

Supplementary material

Identification of water contamination sources using hydrochemical and isotopic studies - the Kozłowa Góra reservoir catchment (Southern Poland)

Table S1. Methods used in measurements of parameters.

Table S2. The results of physicochemical parameters in sampled water.

Table S3. The results of chemical analyses of sampled water.

Table S4. The results of nitrogen compound analyses in sampled water.

Table S5. The results of isotopic analyses of S and O in SO_4 in sampled water.

Table S1. Methods used in measurements of parameters.

Parameter	Method/Equipment	Precision	Detection limit/Range
T	ELMETRON CP-401	± 0.1 °C	-50.0 – 199.9 °C
pH	ELMETRON CP-401	± 0.002	-6.000 – 20.000
EC	ELMETRON CC-411	± 0.25%	0 – 199.9 mS/cm
Eh	ELMETRON CP-315	± 1 mV	± 1,200 mV
O ₂	WTW Oxi 315i	± 0.5%	0.00 – 19.99 mg/L
Ca ²⁺	Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)	± 10%	0.010 – 1,000 mg/L
Mg ²⁺	Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)	± 10%	0.0070 – 1,000 mg/L
Na ⁺	Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)	± 10%	1.0 – 1,000 mg/L
K ⁺	Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)	± 10%	1.0 – 1,000 mg/L
HCO ₃ ⁻	Titration to the phenolphthalein indicator endpoint	± 10%	12 – 6,100 mg/L
SO ₄ ²⁻	Gravimetric determination in hydrated barium chloride	± 20%	10 – 5,000 mg/L
Cl ⁻	Titration with silver nitrate solution in the presence of potassium chromate indicator	± 15%	5.0 – 50,000 mg/L
PO ₄ ³⁻	Ammonium molybdate spectrometric method	± 15%	0.05 – 200 mg/L
TOC	High-temperature combustion and infrared (IR) detection	± 18%	2.0 – 1,000 mg/L
N-NO ₃ ⁻	HACH DR1900 (Cadmium Reduction Method)	± 0.3 mg/L	0.3 – 30.0 mg/L
N-NO ₂ ⁻	HACH DR1900 (USEPA Diazotization Method)	± 0.002 mg/L	0.002 – 0.300 mg/L
N-NH ₄ ⁺	HACH DR1900 (Salicylate Method)	± 0.004 mg/L	0.01 – 0.50 mg/L
δ ³⁴ S _{SO4} δ ¹⁸ O _{SO4}	Elemental analysis isotope ratio mass spectrometry (EA-IRMS)	± 0.08 ‰	-

Table S2. The results of physicochemical parameters in sampled water (Date: I – June 2020; II – January 2021; III – June 2021; IV – September 2021).

Parameter	T				pH				EC				Eh				O ₂				O ₂			
Unit	°C				-				µS/cm				mV				mg/L				%			
Date	I	II	III	IV	I	II	III	IV	I	II	III	IV	I	II	III	IV	I	II	III	IV	I	II	III	IV
BRYNICA RIVER																								
R1	-	-	-	12.3	-	-	-	7.75	-	-	-	606	-	-	-	34	-	-	-	5.65	-	-	-	54.7
R2	16.6	1.0	15.5	11.8	6.96	7.25	7.59	7.14	412	533	445	484	206	147	134	112	6.11	10.50	2.84	5.59	65.5	78.4	81.2	53.2
R3	16.0	3.0	15.7	9.8	7.40	7.51	7.11	7.35	448	545	478	496	205	57	122	85	7.36	8.50	8.75	5.38	78.0	66.7	91.8	48.8
R4	17.8	3.4	16.5	11.1	7.22	7.67	7.31	7.68	374	541	753	559	136	108	132	94	8.2	8.53	8.00	5.91	90.1	67.5	85.5	56.1
R5	-	4.0	16.7	11.0	-	7.52	7.41	7.68	-	742	689	585	-	116	118	92	-	7.71	8.65	6.11	-	62.4	92.6	57.1
R6	15.1	3.2	16.3	9.2	7.26	7.32	7.62	7.47	476	638	532	532	201	87	127	73	8.08	7.76	8.35	5.14	83.6	61.1	88.3	46.0
STREAMS																								
S1	-	-	-	11.2	-	-	-	6.55	-	-	-	268	-	-	-	19	-	-	-	3.14	-	-	-	29.6
S2	15.7	2.6	16.9	11.8	6.93	7.12	7.11	7.01	331	227	271	302	151	108	136	82	4.81	8.27	5.33	3.6	49.9	63.5	56.8	34.3
S3	-	-	-	12.7	-	-	-	7.58	-	-	-	602	-	-	-	74	-	-	-	5.82	-	-	-	56.3
S4	16.0	4.5	16.3	12.5	7.42	7.33	7.48	7.62	540	848	625	684	183	48	11	-40	7.06	7.08	8.15	5.47	74.4	58.1	86.5	52.8
S5	-	-	-	11.5	-	-	-	7.01	-	-	-	368	-	-	-	-6	-	-	-	4.26	-	-	-	40.3
S6	13.8	5.8	14.5	11.2	7.34	7.50	7.47	7.51	543	628	642	599	43	-31	116	-15	9.17	7.20	9.3	5.34	93.9	60.5	93.7	50.1
S7	17.1	4.3	18.8	12.7	7.26	7.35	7.35	7.32	321	930	755	778	-12	-59	-86	-93	7.92	8.06	7.88	4.91	86.3	64.4	87.8	47.7
S8	-	-	-	8.1	-	-	-	6.67	-	-	-	588	-	-	-	78	-	-	-	3.97	-	-	-	34.6
S9	17.6	4.5	16.0	10.8	7.26	7.69	7.64	7.71	404	946	700	685	151	113	117	102	7.4	7.85	8.14	6.15	91.4	64.4	86.0	57.6
S10	-	-	-	11.6	-	-	-	7.94	-	-	-	1010	-	-	-	113	-	-	-	2.60	-	-	-	24.5
S11	16.8	4.1	17.1	7.8	6.95	6.84	6.75	6.98	237	210	223	225	-12	100	77	35	5.85	6.64	5.8	3.73	63.1	52.9	61.7	32.2
KOZŁOWA GÓRA RESERVOIR																								
Z1	20.8	0.5	24.6	13.6	7.86	7.29	8.88	8.38	427	460	408	335	189	143	94	125	8.45	9.70	9.27	6.27	98.4	70.4	114.0	61.5
Z2	20.8	3.0	23.9	14.2	8.03	6.58	8.66	8.54	414	428	404	379	181	171	101	121	8.80	9.27	9.79	6.49	102.3	72.5	112.6	65.1
Z3	-	0.7	23.9	-	-	7.59	8.66	-	-	373	410	-	-	90	114	-	-	10.10	8.61	-	-	78.0	106.0	-
GROUNDWATER																								
W1	13.2	6.8	11.7	13.5	6.37	6.99	7.28	6.65	182	222	253	263	238	166	112	135	6.66	7.08	6.8	5.22	97.2	61.6	65.3	51.5
W2	11.0	8.0	10.5	13.8	6.86	7.27	7.24	7.07	452	346	334	405	82	79	92	-13	5.29	7.35	7.79	4.86	50.2	65.7	72.8	48.2
W3	-	7.5	13.1	14.6	-	7.61	7.45	7.57	-	673	514	598	-	124	86	84	-	5.77	4.09	4.26	-	50.5	40.6	43.2
W4	-	8.3	11.7	11.5	-	7.28	7.11	7.06	-	1500	1650	1290	-	77	109	84	-	6.33	6.25	4.31	-	56.5	59.1	40.6

Table S3. The results of chemical analyses of sampled water (Date: I – June 2020; II – January 2021; III – June 2021; IV – September 2021).

Parameter	Ca ²⁺				Mg ²⁺				Na ⁺				K ⁺				HCO ₃ ⁻				SO ₄ ²⁻				Cl ⁻				PO ₄ ³⁻				TOC			
Unit	mg/L				mg/L				mg/L				mg/L				mg/L				mg/L				mg/L				mg/L							
Date	I	II	III	IV	I	II	III	IV	I	II	III	IV	I	II	III	IV	I	II	III	IV	I	II	III	IV	I	II	III	IV	I	II	III	IV	I	II	III	IV
BRYNICA RIVER																																				
R1	-	-	-	120	-	-	-	4.1	-	-	-	7.7	-	-	-	2.1	-	-	-	291	-	-	-	46	-	-	-	16	-	-	-	<0.05	-	-	-	4.5
R2	96	74	78	85	8.2	5.6	4.5	4.6	16	26	13	12	2.1	2.4	2.2	2.5	204	156	187	209	31	47	35	38	34	54	27	24	<0.05	<0.05	<0.05	<0.05	9.8	9.3	9.5	7.4
R3	88	62	75	68	22	13	19	18	9.9	26	11	11	3.1	14	3.1	3.5	189	147	169	177	64	52	78	68	21	53	23	23	<0.05	<0.05	<0.05	<0.05	5.5	22	8.6	7.7
R4	63	62	83	73	16	13	22	20	15	25	50	15	8.0	14	11	4.6	139	124	204	187	50	56	99	77	26	53	72	31	0.141	<0.05	0.06	0.11	8.1	20	10	7.7
R5	-	69	75	76	-	17	20	21	-	52	37	19	-	18	8.7	5.7	-	211	241	250	-	66	81	70	-	84	54	32	-	<0.05	<0.05	<0.05	-	-	-	-
R6	84	66	84	73	21	16	21	20	18	34	15	19	4.2	15	3.9	5.0	181	172	181	187	69	58	80	78	31	66	30	37	0.200	<0.05	<0.05	<0.05	4.2	16	7.5	6.7
STREAMS																																				
S1	-	-	-	36	-	-	-	5.5	-	-	-	14	-	-	-	1.6	-	-	-	90.9	-	-	-	10	-	-	-	30	-	-	-	<0.05	-	-	-	53
S2	65	32	38	41	21	9.6	12	13	5.3	5.2	6.5	5.9	1.5	1.8	1.6	2.2	206	82	131	142	<10	33	14	13	6.7	10	8.0	9.0	<0.05	<0.05	<0.05	<0.05	17	18	21	23
S3	-	-	-	89	-	-	-	34	-	-	-	5.8	-	-	-	3.6	-	-	-	300	-	-	-	74	-	-	-	19	-	-	-	0.17	-	-	-	3.9
S4	102	80	80	83	33	26	27	27	10	16	18	19	5.2	90	7.1	6.8	244	300	223	220	78	60	87	110	34	39	43	45	<0.05	<0.05	<0.05	<0.05	4.5	63	7.5	7.7
S5	-	-	-	46	-	-	-	12	-	-	-	8.5	-	-	-	7.4	-	-	-	98	-	-	-	73	-	-	-	15	-	-	-	0.12	-	-	-	14
S6	99	88	86	80	38	32	34	32	8.7	9.3	11	10	2.8	2.9	2.6	2.8	272	251	269	245	87	105	93	90	17	17	19	18	<0.05	<0.05	<0.05	<0.05	7.4	11	6.9	7.8
S7	60	93	98	95	22	28	38	36	4.6	42	9.7	14	9.9	89	8.1	22	171	368	364	382	33	69	100	85	7.8	45	20	19	<0.05	<0.05	<0.05	<0.05	4.0	120	13	14
S8	-	-	-	60	-	-	-	16	-	-	-	33	-	-	-	3.8	-	-	-	59	-	-	-	100	-	-	-	92	-	-	-	0.10	-	-	-	6.5
S9	71	87	100	83	21	24	30	25	11	65	22	20	6.3	22	5.9	5.0	166	240	214	219	58	94	110	100	24	114	49	45	0.082	<0.05	<0.05	<0.05	7.9	24	7.0	5.4
S10	-	-	-	73	-	-	-	19	-	-	-	58	-	-	-	15	-	-	-	466	-	-	-	55	-	-	-	83	-	-	-	12.5	-	-	-	50
S11	51	31	35	27	11	6.3	7.4	5.7	4.2	4.8	5.8	5.6	1.1	1.7	1.7	1.7	111	48	61	65	23	110	43	33	8.9	9.3	9.0	9.0	0.086	<0.05	0.05	<0.05	11	14	15	17
KOZŁOWA GÓRA RESERVOIR																																				
Z1	69	64	59	47	18	16	14	12	13	13	16	14	4.8	4.3	4.2	3.9	170	165	128	129	50	66	62	42	32	26	29	27	<0.05	<0.05	<0.05	<0.05	10	10	12	10
Z2	78	62	63	45	20	15	14	12	14	12	15	13	5.3	4.2	4.0	3.8	171	159	131	128	58	62	59	40	32	25	29	27	<0.05	<0.05	<0.05	<0.05	10	8.7	14	10
Z3	52	45	54	-	13	11	12	-	14	9.8	14	-	5.2	3.6	3.8	-	177	119	171	-	47	56	46	-	26	19	24	-	<0.05	<0.05	<0.05	-	-	-	-	
GROUNDWATER																																				
W1	48	38	37	41	7.9	5.1	4.2	5.3	3.2	3.0	4.8	4.4	2.6	2.7	3.0	3.3	57	78	75	78	21	21	34	41	<5	<5	5	<5	<0.05	<0.05	0.098	0.08	8.2	11	9.5	9.8
W2	78	46	42	58	14	8.3	7.5	9.7	15	8.6	9.1	11	11	8.4	8.5	9.2	86	67	63	65	80	44	43	53	26	9.8	11	19	<0.05	<0.05	<0.05	<0.05	2.2	5.8	4.4	5.0
W3	60	90	65	80	19	27	20	23	14	17	10	14	16	18	14	15	281	375	281	336	53	42	31	40	<5	5.1	<5	<5	<0.05	1.496	1.385	3.200	-	-	-	-
W4	180	169	184	152	34	32	34	30	117	107	135	93	38	29	34	28	445	427	592	505	104	95	88	86	256	211	233	158	<0.05	<0.05	<0.05	<0.05	-	-	-	-

Table S4. The results of nitrogen compound analyses in sampled water (Date: I – June 2020; II – January 2021; III – June 2021; IV – September 2021).

Parameter	NO ₃ ⁻				NO ₂ ⁻				NH ₄ ⁺			
Unit	mg/L				mg/L				mg/L			
Date	I	II	III	IV	I	II	III	IV	I	II	III	IV
BRYNICA RIVER												
R1	-	-	-	12.8	-	-	-	0.030	-	-	-	0.03
R2	0.9	8.0	4.0	5.8	-	0.036	0.023	0.010	0.06	0.26	0.08	0.03
R3	6.2	6.2	8.0	7.5	-	0.043	0.046	0.020	0.06	0.06	0.04	<0.01
R4	8.0	7.5	6.2	9.3	-	0.046	0.394	0.020	0.64	0.03	0.85	<0.01
R5	-	8.0	-	10.2	-	0.125	0.253	0.026	-	0.05	0.52	<0.01
R6	4.4	6.2	9.3	8.9	-	0.066	0.089	0.030	0.43	<0.01	0.12	0.03
STREAMS												
S1	-	-	-	1.3	-	-	-	0.036	-	-	-	0.15
S2	0.9	2.2	0.9	0.4	-	0.013	0.023	0.010	0.21	0.10	0.22	0.05
S3	-	-	-	4.9	-	-	-	0.056	-	-	-	0.12
S4	2.7	3.1	4.4	4.9	-	0.056	0.039	0.039	0.18	0.08	0.24	0.15
S5	-	-	-	2.2	-	-	-	0.020	-	-	-	0.10
S6	19.5	22.6	19.0	19.9	-	0.033	0.049	0.030	0.05	0.08	0.03	0.03
S7	3.1	1.3	-	1.3	-	0.148	0.023	0.000	0.63	1.00	1.78	24.47
S8	-	-	-	7.1	-	-	-	0.023	-	-	-	0.01
S9	4.0	8.9	10.2	11.5	-	0.089	0.089	0.030	0.10	<0.01	0.05	0.03
S10	-	-	-	1.8	-	-	-	0.013	-	-	-	51.52
S11	0.4	1.8	-	0.9	-	0.010	0.010	0.007	0.82	0.26	0.19	0.31
KOZŁOWA GÓRA RESERVOIR												
Z1	0.9	3.1	-	0.9	-	0.030	0.023	0.010	0.21	0.08	0.05	0.01
Z2	0.9	3.5	-	0.9	-	0.033	0.030	0.016	0.10	0.10	0.03	<0.01
Z3	-	2.7	-	-	-	0.023	0.020	-	-	0.09	0.03	-
GROUNDWATER												
W1	22.6	9.3	12.0	11.1	-	0.013	0.059	0.010	0.01	<0.01	0.12	0.03
W2	36.7	52.2	29.2	79.7	-	0.016	0.013	0.016	<0.01	<0.01	<0.01	0.30
W3	-	21.7	-	16.4	-	0.069	0.240	0.099	-	0.10	0.12	<0.01
W4	-	16.4	7.5	13.7	-	0.030	0.030	0.033	-	<0.01	0.05	0.03

Table S5. The results of isotopic analyses of S and O in SO₄ in sampled water (Date: I – June 2020; II – January 2021; III – June 2021; IV – September 2021).

Parameter	$\delta^{34}\text{S}_{\text{VCDT}}$			$\delta^{18}\text{O}_{\text{VSMOW}}$		
Unit	‰			‰		
Date	I	II	III	I	II	III
BRYNICA RIVER						
R1	-	-	-	-	-	-
R2	11.85	6.66	9.09	13.30	6.69	8.21
R3	6.88	7.25	7.38	6.36	6.42	5.97
R4	5.81	7.04	5.30	6.11	6.31	4.62
R5	-	-	5.12	-	-	5.38
R6	4.94	6.27	6.48	5.15	5.87	4.82
STREAMS						
S1	-	-	-	-	-	-
S2	-	-	-	-	-	-
S3	-	-	-	-	-	-
S4	6.37	7.45	7.30	8.48	5.29	5.46
S5	-	-	-	-	-	-
S6	6.15	5.94	6.56	6.28	3.59	5.74
S7	8.63	12.28	11.16	7.45	9.76	11.73
S8	-	-	-	-	-	-
S9	4.38	5.63	7.36	7.70	6.80	4.50
S10	-	-	-	-	-	-
S11	13.39	11.74	9.14	10.61	9.11	11.69
KOZŁOWA GÓRA RESERVOIR						
Z1	9.38	7.31	7.46	8.40	6.43	6.43
Z2	9.57	7.12	7.42	8.66	7.07	6.45
Z3	10.09	4.01	7.89	10.46	6.41	6.77
GROUNDWATER						
W1	-	-	-	-	-	-
W2	-	-	-	-	-	-
W3	4.87	7.52	-	3.25	2.69	-
W4	2.96	5.17	5.15	5.24	5.16	6.73