

## Article

# Identification of Water Contamination Sources Using Hydrochemical and Isotopic Studies—The Kozłowa Góra Reservoir Catchment Area (Southern Poland)

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**Abstract:** The application of combined research methods, such as hydrochemical and isotopic analyses, facilitates understanding of the origin of water constituents and migration of contaminants in the aquatic environment. The presented study attempts to identify contamination sources affecting water quality within the Kozłowa Góra reservoir catchment area (southern Poland). A total of 100 water samples were collected from surface water (the Brynica river, streams, and the reservoir) and groundwater (a Quaternary aquifer) in four time periods. During fieldwork, the physicochemical parameters were measured (temperature, pH, electrical conductivity, redox potential, and dissolved oxygen). The chemical analysis included the determination of major ions ( $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and  $\text{K}^+$ ), nutrients ( $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NH}_4^+$ , and  $\text{PO}_4^{3-}$ ), and total organic carbon. The study was complemented by isotopic analysis of sulphur and oxygen in sulphate, which enabled a more precise identification of stressors affecting water quality in different parts of the catchment area. Chemical and isotopic results ( $\delta^{34}\text{S} = 4.38\text{--}13.99\text{‰}$ ;  $\delta^{18}\text{O} = 3.59\text{--}13.30\text{‰}$ ) revealed that wastewater discharges and agricultural activities have a significant influence on the chemistry of the Brynica River and other streams. At some sampling points, a lower quality of water was manifested by elevated concentrations of  $\text{NO}_3^-$  (up to 22.6 mg/L) and several other ions (e.g., up to 114 mg/L for  $\text{Cl}^-$ , up to 51.52 mg/L for  $\text{NH}_4^+$ , and 12.5 mg/L for  $\text{PO}_4^{3-}$ ). The quality of groundwater was deteriorated mainly by infiltration of sewage from leaky septic tanks. The level of groundwater contamination varied depending on the location, as higher concentrations of major ions and values of electrical conductivity were observed in residential areas. The Brynica river, streams, and groundwater recharge the drinking water reservoir, and thus its quality depends on these sources. A dilution of water and the presence of biochemical processes led to a reduction of contaminant concentrations in the Kozłowa Góra reservoir (down to 3.5 mg/L for  $\text{NO}_3^-$ , 32 mg/L for  $\text{Cl}^-$ , 0.21 mg/L for  $\text{NH}_4^+$ , and  $<0.05$  mg/L for  $\text{PO}_4^{3-}$ ) compared to water in the river and streams supplying the reservoir. The study revealed the role of wastewater discharge and agricultural activities in the evolution of surface water chemistry. The results will be used in further research on the origin and migration of other substances in water, including microcontaminants.

**Keywords:** surface water; groundwater; water quality; isotopic study; contamination sources; sulphate



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## 1. Introduction

Safeguarding drinking water resources is one of the key roles of local, regional, and national authorities. It is also one of the major concerns when climate change contributes to a drastic decline in quality water supplies. Additionally, the amount of pollution produced by human activities and emitted into the environment continues to increase. This includes microcontaminants in water, which come from various sources, including wastewater discharge [1], application of manure on arable lands [2], leaky sewer systems and septic tanks [3,4], municipal landfills [5], burial sites [6], and several others [7]. Determination of microcontaminants alone is not sufficient to identify contamination sources. Therefore,

other methods should be applied simultaneously in order to define microcontaminants' origin, such as analysis of other constituents in water (e.g., nitrogen compounds [8]) or stable isotope studies [9]. Basic information on chemical composition and water quality is crucial in further research on microcontaminant migration within a study area and interpreting the monitoring results.

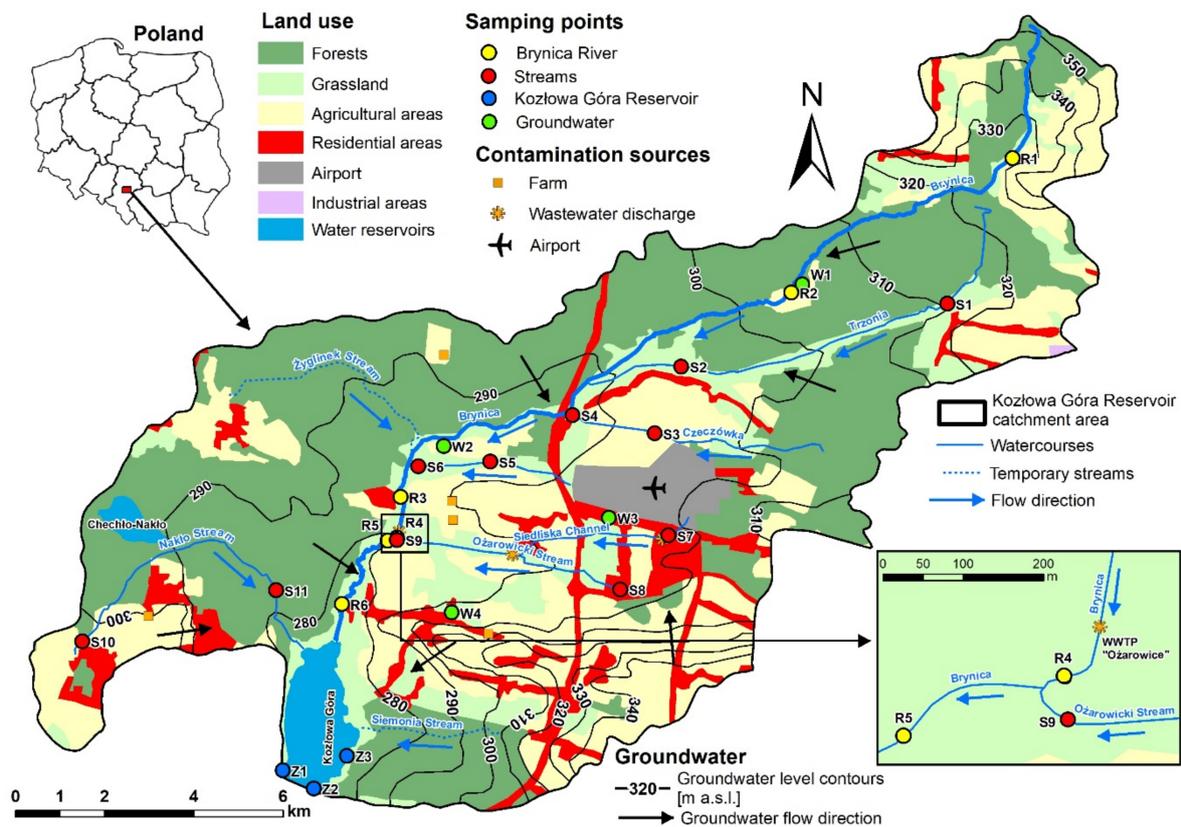
Identification of real and potential contamination sources within a catchment area of a drinking water source is of vital importance for proper water management. In agricultural areas, the potential for surface water and groundwater contamination increases compared to other land-use types. Many studies have focused on groundwater and surface water contamination with  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  [10–16] in rural and urban areas. Their results often reveal a mixed origin of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  in water samples, including fertilisation, wastewater, and natural sources like dissolution of evaporitic minerals and sulphides. Comprehensive research conducted in catchment areas is the basis for assessing the nature of the threat and its sources [17–19]. Isotope investigations are commonly used for areas of mixed land use [15,20–23]. They allow researchers to distinguish sulphate originating from agricultural sources, such as artificial fertilisers [24,25] and livestock manure [24], from natural sources such as oxidation of sulphides [26,27] or sulphate minerals [28]. Combining research monitoring water quality with isotopic studies often yields good results in separating the influence of different sources or in refining the obtained results when isotopes indicate an ambiguous source of contamination.

The purpose of the presented study was to investigate sources of pollution of the surface water and groundwater in the catchment area of the dam reservoir Kozłowa Góra, which is an important source of potable water in the Upper Silesia, Poland. Potential anthropogenic contamination sources are natural and artificial fertilisers, wastewater, and increased exhaust emissions associated with the airport. A substantial part of the catchment area is used for agriculture (39.5%), which entails fertilisation of crop fields with both manure and fertiliser. Another potential source of pollution is wastewater leaking from septic tanks and sewage pipes, because the study area includes a number of villages characterised by single-family housing. An international airport, “Katowice-Pyrzowice”, located in the centre of the catchment area, is another potential source of water pollution. Spatial variation of water chemistry across the catchment of the Kozłowa Góra reservoir was investigated by studying the chemical parameters (major ions, nutrients, total organic carbon) and stable isotopes of sulphate present in the surface water and groundwater. Similar studies have been conducted, e.g., by [10]. The basic information on chemical composition and water quality will be crucial in further studies on microcontaminants occurring in the water environment, which were the main subject of the performed project [29].

## 2. Materials and Methods

### 2.1. Study Area

The study was carried out within the catchment area of the Kozłowa Góra reservoir. It is located in southern Poland, in the central part of the Silesian Province (Figure 1). The catchment area covers an area of about 194 km<sup>2</sup>. In general, five main types of land use can be distinguished, i.e., forests and grassland (approx. 47% of the catchment area), agricultural land (39.5%), artificial surfaces (11%), and water bodies (2.5%). Forests and grassland occur mainly in the eastern and western parts, along the northern boundary and on the west of the Kozłowa Góra reservoir. A significant area is occupied by agricultural land, mainly in the southeast and the northeast. The cultivation of cereals (wheat, rye, oats), rapeseed, and sweetcorn dominates the arable land. Artificial surfaces include the “Katowice-Pyrzowice” airport in the centre-east and residential areas (rural households) situated in the central and south-western areas. The “Katowice-Pyrzowice” airport is one of the largest airports in Poland. In practice, no industrial site is present in the study area. The main water body is the Kozłowa Góra dam reservoir, with a surface area of 5.3 km<sup>2</sup> [30].



**Figure 1.** Land use and identified contamination sources within the Kozłowa Góra catchment area, based on [30–32].

The Kozłowa Góra reservoir serves as a drinking water supply and flood protection. It is recharged mainly by the Brynica river and its tributaries. Other streams flowing into the reservoir are the Nakło and Siemonia streams, but the latter is a temporary stream. The length of the Brynica river, from its source to the dam reservoir, is approx. 28 km, and its flow rate is 0.5–1.5 m<sup>3</sup>/s, depending on the season. Apart from the Brynica river, the area is discharged by numerous drainage ditches and Brynica's tributaries, generally characterised by low flow rates, ranging from several dm<sup>3</sup>/s in dry seasons to several dozens of dm<sup>3</sup>/s in wet seasons [33]. The water quality of the Brynica river is of high importance because it is the main river supplying the drinking water reservoir. The chemical composition of Brynica's water depends on its tributaries; hence other streams must be considered in identifying potential pollution sources.

The area is diversified in terms of geological structure and hydrogeological conditions. Quaternary sediments cover most of the study area and are represented by glacial sands and gravels and fluvial deposits along the watercourses. They form a Quaternary aquifer, discharged by the Brynica river and other streams. Another geological formation within the catchment area is the Triassic multi-aquifer. It consists of two aquifers made up of carbonate deposits (dolomites and limestones) and clastic sediments (gravels and sands underlying the carbonate rocks). Domestic wells draw groundwater from the Quaternary aquifer, the quality of which is affected by anthropogenic activity. Thus, high concentrations of nitrate, sulphate, and chloride are observed locally. The uppermost aquifer is mostly unconfined, and the level of the groundwater table ranges from approx. 280 m a.s.l. in the south to 350 m a.s.l. in the north of the area (Figure 2). Apart from the Quaternary and Triassic deposits, there are also small outcrops of Tertiary, Jurassic, Carboniferous, and Devonian sediments, being of lower significance within the Kozłowa Góra catchment area [34–37].

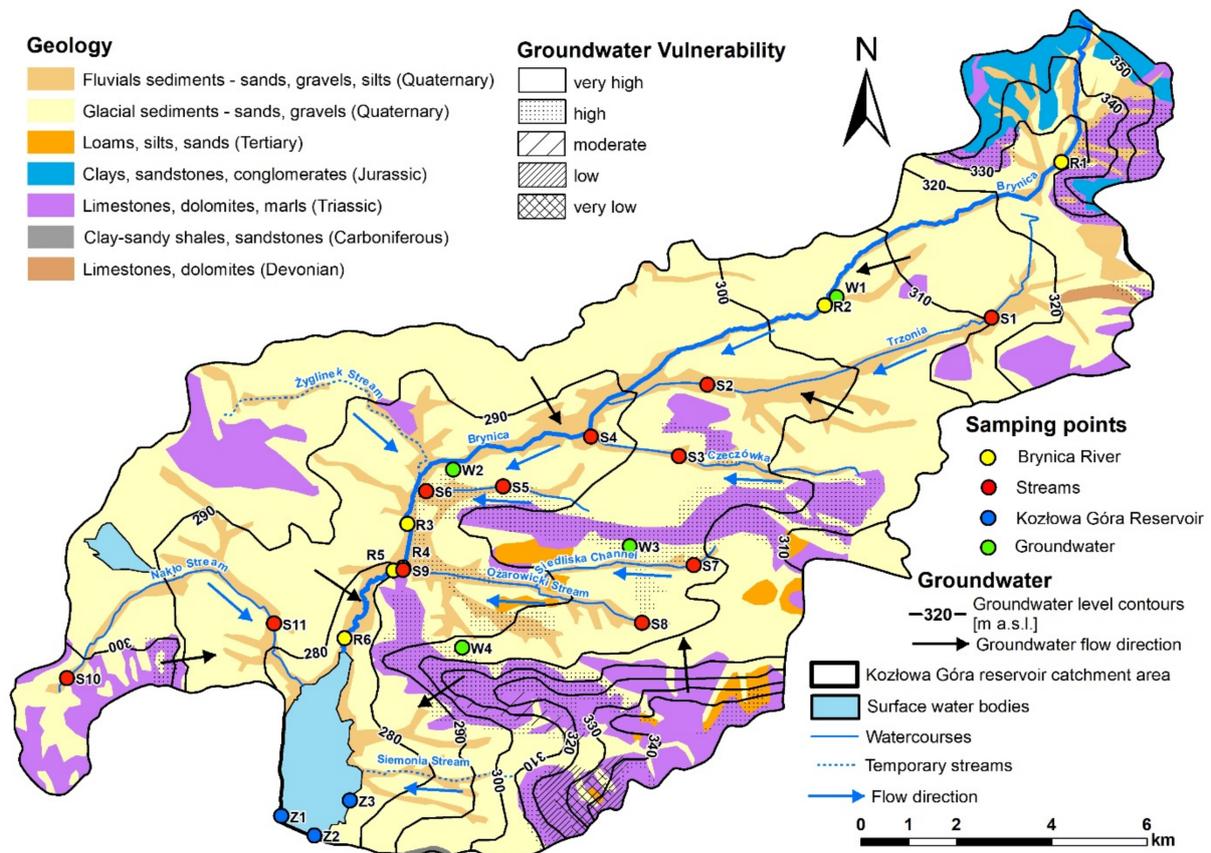


Figure 2. Geology and hydrogeological conditions of the study area based on [31,32].

Given the land use in the study site, municipal wastewater discharges and farming activities are considered as the main contamination sources of the water environment. There is only one active Wastewater Treatment Plant (“Ożarówice”) in the study area, which has operated since 2015. Treated wastewater from the WWTP “Ożarówice” is discharged to the Brynica river. In the past, prior to the construction of WWTP “Ożarówice”, the WWTP “Pyrzowice” functioned in the south of the airport. Wastewater discharges were directed to the Siedliska channel, which flows to the Ożarówicki stream, i.e., the main tributary of the Brynica. Along with a ditch located on the west of the airport, it is a recipient of stormwater discharges from the airport area. The sewage network is poorly developed in this region; hence, household sewage is mainly directed to septic tanks or, sporadically, directly to watercourses. In the former case, it leads to local groundwater contamination.

## 2.2. Sampling and Analyses

A total of 100 water samples for chemical and isotopic analyses were taken in June 2020, January 2021, June 2021, and September 2021 within the Kozłowa Góra catchment area. Sampling periods and location of sampling points were selected based on the scope of the microcontaminant monitoring conducted under the same project. Water samples (63) were taken from surface water, including the Brynica river and streams (52) and the Kozłowa Góra drinking water reservoir (11). The Brynica river was sampled at 6 points. Other streams were sampled at 1 or 2 points (Figure 1). Groundwater samples (16) were taken from shallow domestic wells abstracting the Quaternary aquifer. After sampling campaigns, water samples were stored in a cool box at +4 °C and transported to the laboratory for preparation and analysis. All water samples (except for TOC) were filtered through MF-Millipore membrane filters of 0.45 µm pore size.

During fieldwork, the physicochemical parameters of water were measured using portable equipment. Measurements included temperature (T) and pH of water (EL-

METRON CP-401), electrical conductivity (EC) (ELMETRON CC-411), redox potential (Eh) (ELMETRON CP-315), and dissolved oxygen (O<sub>2</sub>) (WTW Oxi 315i). Additionally, inorganic nitrogen compounds were determined in situ using a HACH DR1900 Portable Spectrophotometer. Concentrations of NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup> were obtained using powder pillows methods for N-NO<sub>3</sub> (Cadmium Reduction Method), N-NO<sub>2</sub> (USEPA Diazotization Method), and N-NH<sub>4</sub> (Salicylate Method).

Each water sample was collected in polyethylene vials of volumes 1000 mL, 500 mL, and 100 mL as well as two 60 mL bottles for chemical analyses. Chemical analyses were performed at an ISO-accredited laboratory, JARS S.A., Poland. Major ions in water comprised HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, and K<sup>+</sup>. In addition, PO<sub>4</sub><sup>3-</sup> and total organic carbon (TOC) were determined. The laboratory methods included titration to the phenolphthalein indicator endpoint (HCO<sub>3</sub><sup>-</sup>, based on alkalinity), gravimetric determination in hydrated barium chloride (SO<sub>4</sub><sup>2-</sup>), titration with silver nitrate solution in the presence of a potassium chromate indicator (Cl<sup>-</sup>), Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES; for Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, and K<sup>+</sup>), the ammonium molybdate spectrometric method (PO<sub>4</sub><sup>3-</sup>), and high-temperature combustion and infrared (IR) detection (TOC). For TOC determination, 60 mL of the samples was acidified by 0.25 mL 18% HCl. Details on precision and detection limits for the applied methods are included in the Supplementary Materials (Table S1).

Isotopic analyses of sulphate were conducted for 15 sampling points, in June 2020, January 2021, and June 2021 (42 samples in total). Surface water samples were taken from 5 points on the Brynica river (R2, R3, R4, R5, and R6), from 5 Brynica tributaries (S4, S6, S7, and S9), from the Nakło stream (S11), and from 3 points at different banks of the Kozłowa Góra reservoir (Z1, Z2, and Z3). The groundwater samples were collected from 2 private wells (W3 and W4). The methodology of SO<sub>4</sub><sup>2-</sup> precipitation from water solution was taken in accordance with previous studies, e.g., [21,32]. In order to perform sulphate isotopic analyses, water samples were collected in 1.5 L plastic bottles. After filtration with a 0.45 µm membrane filter, samples were acidified with HCl to a pH around 2. To precipitate BaSO<sub>4</sub> for analysis, 10% BaCl<sub>2</sub> solution was added. The samples were stored at +4 °C for 24 h. After precipitation of BaSO<sub>4</sub>, samples were centrifuged to separate the water phase from the precipitate. In order to remove chloride ions, the precipitate was rinsed with distilled water and recentrifuged. The obtained BaSO<sub>4</sub> precipitate was dried at +103 °C for 24 h and then placed in 1 mL plastic vials. At least 1.5 mg of BaSO<sub>4</sub> was needed for analysis. Isotopic analysis of sulphur and oxygen in sulphate was conducted at the Institute of Geological Sciences, Polish Academy of Sciences, Poland. The analysis was performed using the elemental analysis isotope ratio mass spectrometry (EA-IRMS) method, and the results are presented as δ<sup>34</sup>S<sub>SO4</sub> and δ<sup>18</sup>O<sub>SO4</sub> values.

### 3. Results

#### 3.1. Water Chemistry

In the sections below, the ranges of measured parameters in different water sample types (the Brynica river, streams, the reservoir, and groundwater) are described. Detailed results of physicochemical, chemical, and isotopic analysis for each sampling campaign are included in the Supplementary Materials (Tables S2–S5).

##### 3.1.1. The Brynica River and Streams

As the field measurements were conducted in different seasons, the temperature of sampled water varied greatly, between 1 °C in winter and 18.8 °C in summer. pH measurements indicated the sampled water as slightly acidic to slightly alkaline, with pH values between 6.55 and 7.94. In the case of electrical conductivity (EC), the results were diversified and ranged from 210 µS/cm to 1010 µS/cm. Redox potential varied from −93 mV to 206 mV. Dissolved oxygen concentration measured in situ was between 2.6 mg/L and 10.5 mg/L (Table 1).

**Table 1.** Results of measured parameters in sampled water (maximum and minimum values).

Parameter (Unit)		Brynica River	Streams	Reservoir	Groundwater
T (°C)	min	1.0 (R2)	2.6 (S2)	0.5 (Z1)	6.8 (W1)
	max	17.8 (R4)	18.8 (S7)	24.6 (Z1)	14.6 (W3)
pH	min	6.96 (R2)	6.55 (S1)	6.58 (Z2)	6.37 (W1)
	max	7.75 (R1)	7.94 (S10)	8.88 (Z1)	7.61 (W3)
EC (µS/cm)	min	374 (R4)	210 (S11)	335 (Z1)	182 (W1)
	max	742 (R5)	1010 (S10)	460 (Z1)	1650 (W4)
Eh (mV)	min	34 (R1)	−93 (S7)	90 (Z3)	−13 (W2)
	max	206 (R2)	183 (S4)	189 (Z1)	238 (W1)
O <sub>2</sub> (mg/L)	min	2.84 (R2)	2.60 (S10)	6.27 (Z1)	4.09 (W3)
	max	10.50 (R2)	9.30 (S6)	10.10 (Z3)	7.79 (W2)
Ca <sup>2+</sup> (mg/L)	min	62 (R3)	27 (S11)	45 (Z2,Z3)	38 (W1)
	max	120 (R1)	102 (S4)	78 (Z2)	184 (W4)
Mg <sup>2+</sup> (mg/L)	min	4.1 (R1)	5.5 (S1)	11 (Z3)	4.2 (W1)
	max	22 (R3,R4)	38 (S6,S7)	20 (Z2)	34 (W4)
Na <sup>+</sup> (mg/L)	min	7.7 (R1)	4.2 (S11)	9.8 (Z3)	3.0 (W1)
	max	52 (R5)	65 (S9)	16 (Z1)	135 (W4)
K <sup>+</sup> (mg/L)	min	2.1 (R1,R2)	1.1 (S11)	3.6 (Z3)	2.6 (W1)
	max	18 (R5)	90 (S4)	5.3 (Z2)	38 (W4)
HCO <sub>3</sub> <sup>−</sup> (mg/L)	min	124 (R4)	48 (S11)	119 (Z3)	57 (W1)
	max	291 (R1)	466 (S10)	177 (Z3)	592 (W4)
SO <sub>4</sub> <sup>2−</sup> (mg/L)	min	31 (R2)	<10 (S2)	40 (Z2)	21 (W1)
	max	99 (R4)	110 (S9,S11)	66 (Z1)	104 (W4)
Cl <sup>−</sup> (mg/L)	min	16 (R1)	7.8 (S7)	19 (Z3)	<5 (W1,W2,W3)
	max	84 (R5)	114 (S9)	32 (Z1,Z2)	256 (W4)
PO <sub>4</sub> <sup>3−</sup> (mg/L)	min	<0.05	<0.05	<0.05	<0.05
	max	0.141 (R4)	12.5 (S10)		3.200 (W3)
TOC (mg/L)	min	4.5 (R1)	3.9 (S1)	8.7 (Z2)	2.2 (W2)
	max	22 (R3)	120 (S7)	14 (Z2)	11 (W1)
NO <sub>3</sub> <sup>−</sup> (mg/L)	min	0.9 (R2)	0.4 (S2,S11)	0.9 (Z1,Z2)	7.5 (W1)
	max	12.8 (R1)	22.6 (S6)	3.5 (Z2)	79.7 (W2)
NO <sub>2</sub> <sup>−</sup> (mg/L)	min	0.010 (R2)	<0.002 (S7)	0.010 (Z1)	0.010 (W1)
	max	0.253 (R5)	0.148 (S7)	0.033 (Z2)	0.240 (W3)
NH <sub>4</sub> <sup>+</sup> (mg/L)	min	<0.01	<0.01 (S9)	<0.01 (Z2)	<0.01
	max	(R3,R4,R5,R6) 0.84 (R4)	51.52 (S10)	0.21 (Z1)	0.30 (W2)

The most abundant ion in the river was HCO<sub>3</sub><sup>−</sup>, whose concentrations ranged between 48.2 mg/L and 466 mg/L. The quantities of other anions, i.e., SO<sub>4</sub><sup>2−</sup> and Cl<sup>−</sup>, were lower and varied from <10 mg/L to 110 mg/L, and from 6.7 mg/L to 114 mg/L, respectively. Ca<sup>2+</sup> was the main cation, and its concentrations in the sampled rivers were between 27 mg/L and 120 mg/L. The rest of the major ions, i.e., Mg<sup>2+</sup>, Na<sup>+</sup>, and K<sup>+</sup>, occurred in lower concentrations and were in the range of 4.1–38 mg/L, 4.2–65 mg/L, and 1.1–90 mg/L, respectively. PO<sub>4</sub><sup>3−</sup> was detected only in a few samples, and its concentration reached 12.5 mg/L. In the case of TOC, the values varied from 3.9 mg/L to 120 mg/L.

The concentrations of NO<sub>3</sub><sup>−</sup> in rivers ranged from 0.4 mg/L to 22.6 mg/L. The concentrations of NO<sub>2</sub><sup>−</sup> were significantly lower, i.e., between <0.002 mg/L and 0.394 mg/L. The observed values of NH<sub>4</sub><sup>+</sup> were usually below or slightly above the detection limit

(0.01 mg/L), but in several river samples, significantly higher results were observed, reaching 51.5 mg/L.

### 3.1.2. The Kozłowa Góra Reservoir

The temperature of the reservoir water varied depending on the season and ranged between 0.5 °C and 24.6 °C. pH measurements also indicated the sampled water as slightly acidic to slightly alkaline, since pH values were between 6.58 and 8.88. EC values ranged between 335 µS/cm and 460 µS/cm. Redox potential in the reservoir varied from 90 mV to 189 mV. The concentration of dissolved oxygen was between 6.27 mg/L and 10.1 mg/L.

HCO<sub>3</sub><sup>−</sup> was the dominant ion in the reservoir, and the concentrations were between 119 mg/L and 177 mg/L. SO<sub>4</sub><sup>2−</sup> and Cl<sup>−</sup> concentrations were in the range of 40–66 mg/L and 19–32 mg/L, respectively. In the case of major cations, the observed values were 45–78 mg/L for Ca<sup>2+</sup>, 11–20 mg/L for Mg<sup>2+</sup>, 9.7–16 mg/L for Na<sup>+</sup>, and 3.6–5.3 mg/L for K<sup>+</sup>. PO<sub>4</sub><sup>3−</sup> was not detected in any of the reservoir water samples (<0.05 mg/L). TOC values ranged between 8.7 mg/L and 14 mg/L.

Among the analysed inorganic nitrogen compounds, the highest concentrations were observed for NO<sub>3</sub><sup>−</sup>, i.e., from 0.9 mg/L to 3.5 mg/L. The concentrations of NO<sub>2</sub><sup>−</sup> and NH<sub>4</sub><sup>+</sup> were considerably lower, and the values were in the range of 0.010–0.033 mg/L and <0.01–0.21 mg/L, respectively.

### 3.1.3. Groundwater

The depth of sampled wells ranged between 2.8 m and 5.4 m. The temperature of groundwater was between 6.8 °C (in winter) and 14.6 °C (in summer). pH values ranged from 6.37 to 7.61. The results of EC were diverse, i.e., from 181 µS/cm to 1650 µS/cm. Redox potential varied from −13 mV to 238 mV. O<sub>2</sub> concentrations measured in situ in groundwater were between 4.09 mg/L and 7.79 mg/L.

Seasonal changes in major ion concentrations were small. Similar to surface water, HCO<sub>3</sub><sup>−</sup> was the main constituent in groundwater (from 57.3 mg/L to 592 mg/L). The lowest concentrations of SO<sub>4</sub><sup>2−</sup> and Cl<sup>−</sup> were 21 mg/L and <5 mg/L, whereas the highest concentrations were 104 mg/L and 256 mg/L, respectively. Ca<sup>2+</sup> was the dominant cation, and its concentration varied from 37 mg/L to 184 mg/L. Mg<sup>2+</sup>, Na<sup>+</sup>, and K<sup>+</sup> occurred in lower concentrations, i.e., 4.2–34 mg/L, 3.0–135 mg/L, and 2.6–38 mg/L, respectively. PO<sub>4</sub><sup>3−</sup> concentrations usually did not exceed the detection limit (<0.05 mg/L), except for groundwater samples taken from the W3 well, where the values reached 3.2 mg/L. TOC values in the analysed groundwater were between 2.2 mg/L and 11 mg/L.

The groundwater contained higher concentrations of NO<sub>3</sub><sup>−</sup> compared to sampled surface water, as concentrations ranged from 7.5 mg/L to 79.7 mg/L. Lower values were observed for NO<sub>2</sub><sup>−</sup>. The concentrations varied between 0.01 mg/L and 0.24 mg/L. NH<sub>4</sub><sup>+</sup> was mostly observed in concentrations <0.01 mg/L, but in one groundwater sample (W4), it reached 0.3 mg/L.

## 3.2. Isotopic Composition of Sulphate

The results of measurements of δ<sup>34</sup>S and δ<sup>18</sup>O in sulphate in surface water and groundwater sampled in 15 sites are summarised in Table 2 as minimum and maximum values from the three sampling campaigns (June 2020, January 2021, and June 2021).

**Table 2.** Results of measured  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  in sampled water (maximum and minimum values).

Parameter (Unit)		R2	R3	R4	R5 <sup>1</sup>	R6	S4	S6	S7	S9	S11	Z1	Z2	Z3	W3	W4
$\delta^{34}\text{S}_{\text{VCDT}}$ (‰)	min	6.66	6.88	5.30	5.12	4.94	6.37	5.94	8.63	4.38	9.14	7.31	7.12	4.01	4.87	2.96
	max	11.85	7.38	7.04		6.48	7.45	6.56	12.28	7.36	13.39	9.38	9.57	10.09	7.52	5.17
$\delta^{18}\text{O}_{\text{VSMOW}}$ (‰)	min	6.69	5.97	4.62	5.38	4.82	5.29	3.59	7.45	4.50	9.11	6.43	6.45	6.41	2.69	5.16
	max	13.30	6.42	6.31		5.87	8.48	6.28	11.73	7.70	11.69	8.40	8.66	10.46	3.25	6.73

<sup>1</sup> Isotopic composition of  $\text{SO}_4^{2-}$  was measured only once, in June 2021.

Based on the results of the performed isotopic analyses, one can observe relatively stable values for groundwater samples (W3 and W4) in all three sampling campaigns. Values of  $\delta^{18}\text{O}$  in the W3 sample were the lowest of all the results (from 2.69 to 3.25‰), and  $\delta^{34}\text{S}$  ranged from 4.87 to 7.52‰. In the W4 sample,  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  values were in the ranges of 2.96 to 5.17‰ and 5.16 to 6.73‰, respectively. Water samples collected from the Kozłowa Góra reservoir showed seasonal changes in the isotopic composition of  $\text{SO}_4^{2-}$ . The values of  $\delta^{34}\text{S}$  in the three sampling points (Z1, Z2, and Z3) ranged from 4.01 to 10.09‰, and  $\delta^{18}\text{O}$  ranged from 6.41 to 10.46‰. In general, higher values of  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  were observed in summer compared to the winter sampling campaign. Samples taken from the Brynica river and other streams were characterised by  $\delta^{34}\text{S}$  values ranging from 4.38‰ (S3) to 13.39‰ (S11) and  $\delta^{18}\text{O}$  values ranging from 3.59‰ (S6) to 13.30‰ (R2).

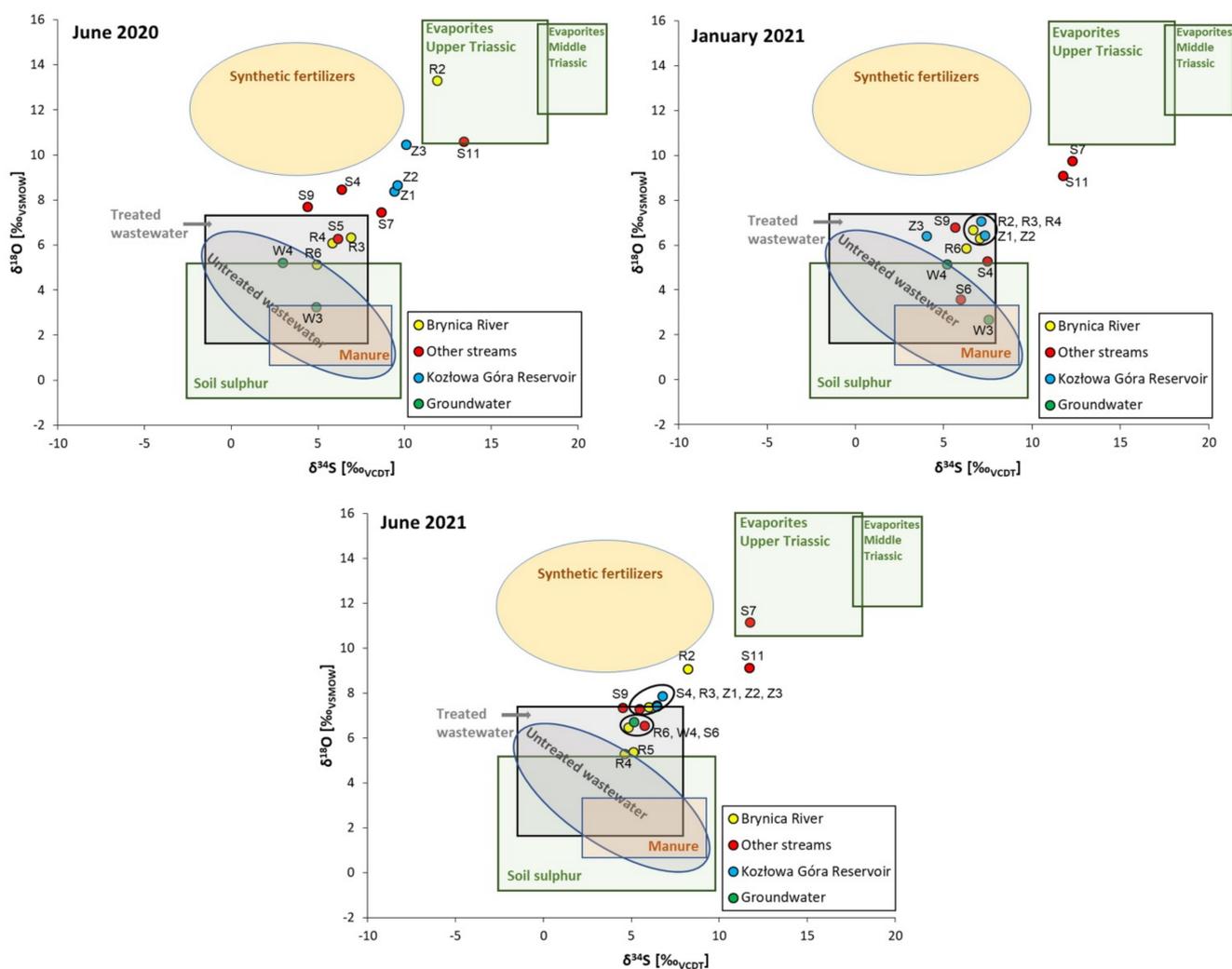
#### 4. Discussion

The Quaternary aquifer represents a shallow groundwater system, which is manifested by a significant variation in measured physicochemical parameters within the study period. In addition, all sampled wells were located within areas of very high groundwater vulnerability (Figure 2).

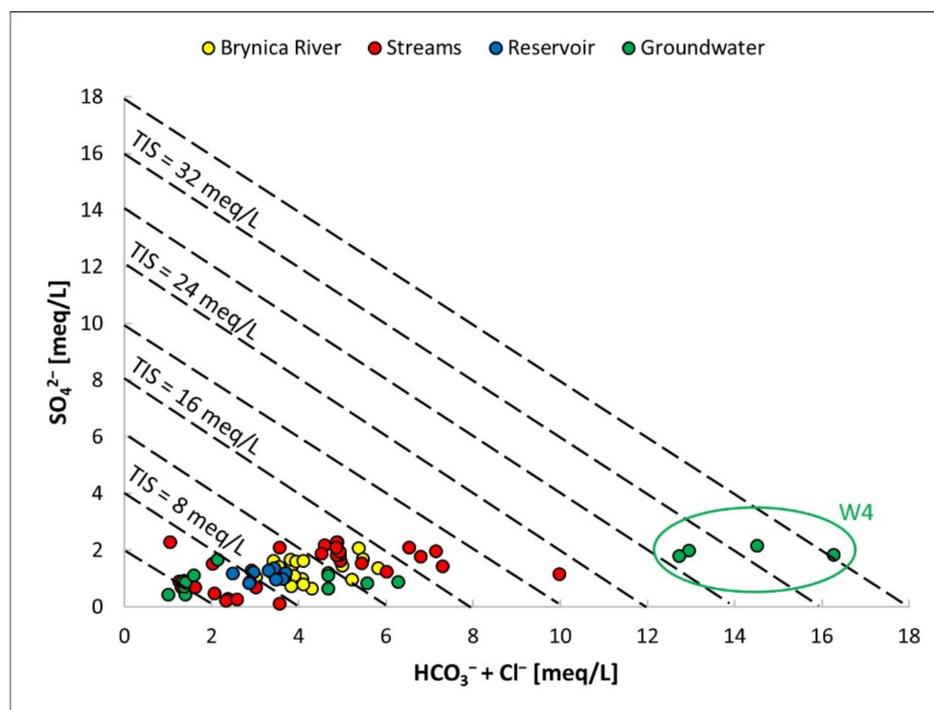
The results indicate that the groundwater contamination level varies depending on the location within the catchment area. The W1 and W2 samples revealed relatively low concentrations of analysed constituents in each season. This is particularly noticeable in the case of W1, as groundwater was characterised by very low EC values and  $\text{Cl}^-$  concentrations, regardless of the period (Tables S2 and S3). Among the groundwater samples, the highest concentrations of  $\text{NO}_3^-$  were reported for W2, which exceeded the drinking water limit (i.e., 50 mg/L [38]) in two sampling campaigns. In the past, elevated concentrations of  $\text{NO}_3^-$  in groundwater from this well were also observed [39]. Given the land use in the vicinity of these wells, the probable source of nitrate is agricultural activities, i.e., the application of manure or fertilisers. Elevated concentration of nitrate was a major concern in W2; therefore, another method, such as  $\text{NO}_3^-$  isotopic studies [40], should be considered to investigate the origin of groundwater contamination in this area. Isotopic analyses of  $\text{NO}_3^-$  were not planned under the current project, but this method should be applied in future studies.

The W3 and W4 wells located in residential areas south of the airport revealed higher EC values and ion concentrations in the groundwater. However, the  $\text{NO}_3^-$  concentration was lower compared to the groundwater sampled in agricultural areas (W2). According to the isotopic results, sulphate in both W3 and W4 originates mainly from wastewater (Figure 3). Most of the catchment area does not have sewers, and domestic sewage is discharged to septic tanks. In this case, leaky septic tanks presumably lead to groundwater contamination. High concentrations of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  and relatively high EC values (up to 1650  $\mu\text{S}/\text{cm}$ ) in W4 seem to confirm this assumption. The correlation diagram of  $\text{SO}_4^{2-}$  vs.  $\text{HCO}_3^- + \text{Cl}^-$  (prepared after [41,42]) confirms the distinct chemistry of groundwater from W4 compared to other collected water samples (Figure 4). Moreover, the results plotted on the TIS diagram show that  $\text{SO}_4^{2-}$ , although originating from different sources, is not responsible for degradation of the water quality and plays a minor role in the observed total ionic salinity. Based on the groundwater level contours and flow directions to the east

of the Kozłowa Góra reservoir, the migration of pollutants from south-eastern residential areas may also influence groundwater quality south of the airport. The observed ion concentrations and parameter values in W3 were not as high as in W4, but the results suggest that the groundwater is of lower quality compared to W1 and W2, mainly due to elevated concentrations of  $\text{PO}_4^{3-}$ . It is noteworthy that only in the W3 sample was  $\text{PO}_4^{3-}$  detected in concentrations exceeding the natural hydrogeological background (i.e., 1 mg/L [43]). Although  $\text{PO}_4^{3-}$  is usually associated with agriculture, it may also come from laundry and dishwashing detergents used in households [44]. Therefore, the presence of  $\text{PO}_4^{3-}$  in domestic sewage and its migration to the aquifer through leaky septic tanks may result in elevated concentrations of  $\text{PO}_4^{3-}$  in groundwater.



**Figure 3.** Isotopic composition of sulphate in surface water and groundwater in the catchment area of the Kozłowa Góra reservoir sampled in June 2020, January 2021, and June 2021. Coloured boxes represent typical isotopic signatures of different  $\text{SO}_4^{2-}$  sources [12,26,45–49]. Isotopic signatures of treated and untreated wastewater and synthetic fertilisers are from another study based on local sources (unpublished).



**Figure 4.** Concentrations of  $\text{SO}_4^{2-}$  vs.  $(\text{HCO}_3^- + \text{Cl}^-)$  in the collected water samples.

Concentrations of major ions in surface water were similar in warm seasons, i.e., summer and early autumn. In winter, some changes were observed in the Brynica river and other streams (Figure 5). In that period, most of the samples revealed higher concentrations of  $\text{Cl}^-$  and  $\text{Na}^+$ , especially in the Brynica river and the Ożarówicki and Nakło streams. An increase in EC values was also observed in winter. The results presented in Figure 4 confirm that  $\text{Cl}^-$  contributes significantly to the total ionic salinity in some of the sampled waters. The mentioned river and streams are the largest ones within the analysed catchment area and intersect major roads at several points. During the winter sampling campaign, de-icing roads could release additional  $\text{Cl}^-$  and  $\text{Na}^+$  into the water environment. At the same time, higher TOC values were reported in winter. This suggests a continuous supply of contaminants to the surface water and slow biodegradation of organic matter due to the prevailing conditions (i.e., low temperatures and reducing conditions). According to isotopic analyses,  $\text{SO}_4^{2-}$  originates primarily from wastewater in winter. Furthermore, no significant changes were observed in  $\text{SO}_4^{2-}$  concentrations ( $<100$  mg/L in most samples), except for the S7 and S11 sampling points. The increase in sulphate concentrations and the distinct isotopic composition suggest mixed pollution sources for these samples. In most cases, the isotopic results of sampled rivers and streams were comparable in winter, whereas in summer seasons,  $\delta^{18}\text{O}$  values were slightly higher (Figure 3). This suggests the application of fertilisers as an additional factor affecting surface water quality in warm seasons. Apart from the isotopic results, the relationship between  $\text{NO}_3^-/\text{Cl}^-$  ratio and  $\text{Cl}^-$  (adapted from [15]) also suggests mixed sources of contamination in sampled waters. In Figure 6, points representing surface waters show diversified relations, ranging between results for highly contaminated groundwater (W4, high values of  $\text{Cl}^-$ ) and groundwater with low anthropogenic impact (e.g., W1, high values of  $\text{NO}_3^-/\text{Cl}^-$  ratio).

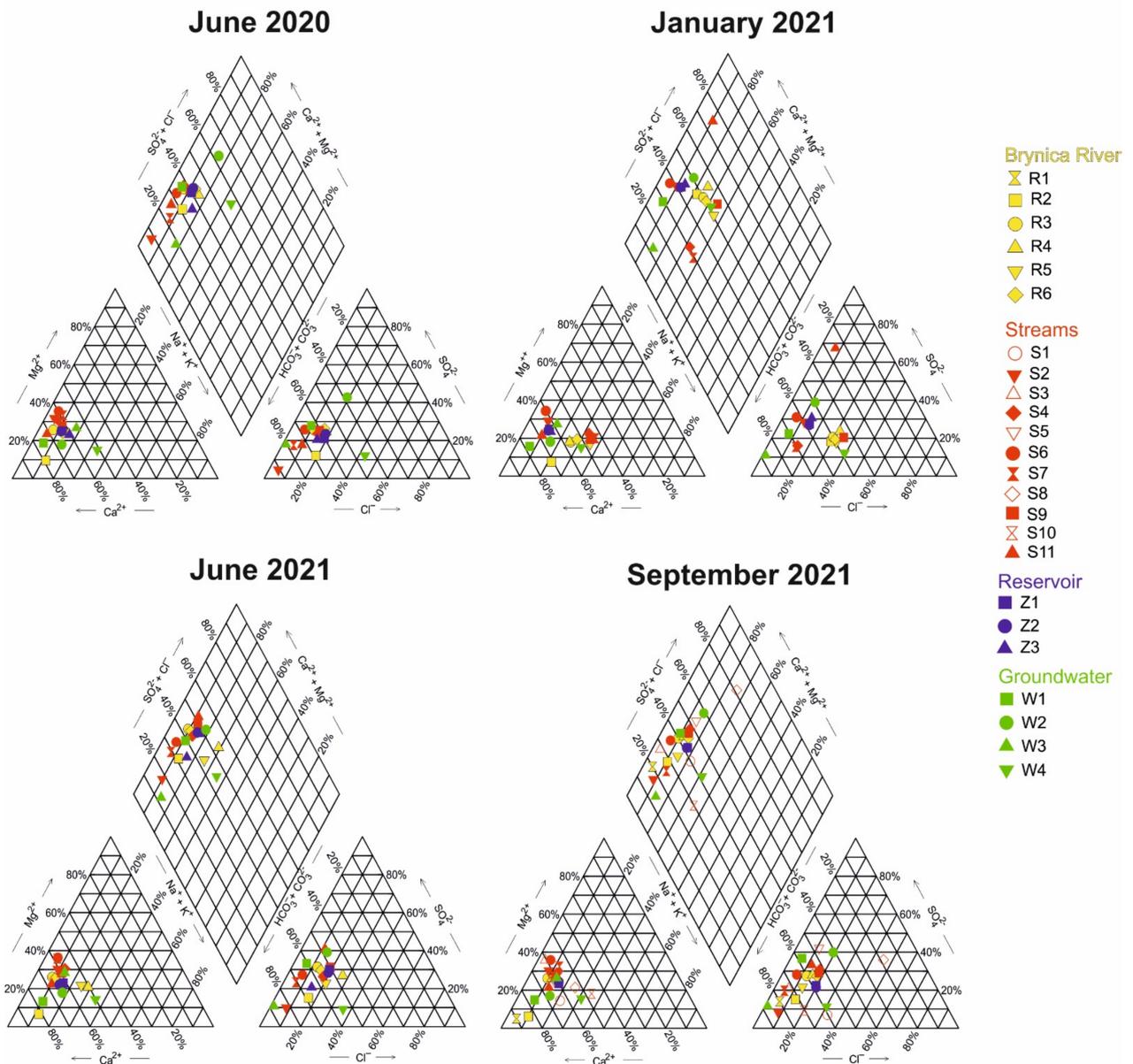


Figure 5. Piper diagrams for water samples collected in four sampling campaigns.

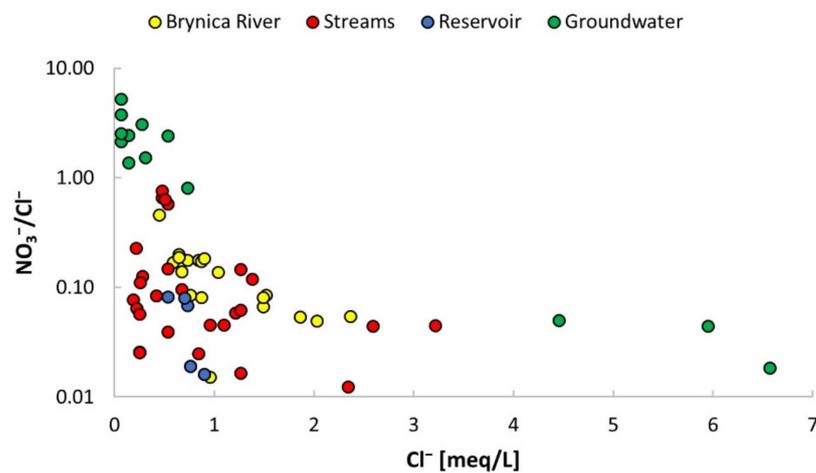


Figure 6. Relationship between  $\text{NO}_3^-/\text{Cl}^-$  ratio and concentrations of  $\text{Cl}^-$ .

As already mentioned, EC values and ion concentrations in surface water were slightly lower in warmer periods. In contrast to the winter sampling, chemical analyses revealed the presence of  $\text{PO}_4^{3-}$  in some river water samples. Although water drained from arable lands may affect the chemical composition of water from the Brynica river (Figure 1),  $\text{PO}_4^{3-}$  occurred in this river, starting from the R4 point, i.e., right below the wastewater discharge from the WWTP “Ożarówice”. The WWTP seems to be the main source of  $\text{PO}_4^{3-}$  in the Brynica river; however, it is noteworthy that in June 2021, this ion was also detected in Brynica’s tributaries, i.e., the Czechówka stream (S3) and the drainage ditch west of the airport (S6). Both streams run across agricultural lands, away from residential areas. Furthermore, low concentrations of dissolved oxygen were observed in the Czechówka stream in the last sampling campaign (3.14–3.73 mg/L), which may indicate decomposition of organic waste (e.g., manure). Therefore, the tributaries may carry contaminants of agricultural origin to the Brynica river between R2 and R3, but their quantities decrease significantly, reaching values below the detection limit, presumably due to dilution. Moreover, a relatively high concentration of  $\text{PO}_4^{3-}$  was reported in the last sampling campaign for the Nakło stream in the vicinity of its spring (S10). The S10 point was surrounded by arable lands. High concentrations of  $\text{NH}_4^+$  and organic matter suggest the agricultural origin of  $\text{PO}_4^{3-}$  in this region. High TOC values may be associated with manure applied on arable lands. As a result of organic matter decomposition,  $\text{NH}_4^+$  is released into the water, and dissolved oxygen occurs in a low concentration (2.60 mg/L). High concentrations of  $\text{NH}_4^+$  and low values of  $\text{NO}_3^-$  in the observed redox conditions ( $E_h = 113$  mV) suggest recent contamination. Interestingly, in the S11 sampling point, located closer to the Nakło stream mouth,  $\text{SO}_4^{2-}$  is characterised with high values of  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$ , close to the ranges for natural sources (Figure 3). Moreover, the S11 water samples revealed low values of parameters, indicating influence of anthropogenic activity, such as  $\text{NO}_3^-$ ,  $\text{Cl}^-$ , and EC. However, elevated concentrations of  $\text{NH}_4^+$  (0.19–0.82 mg/L) and low concentrations of dissolved oxygen (3.73–6.64 mg/L) were observed, which may be associated with the presence of organic matter (TOC = 11–17 mg/L). All facts considered, nutrients entering the Kozłowa Góra reservoir are of a mixed origin and come from both wastewater and agricultural activities.

Some level of diversity was also observed in the distribution of inorganic nitrogen compounds within the catchment area (Figure 7). Three forms, i.e.,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , and  $\text{NH}_4^+$ , were detected above the quantification limits in most river samples. This indicates nitrification/denitrification processes and permanent contamination of surface water [44].

In the north-eastern part of the catchment area, i.e., upstream of the Brynica river, the area is covered mostly by forests and arable lands. Sampling points on the Brynica river in this area (R1 and R2) revealed  $\text{NO}_3^-$  reaching 12.8 mg/L in R1 in September 2021. In natural areas and regions less impacted by anthropogenic activity, such as forests,  $\text{NO}_3^-$  concentrations are lower compared to other land use types [50]. Relatively low concentrations of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  indicate distant contamination sources. R1 and R2 are the sampling points closest to the Brynica’s source (Figure 1). Based on the results obtained in September 2021, ion concentrations in the R1 and R2 samples are similar. Isotopic composition of  $\text{SO}_4^{2-}$  differed depending on the season, in contrast to  $\text{SO}_4^{2-}$  concentrations, which were low in each sampling period (31–47 mg/L). The Brynica river flows across forests and agricultural lands in the northeast, away from residential areas. Therefore, the most probable source of contaminants is agriculture, possibly a mix of synthetic fertilisers and livestock manure.

The agricultural impact is also seen in other streams in the north-eastern part of the catchment area, i.e., Trzonka and Czechówka streams. Although  $\text{NH}_4^+$  and  $\text{NO}_2^-$  concentrations in these streams were similar,  $\text{NO}_3^-$  concentrations were higher in the Czechówka stream, which runs across arable lands, unlike the Trzonka stream (Figure 1). The influence of manure and synthetic fertilisers in summer was confirmed for S4 by  $\text{SO}_4^{2-}$  isotopic studies. Lower concentrations of ions in the Trzonka stream also suggests a lower level of anthropogenic impact.

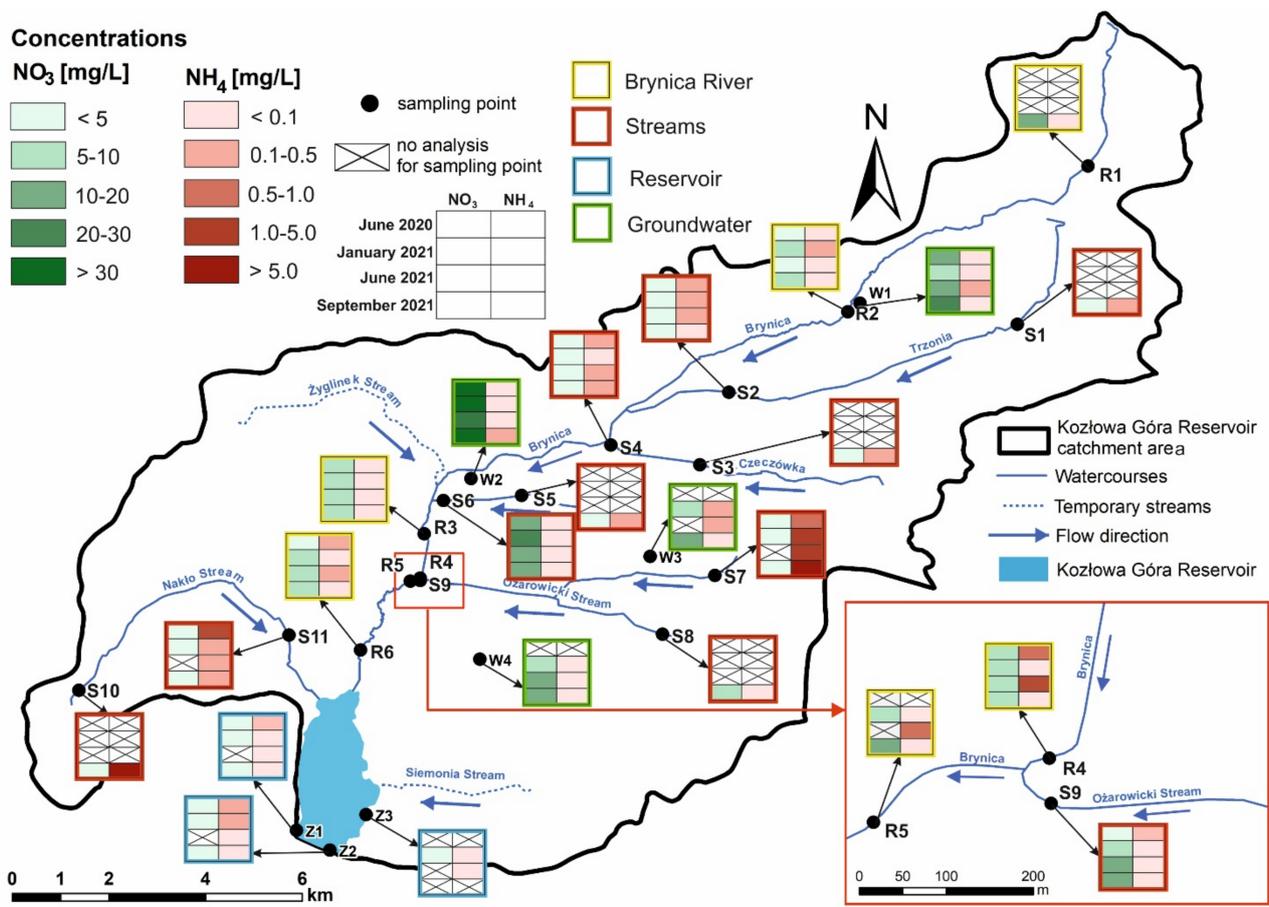


Figure 7. Variations in NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> concentrations within the study area.

In the central part of the catchment area, starting from the R3 point, NO<sub>3</sub><sup>-</sup> concentrations increased in the Brynica river. The R3 sampling point was situated upstream the WWTP “Ożarowice”, and the increase in nitrate concentrations is related to another contamination source. Based on the land-use pattern and the chemical results, the drainage ditch (sampled as S5 and S6) is likely to carry a certain amount of NO<sub>3</sub><sup>-</sup> to the Brynica river. Based on the isotopic analyses, the water quality of the ditch could be deteriorated by wastewater, possibly coming from the airport area.

Downstream the WWTP discharge (R4), NO<sub>3</sub><sup>-</sup> concentrations remained similar to upstream the WWTP (R3). However, NH<sub>4</sub><sup>+</sup> concentrations increased (up to 0.85 mg/L), which resulted from recent contamination caused by the wastewater discharge. In this part of the catchment area, the Ożarowicki stream influences Brynica’s quality, as it provides an additional load of NO<sub>3</sub><sup>-</sup> and slightly reduces NH<sub>4</sub><sup>+</sup> concentrations due to water mixing. Presumably, a portion of contamination in the Ożarowicki stream is derived from the Siedliska channel, which is the drainage ditch on the south of the airport. The S7 sample revealed the dominance of NH<sub>4</sub><sup>+</sup> over nitrate, regardless of the season. In this stream, the most reduced conditions were also observed. Isotopic analyses of sulphate revealed higher values of δ<sup>34</sup>S and δ<sup>18</sup>O in January 2021 and June 2021. Although the results suggest a natural origin of SO<sub>4</sub><sup>2-</sup> (Figure 3), it seems unlikely, considering the contamination sources in the vicinity of the S7 sampling point. This sample was collected at a short distance from a wastewater discharge identified at the Siedliska channel, which significantly influences the water quality. The wastewater probably comes from the areas of car parks next to the airport and/or from the allotments west of the Siedliska channel. Elevated concentrations of ions and TOC indicate the influence of wastewater from a local contamination source, which is the reason for a specific isotopic signature different from the literature values. In the Ożarowicki stream alone, the redox conditions are more oxidising, and other potential

contamination sources are possible, such as another wastewater discharge and arable lands (Figure 1).

The quality of the R6 sample reflects a combined impact of the Brynica river and its tributaries. Isotopic results showed that the  $\delta^{18}\text{O}$  and  $\delta^{34}\text{S}$  values changed gradually downstream the river.  $\text{SO}_4^{2-}$  and other ions are of mixed origin in R6. Inorganic nitrogen compounds are not as abundant as in Brynica close to the WWTP "Ożarówice", but the river is still the main input of contamination to the reservoir. Another tributary of the Kozłowa Góra, the Nakło stream, supplies the  $\text{NH}_4^+$  load on a larger scale compared to the Brynica river (Figure 7). This points to a local source, probably of agricultural origin. Redox conditions in the Nakło stream differed throughout the year, but were reduced in each sampling campaign as compared to Brynica.

Undoubtedly, the water quality of the rivers affects the chemical composition of the reservoir. However, both inflowing streams and groundwater recharge the Kozłowa Góra reservoir; thus, contaminants may enter the surface water body along with the groundwater. The groundwater level contours show higher hydraulic gradient on the southeast, which means that this part of the catchment area contributes to significant recharge of the reservoir by groundwater. This implies that contaminants from agricultural and residential areas in this part of the study area can enter the reservoir (Figure 1). Migration of contaminants to the reservoir via rivers, groundwater, and surface run-off may be responsible for water quality deterioration, but the observed contamination level of the reservoir water is lower compared to its tributaries and to groundwater. This means that natural processes must influence the chemical composition of the reservoir water and lead to a decrease in contaminant concentrations.

The Kozłowa Góra reservoir was sampled at three of its banks (west, south, and east), and no significant differences in the chemical composition of water were found. The results of  $\text{SO}_4^{2-}$  isotopic analyses indicate that this ion originates partially from agricultural activities in summer and predominantly from wastewater discharges in winter. Although the Brynica river is considered to have a significant impact on the water quality of the reservoir, other factors seem to play an important role in the formation of the chemical composition of the reservoir water. Ions related to agriculture were either not present in the reservoir water ( $\text{PO}_4^{3-}$ ) or occurred in low concentrations ( $\text{NO}_3^-$ ). The highest concentrations of  $\text{NO}_3^-$  in the reservoir water were reported in winter, but they were still considerably lower in comparison to most of the river water samples. One of the processes altering water chemistry in the reservoir is dilution by the Nakło stream and rainwater. Chemical results for the Nakło stream (S11) revealed much lower EC values and concentrations of most analysed ions than in the Brynica river (R6). Moreover, archival data for this area showed low concentrations of  $\text{NO}_3^-$  in precipitation (the sum of  $\text{NO}_3^-$  and  $\text{NO}_2^- = 0.32 \text{ mg/L}$ , [51]). This suggests that rainwater could partially contribute to dilution and decrease  $\text{NO}_3^-$  concentrations in the reservoir. This involves other constituents as well.

The reservoir is partially recharged by groundwater, mainly at its eastern bank. Previous studies conducted in this area revealed the influence of groundwater recharge on water chemistry in the eastern part of the Kozłowa Góra reservoir, resulting in elevated concentrations of  $\text{NO}_3^-$  in the north-eastern part of the reservoir compared to the south-western part [32]. This proves that contaminants may reach the reservoir through groundwater recharge. Based on the study results and archival data [32], processes other than dilution influence the chemical composition of the reservoir water. These can be biochemical processes occurring in plant organisms. Dissolved oxygen in the reservoir occurred in higher concentrations compared to the Brynica river and other streams, regardless of the season. As the primary source of  $\text{O}_2$  is photosynthesis, the results confirm the role of phytoplankton and aquatic plants in the evolution of the reservoir water chemistry. Moreover, plant organisms consume a portion of nutrients.  $\text{NO}_3^-$  concentrations in surface water bodies may vary throughout the year, as the growth of plant organisms differs depending on the season. In winter, plant growth and development are slower, and thus organisms absorb a smaller amount of  $\text{NO}_3^-$  [52–54].

## 5. Conclusions

The application of combined chemical and isotopic analyses enabled more accurate identification of the anthropogenic factors affecting water quality within the Kozłowa Góra catchment area. The distribution of ion concentrations in the sampled water shows that the contamination risk and contamination level differ depending on land use and the season. Groundwater contamination is a result of a poorly developed sewer system. The highest level of groundwater contamination was observed in residential areas located to the east of the Kozłowa Góra reservoir. Isotopic analyses of  $\text{SO}_4^{2-}$  confirmed that the deteriorated water quality in some streams, including the Brynica river, is related mainly to wastewater discharge. In some parts of the catchment area, the overlapping effects of agricultural activities and wastewater discharge are noticeable in warm seasons. Isotopic studies of  $\text{SO}_4^{2-}$  facilitated interpretation of contamination origin; however, constituents other than  $\text{SO}_4^{2-}$  played an important role in water quality, e.g.,  $\text{Cl}^-$  and nutrients. Both the isotopic results and relations between the analysed ions indicated a mixed origin of contamination at some sampling points. The measurement of inorganic nitrogen compounds revealed the highest concentrations of  $\text{NO}_3^-$  in groundwater. Among the surface water samples, the lowest water quality, manifested by high EC values and ion concentrations, was observed in the Brynica river, the Ożarówicki stream, and the Siedliska channel, i.e., streams where wastewater discharges were identified. Elevated concentrations of  $\text{NH}_4^+$  and TOC, as well as the presence of the other nitrogen compounds ( $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ), confirm long-term contamination and the role of denitrification and nitrification processes in the modification of the chemical composition of the river water. Although the Brynica river carries a significant part of the analysed constituents, groundwater recharge, precipitation, inflow of the Nakło stream, and processes occurring in the reservoir control contaminant concentrations in the Kozłowa Góra, which is a drinking water source for the local community.

Undoubtedly, the application of the two research methods facilitated understanding of the types and the range of human impact on the water environment and water quality. Nevertheless, the involvement of another method, e.g., isotopic analysis of  $\text{NO}_3^-$ , would allow for a more precise assessment. This primarily concerns streams that run across areas representing different land-use types or reveal misleading results for  $\text{SO}_4^{2-}$  isotopic composition.

The identification of contamination sources responsible for water quality deterioration in different parts of the catchment area can be used in further studies within this area, such as the monitoring of microcontaminants in the water environment. The knowledge on existing risks and contamination sources may prove useful in a future interpretation of the origin and migration patterns of monitored substances.

**Supplementary Materials:** The following are available online at <https://www.mdpi.com/article/10.3390/w14060846/s1>, Table S1: Methods used in measurements of parameters, Table S2: The results of physico-chemical parameters in sampled water (Date: I—June 2020; II—January 2021; III—June 2021; IV—September 2021), Table S3: The results of chemical analyses of sampled water (Date: I—June 2020; II—January 2021; III—June 2021; IV—September 2021), Table S4: The results of nitrogen compound analyses in sampled water (Date: I—June 2020; II—January 2021; III—June 2021; IV—September 2021), Table S5: The results of isotopic analyses of S and O in  $\text{SO}_4$  in sampled water (Date: I—June 2020; II—January 2021; III—June 2021; IV—September 2021).

**Author Contributions:** Conceptualization, K.Ś.; methodology, K.Ś. and S.J.-K.; software, K.Ś. and S.J.-K.; analysis, K.Ś. and S.J.-K.; investigation, K.Ś. and S.J.-K.; resources, K.Ś. and S.J.-K.; data curation, K.Ś.; writing—original draft preparation, K.Ś. and S.J.-K.; writing—review and editing, S.J.-K. and A.J.W.; visualization, K.Ś. and S.J.-K.; supervision, K.Ś. and A.J.W. All authors have read and agreed to the published version of the manuscript.

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**Data Availability Statement:** All data presented in this study are available within this article.

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