

Article

Overview of the Chemical and Isotopic Investigations of the Mareza Springs and the Zeta River in Montenegro

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Supplementary Materials

Table S1 Results of major physicochemical properties of spring and surface water during research period.

Parameter	S1	S2	S3	S4	RU	RD	Sampling date
T _{water} (°C)	10.5	10.5	10.3	10.5	10	10.1	February 22, 2017
	10.4	10.9	10.6	10.7	10.5	10.7	March 15, 2017
	10.5	10.6	10.4	10.5	10.3	10.4	April 9, 2017
	10.7	10.7	10.8	11.5	11.8	11	April 23, 2017
	10.5	8.5	9.9	10.9	11.8	11.9	May 10, 2017
	11.1	12.3	12.6	13.3	13.6	17.7	June 3, 2017
	12.1	12.3	13.3	12.7	19.9		June 25, 2017
	12.2	11.6	11.9	12.9	19.9	19.4	July 5, 2017
	12.5	12.1	12.4	13.3	17.7	21.3	August 2, 2017
	12.6	12.7	13.3	13.3	18.5	19.8	September 2, 2017
	12.1	12	12.1	12	14.6		September 23, 2017
	11.9	12.1	11.9	12	14.3	14.7	October 7, 2017
	12.4	12.7	12.1	12.7	13.7	14.2	November 14, 2017
	11.1	11.1	11.1	11.3	10.8	10.9	November 30, 2017
	6	6.5	8	8	6.5	8.5	December 24, 2017
	10.1	10.2	10.8	10.2	9	11.3	January 10, 2018
pH			12.1	12	12	11.2	February 3, 2018
			11.7	11.9	10.1	11.5	March 4, 2018
	7.81	7.77	7.85	7.82	7.86	7.73	February 22, 2017
	7.83	7.81	7.84	7.84	7.91	7.73	March 15, 2017
	7.8	7.78	7.84	7.81	7.94	7.88	March 26, 2017.
	7.76	7.79	7.77	7.8	7.92	7.88	April 9, 2017
	7.6	7.69	7.72	7.73	7.84	7.75	April 23, 2017
	7.87	7.9	7.88	7.88	7.92	7.89	May 10, 2017
	7.81	7.84	7.83	7.83	7.96	8.05	June 3, 2017
	7.82	7.8	7.83	7.79	7.98		June 25, 2017
	7.78	7.74	7.75	7.7	7.97	8.05	July 5, 2017
	7.69	7.65	7.71	7.67	7.92	7.93	August 2, 2017
	7.71				8		August 21, 2017
	7.73	7.72	7.76	7.79	8.03	8	September 2, 2017
	7.78	7.76	7.76	7.75	7.86		September 23, 2017
	7.81	7.8	7.77	7.79	7.92	7.98	October 7, 2017
7.6	7.62	7.61	7.61	7.7	7.7	November 14, 2017	
7.39	7.35	7.42	7.42	7.86	7.77	November 30, 2017	
7.58	7.67	7.67	7.74	7.84	7.66	December 24, 2017	
7.76	7.73	7.79	7.84	7.87	7.57	January 10, 2018	
		7.53	7.56	7.65	7.82	February 3, 2018	
		7.72	7.71	7.93	7.88	March 4, 2018	
	238	240	236	236	237		February 11, 2017

	253	249	249	250	277	268	February 22, 2017
	237	237	234	233	271	289	March 15, 2017
	256	256	257	256	277	271	March 26, 2017.
	260	260	263	264	260	268	April 9, 2017
	282	281	280	280	259	279	April 23, 2017
	261	259	260	266	249	261	May 10, 2017
	268	270	272	274	266	255	June 3, 2017
EC	283	285	288	275	279		June 25, 2017
μS/cm	275	286	274	289	279	270	July 5, 2017
	287	290	288	290	284	273	August 2, 2017
	297				269		August 21, 2017
	269	271	270	268	252	260	September 2, 2017
	284	285	286	285	254		September 23, 2017
	290	288	285	283	222	268	October 7, 2017
	322	324	322	321	240	248	November 14, 2017
	302	296	315	309	279	277	November 30, 2017
	236	226	221	227	258	276	December 24, 2017
	256	258	246	254	267	283	January 10, 2018
			322	321	280	233	February 3, 2018
			288	294	258	261	March 4, 2018
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	171	171	171	171	201	195	February 22, 2017
	171	171	171	171	189	207	March 15, 2017
	177	177	177	177	195	189	March 26, 2017.
	177	177	177	177	177	183	April 9, 2017
	189	189	189	189	177	183	April 23, 2017
	183	183	183	183	177	177	May 10, 2017
	201	201	201	201	189	183	June 3, 2017
	207	207	207	207	201		June 25, 2017
HCO₃⁻	201	201	201	201	195	189	July 5, 2017
mg/L	201	201	201	201	195	195	August 2, 2017
	201				201		August 21, 2017
	189	189	189	189	177	177	September 2, 2017
	201	201	201	201	177		September 23, 2017
	207	201	201	207	171	183	October 7, 2017
	220	220	220	220	177	177	November 14, 2017
	207	207	207	207	189	189	November 30, 2017
	165	165	165	165	177	195	December 24, 2017
	165	165	165	165	177	177	January 10, 2018
			207	207	189	183	February 3, 2018
			195	195	171	177	March 4, 2018
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	49.85	48.57	48.6	48.03	50.38		February 11, 2017
	46.14	46.97	46.55	46.2	57.7	53.9	February 22, 2017
	45.72	45.87	44.91	45.55	53.27	58.4	March 15, 2017
	51.47	50.8	50.1	50.4	55.76	53.8	March 26, 2017.
	46.3	46.14	46.3	45.9	49.1	49.2	April 9, 2017
Ca²⁺	49.6	49	47.97	48.36	47.3	50.1	April 23, 2017
mg/L	47.3	47.8	47.6	47.6	48.9	50.9	May 10, 2017
	53.4	52.6	53.11	52.6	54.1	51.41	June 3, 2017
	56.7	56.97	56.4	56.05	57.3		June 25, 2017
	56.26	55.45	55.67	56.04	55.6	52.7	July 5, 2017
	53.4	53.49	53.15	52	54.7	51.5	August 2, 2017
	54				54.35		August 21, 2017
	51.51	51.35	51.58	51.5	48.04	49.69	September 2, 2017
	52.94	53.81	53.35	53.31	47.29		September 23, 2017

	53.93	55.69	54.9	54.41	45.03	52.88	October 7, 2017
	66.29	66.81	64.53	64.08	53.99	57.81	November 14, 2017
	64.97	63.39	65.52		55.07	60.2	November 30, 2017
	44.5	44.6	43.5	43.64	52.5	56.9	December 24, 2017
	45.4	45.8	45.5	45.4	51.1	51.5	January 10, 2018
			62.6	62	56.95	45.16	February 3, 2018
			56	56.9	50.1	52.3	March 4, 2018
	6.34	6.14	6.53	6.43	4.97		February 11, 2017
	5.40	5.57	5.70	5.68	5.20	5.00	February 22, 2017
	5.88	5.82	5.98	6.11	4.89	5.37	March 15, 2017
	6.70	6.83	6.95	6.95	5.66	6.20	March 26, 2017.
	6.98	6.89	7.01	6.92	4.34	5.68	April 9, 2017
	6.87	6.74	6.80	6.82	4.48	5.50	April 23, 2017
Mg²⁺	6.41	6.47	6.42	6.5	4.5	5.30	May 10, 2017
mg/L	6.30	6.22	6.30	6.32	4.94	4.78	June 3, 2017
	7.44	7.44	7.45	7.34	6.12		June 25, 2017
	7.22	7.08	7.11	7.19	6.03	5.89	July 5, 2017
	7.05	7.09	7.03	6.89	6.28	6.10	August 2, 2017
	7.29				6.44		August 21, 2017
	7.16	7.02	7.1	7.11	6.07	6.50	September 2, 2017
	7.84	8.051	7.95	7.99	6.53		September 23, 2017
	7.84	7.96	7.80	7.83	5.138	6.40	October 7, 2017
	6.51	6.54	6.70	6.52	4.97	4.95	November 14, 2017
	5.12	4.79	5.50		4.6	4.32	November 30, 2017
	5.5	5.51	5.53	5.60	3.97	4.98	December 24, 2017
	5.85	5.91	5.87	5.80	4.54	5.18	January 10, 2018
			4.59	4.48	2.67	3.24	February 3, 2018
			5.49	5.32	4.59	4.54	March 4, 2018
	2.84	3.03	2.87	2.74	3.13		February 11, 2017
	3.06	3.14	3.05	3.09	3.97	3.83	February 22, 2017
	2.67	2.73	2.97	2.57	3.6	3.65	March 15, 2017
	3.6	3.55	3.8	3.72	3.79	3.78	March 26, 2017.
	4.15	4.03	4.14	4.3	3.23	3.77	April 9, 2017
	4.59	4.57	4.54	4.63	3.37	3.83	April 23, 2017
	4.15	4.11	4.17	4.14	3.25	3.85	May 10, 2017
	4.9	4.86	4.9	4.9	3.9	3.8	June 3, 2017
SO₄²⁻	5.62	5.81	5.57	5.49	3.2		June 25, 2017
mg/L	5.83	5.76	5.73	5.74	3.3	4.14	July 5, 2017
	5.93	5.86	5.84	5.86	4.11	4.13	August 2, 2017
	6.06	6.05	6.03	6.04	4.18	4.49	September 2, 2017
	6.3	6.3	6.37	6.5	4.19		September 23, 2017
	6	6.03	5.86	6.056	3.85	4.2	October 7, 2017
	5.83	5.95	5.94	5.97	4.46	5.19	November 14, 2017
	4.59	4.58	4.5	4.59	4.19	4.09	November 30, 2017
	2.57	2.764	2.53	2.57	3.1	3.4	December 24, 2017
	2.63	2.74	2.6	2.67	3.82	3.65	January 10, 2018
			3.56	3.79	3.08	2.74	February 3, 2018
			4.2	4.15	3.68	3.8	March 4, 2018
	1.65	1.64	1.64	1.61	1.98		February 11, 2017
	1.75	1.96	1.6	1.6	3.15	2.06	February 22, 2017
	1.55	1.45	1.46	1.55	2.20	1.80	March 15, 2017
	2.06	1.84	2.48	2.07	2.20	2.00	March 26, 2017.
	1.87	1.83	2.37	2.53	1.95	2.44	April 9, 2017
	1.95	2.10	1.85	1.85	1.8	1.95	April 23, 2017

Cl ⁻ mg/L	2.15	2.00	2.20	2.50	2.15	2.32	May 10, 2017
	1.7	1.90	1.70	1.80	2.30	1.60	June 3, 2017
	2.64	2.53	2.11	2.08	2.50		June 25, 2017
	2.4	2.35	2.35	2.4	2.45	3.20	July 5, 2017
	2.2	2.16	2.03	2.1	1.98	2.09	August 2, 2017
	2.05				3.15		August 21, 2017
	2.15	2.12	2.19	2.32	2.66	2.88	September 2, 2017
	2.00	1.75	2.00	2.00	1.50		September 23, 2017
	2.52	2.59	2.38	2.32	2.15	2.41	October 7, 2017
	3.05	3.00	4.00	3.78	2.13	2.46	November 14, 2017
	2.61	2.52	2.60	2.79	2.72	2.38	November 30, 2017
	1.76	1.82	1.78	1.91	2.76	2.31	December 24, 2017
	2.05	2.20	2.14	2.11	2.45	2.41	January 10, 2018
			2.96	2.96	2.41	2.69	February 3, 2018
			2.56	2.71	2.52	2.31	March 4, 2018
Hardness mg (CaCO ₃)/ L	151	147	148	146	146	155	February 11, 2017
	137	140	140	139	166	168	February 22, 2017
	138	139	137	139	153	160	March 15, 2017
	156	155	154	154	163	146	March 26, 2017.
	144	144	144	143	141	148	April 9, 2017
	152	150	148	149	137	149	April 23, 2017
	145	146	145	146	141	148	May 10, 2017
	159	157	159	157	156		June 3, 2017
	172	173	172	170	168	156	June 25, 2017
	170	168	168	170	164	154	July 5, 2017
	162	163	162	158	162		August 2, 2017
	165				162	151	August 21, 2017
	158	157	158	158	145		September 2, 2017
	164	168	166	166	145	158	September 23, 2017
	167	172	169	168	134	165	October 7, 2017
192	194	189	187	155	168	November 14, 2017	
183	178	186		157	163	November 30, 2017	
134	134	131	132	148	150	December 24, 2017	
137		138	137	146	126	January 10, 2018	
		175	173	153	149	February 3, 2018	
		163	164	144		March 4, 2018	

Table S2. Average, minimum, maximum and median values for in situ field parameters and for major ion concentrations for the six sampling locations.

Parameter	Values	S1	S2	S3	S4	RU	RD	Mareza Aquifer	Zeta River
T °C	Average	11.0	11	11.5	11.7	12.5	13.4	11.3	12.9
	Min	6.0	6.5	8	8	6.5	8.5	6	6.5
	Max	12.6	12.7	13.3	13.3	19.9	21.3	13.3	21.3
	Median	11.1	11.4	11.8	12	11.8	11.4	11.6	11.7
pH	Average	7.73	7.73	7.74	7.74	7.89	7.84	7.74	7.87
	Min	7.39	7.35	7.42	7.42	7.65	7.57	7.35	7.57
	Max	7.87	7.9	7.88	7.88	8.03	8.05	7.9	8.05
	Median	7.77	7.76	7.76	7.79	7.92	7.88	7.76	7.88
EC µS/cm	Average	271.3	270.1	272.8	273.7	262.7	267.1	272.1	264.7
	Min	236	226	221	227	222	233	221	222
	Max	322	324	322	321	284	289	324	289
	Median	269	270.5	273	274.5	266	268	272	268

Hardness mgCaCO ₃ /L	Average	157	158	158	156	152	154	157	153
	Min	134	134	131	132	134	126	133	130
	Max	192	194	189	187	168	168	190	168
	Median	158	157	158	157	153	154	158	153
SO ₄ ²⁻ mg/L	Average	4.54	4.54	4.46	4.47	3.67	3.9	4.50	3.79
	Min	2.57	2.73	2.53	2.57	3.08	2.74	2.53	2.74
	Max	6.3	6.3	6.37	6.5	4.46	5.19	6.50	5.19
	Median	4.59	4.57	4.35	4.44	3.74	3.83	4.57	3.81
HCO ₃ ⁻ mg/L	Average	190	190	191	191	185	186	189	188
	Min	165	165	165	165	170.8	176.9	165	177
	Max	219	219	219	219	201	207	219	207
	Median	189	189	195	195	183	183	189	189
Ca ²⁺ mg/L	Average	52.08	51.95	52.39	51.57	52.31	52.84	51.94	52.56
	Min	44.5	44.6	43.5	43.64	45.03	45.16	43.50	45.03
	Max	66.29	66.81	65.52	64.08	57.7	60.2	66.81	60.20
	Median	51.51	51.07	52.34	51.5	53.27	52.3	51.50	52.70
Mg ²⁺ mg/L	Average	6.62	6.55	6.49	6.51	52.31	52.84	6.54	5.20
	Min	5.12	4.79	4.59	4.48	45.03	45.16	4.48	2.67
	Max	7.84	8.05	7.95	7.99	57.7	60.2	8.05	6.53
	Median	6.7	6.64	6.62	6.52	53.27	52.3	6.62	5.14
SO ₄ ²⁺ mg/L	Average	4.5	4.5	4.5	4.5	3.70	3.90	4.5	3.80
	Min	2.6	2.7	2.5	2.6	3.08	2.74	2.6	2.91
	Max	6.3	6.3	6.4	6.5	4.46	5.19	6.4	4.83
	Median	4.6	4.6	4.4	4.4	3.79	3.83	4.5	3.81

Table S3. Isotopic contents of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ and d-excess values in monthly precipitation collected at P1 and P2, in the period March 2017–February 2018.

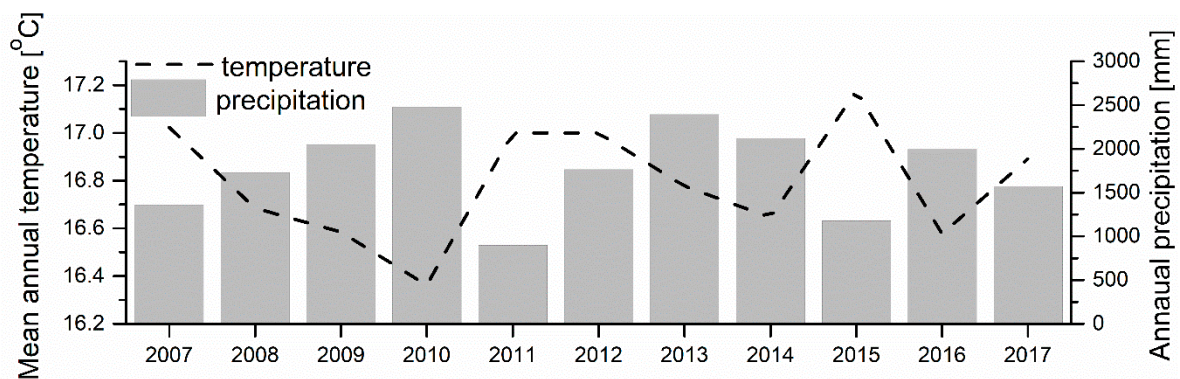
	P1	P1	P1	P2	P2	P2
	$\delta^{18}\text{O}$	$\delta^2\text{H}$	d	$\delta^{18}\text{O}$	$\delta^2\text{H}$	d
March 2017	-4.37	-29.3	5.66	-6.14	-37.0	12.12
April 2017	-5.50	-32	12.00	-4.82	-25.6	12.96
May 2017	-6.13	-44.8	4.24	-6.00	-43.1	4.90
June 2017	-3.82	-21.6	8.96	Without rain	Without rain	-
July 2017	-5.02	-31.1	9.06	-2.13	-10.8	6.24
August 2017	-3.80	-21.5	8.90	-4.40	-25.1	10.10
September 2017	-4.96	-29.1	10.58	-4.46	-26.8	8.88
October 2017	Without rain	Without rain	-	Without rain	Without rain	-
November 2017	-5.63	-29	16.04	-5.25	-24.0	18.00
December 2017	-6.71	-36.6	17.08	-6.81	-37.7	16.78
January 2018	-4.52	-20.6	15.56	-4.44	-19.2	16.32
February 2018	-8.89	-56.9	14.22	-9.09	-57.9	14.82

Table 4. Isotopic data of all water samples (springs and surface water) through 21 series of sampling.

Date	S1 ‰			S2 ‰			S3 ‰			S4 ‰			RU ‰			RD ‰		
	$\delta^{18}\text{O}$	$\delta^2\text{H}$	d	$\delta^{18}\text{O}$	$\delta^2\text{H}$	d	$\delta^{18}\text{O}$	$\delta^2\text{H}$	d	$\delta^{18}\text{O}$	$\delta^2\text{H}$	d	$\delta^{18}\text{O}$	$\delta^2\text{H}$	d	$\delta^{18}\text{O}$	$\delta^2\text{H}$	d
02/11/17	-7.26	-40.8	17.3	-7.22	-39.42	18.3	-7.25	-40.5	17.5	-7.27	-39.9	18.3	-7.57	-43.66	16.9			
02/22/17	-7.23	-40.6	17.2	-7.22	-40.7	17.1	-7.3	-41.5	16.9	-7.25	-41.1	16.9	-7.56	-45.5	15	-7.08	-41.2	15.4
03/15/17	-7.23	-40	17.8	-7.25	-40.7	17.3	-7.24	-40.5	17.4	-7.23	-40.7	17.1	-7.66	-45.9	15.4			
03/26/17	-7.39	-42.4	16.7	-7.38	-42.4	16.6	-7.41	-42.9	16.4	-7.42	-42.1	17.3	-7.89	-48.2	14.9	-7.17	-41.5	15.9
04/09/17				-7.72	-45	16.8	-7.76	-45.5	16.6				-8.01	-49.1	15	-7.76	-46.4	15.7
04/23/17				-7.73	-45.4	16.4	-7.76	-45.6	16.5	-7.72	-45.1	16.7	-7.78	-47.1	15.1	-7.58	-44.8	15.8
05/10/17	-7.69	-45.1	16.4	-7.7	-45.2	16.4	-7.73	-45	16.8	-7.73	-44.8	17	-8.01	-48.6	15.5	-7.74	-46.4	15.5
06/03/17	-7.68	-45.4	16	-7.71	-45.5	16.2	-7.69	-45.2	16.3	-7.7	-45.3	16.3	-7.89	-48.6	14.5	-7.64	-46.5	14.6
06/25/17	-7.79	-46.2	16.1	-7.81	-45.9	16.6	-7.8	-46.5	15.9	-7.78	-45.9	16.3	-7.94	-49.2	14.3			
07/05/17	-7.82	-46.3	16.3	-7.83	-46.2	16.4	-7.82	-46.8	15.8	-7.82	-46.1	16.5	-7.8	-48.1	14.3	-7.59	-46.6	14.1
08/02/17	-7.93	-47.2	16.2	-7.91	-47	16.3	-7.92	-47.3	16.1	-7.88	-47.3	15.7	-7.66	-47.3	14	-7.52	-46.3	13.9
08/21/17	-7.92	-47.1	16.3										-7.68	-47.5	13.9			
09/02/17	-7.83	-47.7	14.9	-7.86	-47.4	15.5	-7.92	-47.3	16.1	-7.92	-47.6	15.8	-7.37	-46.6	12.4	-7.55	-46.9	13.5
09/23/17	-7.85	-47.1	15.7	-7.87	-47	16	-7.86	-46.8	16.1	-7.89	-46.6	16.5	-7.25	-45	13			
10/07/17	-7.9	-47.6	15.6	-7.9	-47.4	15.8	-7.95	-47.5	16.1	-7.87	-47.5	15.5	-6.36	-41.1	9.78	-7.2	-45	12.6
11/14/17	-7.3	-43.3	15.1	-7.28	-43.2	15	-7.4	-43.6	15.6	-7.33	-43.4	15.2	-7.11	-42.5	14.4	-6.85	-39.5	15.3
11/30/17	-6.68	-37.5	15.9	-6.64	-36.9	16.2	-6.65	-37.6	15.6	-6.7	-38	15.6	-7.18	-41.7	15.7	-6.73	-38.5	15.3
12/24/17	-7.39	-39.5	19.6	-7.39	-39.3	19.8	-7.39	-39	20.1	-7.36	-39	19.9	-8.06	-47.6	16.9	-7.4	-41.6	17.6
01/10/18	-7.31	-40.2	18.3	-7.32	-40.3	18.3	-7.3	-39.8	18.6	-6.67	-36	17.4	-7.91	-47.1	16.2	-7.07	-38.7	17.9
02/03/18							-6.7	-36.3	17.3				-6.38	-34.5	16.5	-6.67	-36.7	16.7
03/04/18							-6.96	-37.6	18.1	-6.97	-37.8	18	-7.89	-46.3	16.8	-7.47	-42.7	17.1

Table S5. Average, minimum, maximum and median values for isotope composition of spring and surface water samples collected in study period.

Locality	Values	$\delta^{18}\text{O}(\text{‰})$	$\delta^2\text{H}(\text{‰})$	d (‰)
S1	Average	-7.54	-43.76	16.56
	Min	-7.93	-47.70	14.94
	Max	-6.68	-37.50	19.62
	Median	-7.68	-45.10	16.26
S2	Average	-7.54	-43.61	16.72
	Min	-7.91	-47.40	15.04
	Max	-6.64	-36.90	19.82
	Median	-7.70	-45.10	16.44
S3	Average	-7.49	-43.14	16.79
	Min	-7.95	-47.50	15.60
	Max	-6.65	-36.30	20.12
	Median	-7.55	-44.30	16.43
S4	Average	-7.47	-43.00	16.77
	Min	-7.92	-47.60	15.24
	Max	-6.67	-36.00	19.88
	Median	-7.56	-44.10	16.59
RU	Average	-7.57	-45.77	14.79
	Min	-8.06	-49.20	9.78
	Max	-6.36	-34.50	16.90
	Median	-7.68	-47.10	14.98
RD	Average	-7.31	-43.08	15.43
	Min	-7.76	-46.90	12.60
	Max	-6.67	-36.70	17.86
	Median	-7.43	-43.75	15.48

**Figure S1.** Mean annual air temperature and annual precipitation in study area, for the long term period (2007–2017).