Sr, Li, Pb, Cs, Se; SO_4 → Na, TDS → EC.

According to the obtained values for total hardness investigated waters are hard, moderately hard and very hard. High values for total hardness are mainly due to solubility of carbonate rocks. Positive CAI values noted in Neokazi (samples 1 and 2), Jargulica (samples 1 and 2), Novo Selo, Murtino, Robovo, Gabrovo and Smolare suggest that sodium and potassium from water are exchanged with magnesium and calcium in rocks following base exchange reactions (chloro-alkaline equilibrium), whereas negative CAI (Chloro-Alkaline Indices) noted at Trabotivište, Istibanja, Karaorman Plačkovica, Lakavica (samples 1 and 2) suggest that magnesium and calcium from water are exchanged with sodium and potassium in rocks favouring cation-anion exchange reactions (chloro-alkaline disequilibrium). After Piper diagram the type of water in the study area is mainly calcium / magnesium bicarbonate.

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Резиме

ГЕОХЕМИСКА ПРОЦЕНА НА НЕКОИ ПРИРОДНИ ВОДИ ОД ИСТОЧНА И ЈУГОИСТОЧНА МАКЕДОНИЈА

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Клучни зборови: природни води; елементи во треги; pH; TDS

Во овој труд е дадена геохемиска процена на некои природни води од источна и југоиситочна Македонија. Анализирани се 16 примероци вода од селата Тработивиште, Истибања, Неокази (два примерока), Горни Балван, Плачковица, Караорман ,Лакавица (два примерока), Јаргулица (два примерока), Ново Село, Муртино, Робово, Габрово и Смоларе. Добиените податоци покажаа дека поголем дел од испитуваните елементи се во границите на максимално дозволените концентрации пропишани од Светската здравствена организација. Зголементите концентрации на некои од елементите се резултат од антропогено загадување на водата преку ѓубрењето на нивите и од сточарските фарми. Позитивна корелација постои помеѓу: Ca → SO_4, Na, Mg; Ti → Ca, Mg, Na, K, B; U → Mo, Rb, Cs, As; B → Ca, Ti, Ge, Cl, HCO_3; Li → Mg, Na, K, B, Sr, Rb; Ge → Ca, Mg, Na, B, Ti, Li, Cl, Pb; Cl → Mg, Na, K, B, Sr, Li, Pb; HCO_3 → Ca, Mg, Na, K, B, Ti, Sr, Li, Pb, Co, Se, Ge; NO_3 → Na, Sr, Li, Pb, Cs, Se; SO_4 → Na, TDS → EC. Според добиените вредности за тврдоста на водата, испитуваните води се тврди, умерено тврди и многу тврди со исклучок на водата од Плачковица која е мека. Високи вредности за тврдоста на водата се должат главно на растворливоста на карбонатните карпи. Според дијаграмот на Piper испитуваните води се главно калциум/магнезиумбикарбонатни.