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Identification of Sulfate Sources and Biogeochemical Processes in an Aquifer Affected by Peatland: Insights from Monitoring the Isotopic Composition of Groundwater Sulfate in Kampinos National Park, Poland

Adam Porowski [1,*], **Dorota Porowska** [2] **and Stanislaw Halas** [3,†]

[1] Institute of Geological Sciences Polish Academy of Sciences (ING PAN), Ul. Twarda 51/55, 00-818 Warszawa, Poland
[2] Faculty of Geology, University of Warsaw, Ul. Żwirki i Wigury 93, 02-089 Warsaw, Poland
[3] Mass Spectrometry Laboratory, Maria Curie-Skłodowska University, plac M. Curie-Skłodowskiej 1, 20-031 Lublin, Poland
* Correspondence: adamp@twarda.pan.pl
† Stanislaw Halas passed away in 2017.

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Abstract: Temporal and spatial variations of the concentration and the isotopic composition of groundwater sulfate in an unconfined sandy aquifer covered by peatland have been studied to better understand the sources and biogeochemical processes that affect sulfate distribution in shallow groundwater systems influenced by organic rich sediments. The groundwater monitoring was carried out for one year at hydrogeological station Pożary located within the protected zone of the Kampinos National Park. Sulfur ($\delta^{34}S_{SO4}$) and oxygen ($\delta^{18}O_{SO4}$) isotopic composition of dissolved sulfates were analyzed together with oxygen ($\delta^{18}O_{H2O}$) and hydrogen ($\delta^{2}H_{H2O}$) isotopic composition of water and major ions concentration at monthly intervals. The research revealed three main sources of sulfates dissolved in groundwater, namely, (a) atmospheric sulfates—supplied to the aquifer by atmospheric deposition (rain and snow melt), (b) sulfates formed by dissolution of evaporite sulfate minerals, mainly gypsum—considerably enriched in ^{34}S and ^{18}O, and (c) sulfate formed during oxidation of reduced inorganic sulfur compounds (RIS), mainly pyrite—depleted in ^{34}S and ^{18}O. The final isotopic composition and concentration of dissolved SO_4^{2-} in groundwater are the result of overlapping processes of dissimilatory sulfate reduction, oxidation of sulfide minerals, and mixing of water in aquifer profile.

Keywords: oxygen isotopes; sulfur isotopes; isotopic composition of water; bacterial sulfate reduction; sulfide oxidation; atmospheric sulfate; peatland; unconfined aquifer; mineralization of organic matter

1. Introduction

Organic-rich sediments in hydrogeological profile, their high productivity and complex biogeochemistry have a globally significant influence on the quality of adjacent groundwaters, their chemical composition, trace elements cycling and the composition of atmospheric trace gases [1]. Wetlands, bogs, fens, and peatlands, which cover nearly 5% of the Earth's surface, are such ecosystems where the accumulation of reactive organic matter always implies a series of redox processes which control not only the content of carbon in groundwater but also the distribution of major dissolved compounds, including, for example, nitrogen or sulfur species [1–13]. Peatlands are very heterogeneous environments: inside the peatland bed, macro and micro gradients of redox conditions enable the development of a highly diverse microbial community capable of different redox reactions occurring simultaneously (e.g., nitrification, denitrification, sulfate reduction, oxidation of reduced inorganic sulfides, etc.) on a small spatial scale [7,9,10]. The biotic and abiotic transformations of sulfur compounds are interconnected with other geochemical processes through their common substrates or products. Sulfates reduction in peatlands can result in Eh and pH changes in groundwater, alkalinity generation, and C transformation, and, indirectly, the mobilization and removal of nutrients such as N, P, and C [2,3,6,7]. Moreover, sulfide as a product of dissimilatory sulfate reduction may remove heavy metals contained in waters via the formation of metal sulfides.

Numerous studies concerning wetland systems are focused first of all on the investigation of sulfur compounds transformation, sulfate reduction and generation directly in the organic-reach beds under environmentally relevant conditions in order to better understand the overall sulfur cycle dynamic and net sulfur compounds storage within freshwater peatlands [1,7,9,10,13,14]. Some of these researches are aimed at the direct application of wetlands to natural restoration of water quality e.g., [1,9]. An important part of the sulfur cycle in peatland systems involves the formation and sink of the organic sulfur species, the formation of biogenic minerals, and the interaction between mineral matter and organic matter [4,6,10].

Stable isotopes of O and S are used first of all to investigate the sulfate sources, the sulfate reduction and oxidation zones in the peat, and to compare sulfate sources in various wetland systems often located in different hydrogeological and climatic conditions [4,5,7,14]. Isotopic composition of sulfates is also used to explain the mechanisms and sources of SO_4^{2-} released from peatlands to streams, lakes, or soils [11,13,14].

Still insufficient attention is addressed to investigation the long term, direct influence of the peatland ecosystems on the geochemistry of groundwater masses in adjacent aquifers, especially in changing climate conditions. In this study we utilize an approach involving O and S isotopic composition of sulfates to identify the sulfate sources and biogeochemical processes that affect sulfate distribution in a shallow alluvial aquifer covered by peatland. The research was performed at the Pożary monitoring station, located in an area of Holocene peats of the Vistula River terrace in the Kampinos National Park, Central Poland (52°17′5″ N, 20°29′4″ E). The monitoring station was equipped with four piezometers installed at different depths in a sandy aquifer, namely 2.1, 3.3, 4.75, and 8.35 m (Figure 1). A previous study performed in this area by Porowska and Lesniak [15] focused on the distribution of dissolved inorganic carbon (DIC) and its C isotope composition, as well as on dissolved organic carbon (DOC) and dissolved oxygen (DO) in the aquifer profile. The study indicated that the mineralization of organic matter and the presence of organic carbon in the geological profile may have a significant effect on the biogeochemical processes controlling the chemical composition of groundwater in the aquifer. For example, the concentration of dissolved sulfate showed one of the largest seasonal variations in comparison to other major constituents. Seasonal and spatial variation of sulfates concentration and their stable O and S isotopic compositions is an important tracer of the sulfate sources, the biogeochemical processes in groundwater environment, and the geochemical conditions in the aquifer [4,11,12].

The major forms of sulfur in the hydrogeological subsurface environment include sulfate (SO_4^{2-}) and sulfide (HS^-) minerals, sulfate and sulfide dissolved in water, and hydrogen sulfide gas (H_2S) and sulfur in organic compounds (DOS) [2,3]. These various sources of sulfur may participate in the evolution of the chemical composition of water masses below the ground. Dissolved sulfates (SO_4^{2-}) are usually the dominant form of sulfur, and are one of the most common sulfur species in various natural groundwater environments. The geochemistry of sulfur is complicated by its wide range of oxidation states. However, the key reaction in the global sulfur cycle, i.e., the reduction of sulfate (SO_4^{2-} to hydrogen sulfide (H_2S), may be identified by the distribution of sulfate concentrations and its O and S isotopic composition. When sulfate ions reach the anaerobic zone within the saturated soil, peatland or groundwater, the sulfate reducing bacteria start producing sulfides (S^{2-}); consequently, the concentration of dissolved SO_4^{2-} in water decreases and considerable fractionation of $^{34}S/^{32}S$ and

$^{18}O/^{16}O$ isotope occurs. The residual SO_4^{2-} becomes progressively enriched in the heavy isotopes ^{18}O and ^{34}S [5,7,9,11].

This paper gives the results of a thorough one-year monitoring study of the concentration of dissolved sulfate and its sulfur ($\delta^{34}S$) and oxygen ($\delta^{18}O$) isotopic composition together with the chemical and isotopic ($\delta^{2}H$ and $\delta^{18}O$) composition of groundwater in the aquifer vertical profile. The performed study had three principal objectives, namely (i) to distinguish between sulfate sources in the groundwater of the shallow unconfined aquifer covered by peatland, (ii) to identify the biogeochemical processes controlling the distribution and isotopic transformation of sulfates in the shallow groundwater system, and (iii) to evaluate the influence of organic-rich sediments on the geochemical conditions in the groundwater flow system. Explaining these phenomena is essential to obtain a better understanding of the sulfur cycling between the peat and the groundwater, and the influence of organic-rich sediments on the evolution of water chemistry in adjacent unconfined aquifers.

2. Study Area and Hydrogeological Settings

Kampinos National Park, located several kilometers northwest of Warsaw, Poland, is a special protection area where extensive ecological and climatic studies have been conducted for several years. There is one fully equipped meteorological station in this area, as well as several smaller research stations where only piezometers or observation wells are installed to monitor the level and the quality of groundwater for the needs of the Polish National Groundwater Monitoring Network. Our investigation was performed at the Pożary research station, located in an area of Holocene peats on the Vistula River terrace (Figure 1) [16]. The research station was equipped with four piezometers installed in the same aquifer at different depths. The shallowest one (depth: 2.10 m) was installed at a contact between fine- and medium-grained sands. The next two piezometers (depths: 3.30 and 4.75 m) were set into medium-grained sands, and the deepest one (depth: 8.35 m) was set into coarse-grained sands and gravels (Figure 1). The organic matter was accumulated within a peat layer with a thickness of 0.5 m in the uppermost part of the geological profile, within the vadose zone.

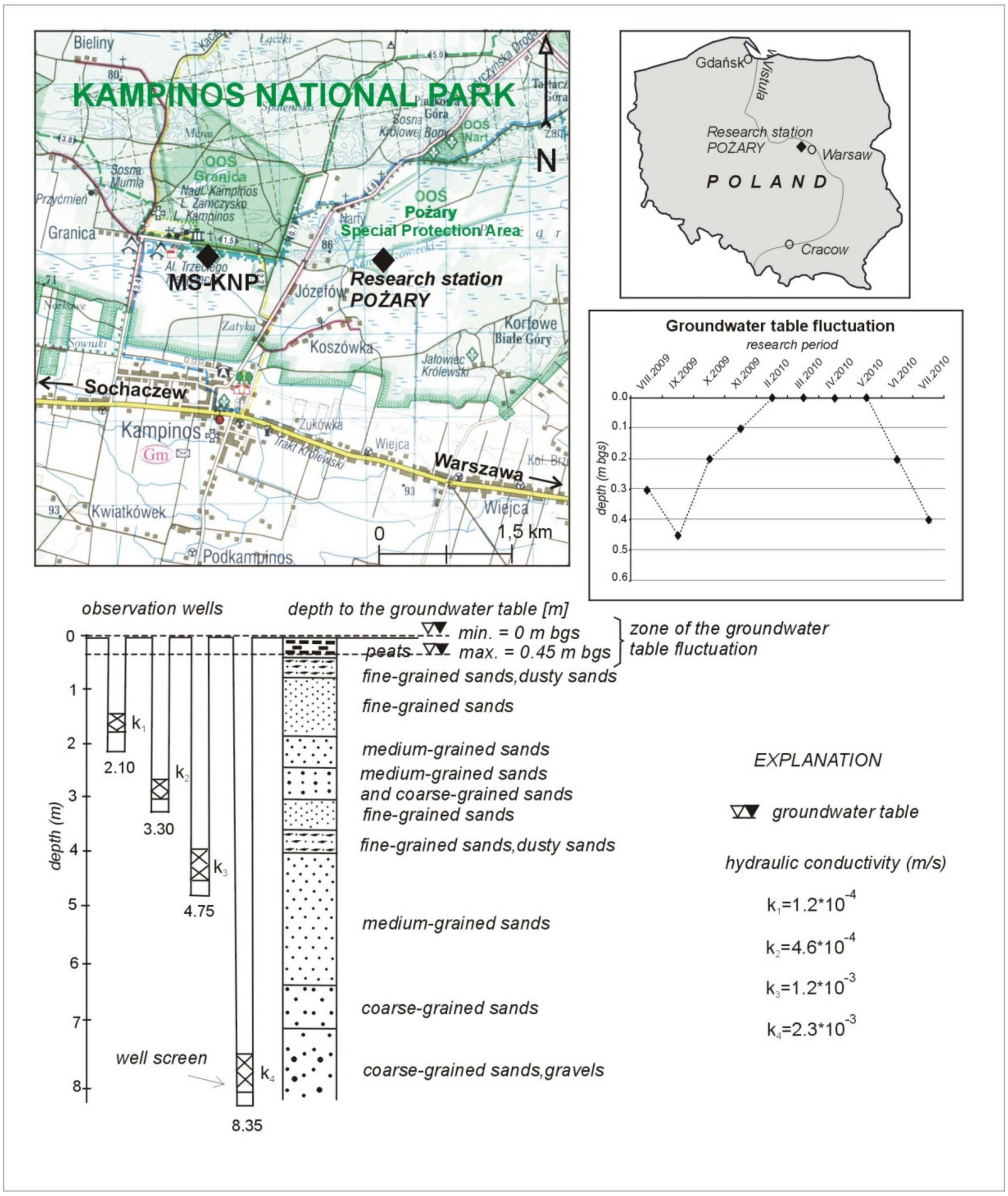

Figure 1. Location of the Pożary research station, geologic profile, and arrangement of piezometers for groundwater sampling. MS-KNP—meteorological station of Integrated Monitoring of the Natural Environment of the Kampinos National Park (KNP). Geological profile after Fic and Wierzbicki [17] modified by the authors.

Depending on the season and position of the groundwater level, the layer of peat may occur within either the saturation or vadose zone. During the one year of monitoring studies, the groundwater table fluctuated in the range from 0.0 to 0.45 m below ground surface (bgs). Generally, the groundwater level was above the peat surface during winter and spring, i.e., from February 2009 to May 2010, and was below the ground surface at depths from 0.10 to 0.45 m during summer and autumn, i.e., from August 2009 to November 2009 and from June 2010 to July 2010. It is important to note that the capillary fringe in the peat can extend to 0.2 m above the water table [18]. The hydraulic conductivity in the aquifer increases with depth, from $1.2 \cdot 10^{-4}$ to $2.3 \cdot 10^{-3}$ m/s (Figure 1)

3. Materials and Methods

Samples of groundwater were collected from four observation piezometers installed close to each other in the same aquifer. The piezometers were simple PVC standpipes slotted in the saturated zone at various depths, i.e., 2.1 (the shallowest one), 3.30, 4.75, and 8.35 m (the deepest one). The samples of groundwater were collected at monthly intervals from August 2009 to July 2010. In December 2009 and January 2010, the field campaign was suspended due to harsh weather and thick snow cover, which caused the piezometers and groundwater to be unavailable for sampling. To collect representative samples of water from the aquifer, sampling procedures were strictly followed [19–22]. Field measurements were made of basic physicochemical water quality parameters such as temperature (T), pH, electrical conductivity (EC), and oxygen/reduction potential (ORP), using a small electrical water pump, an in-line flow-through cell, and portable meters such as a HQ40D multi meter (Hach®, Hach-Lange GMBH, Berlin, Germany) equipped with Intellical™ (Hach-Lange GMBH, Berlin, Germany) pH, EC, and ORP electrodes with temperature sensors. The EC and ORP values were used to determine when formation-quality water was available for sample collection [20].

For chemical analysis, water was filtered through 0.7 µm GF/F (glass microfiber) Whatman's syringe filters and collected in polyethylene bottles—150 mL aliquots for anions and 30 mL aliquots for cations. Then, bottles were put into a refrigerator and delivered to the laboratory within 48 h. A High-Performance Liquid Chromatography (HPLC) method was used for major anion analysis (except bicarbonates and nitrates), and the Inductively Coupled Plasma Absorption Emission Spectrometry (ICP-AES) method was used for cation analysis. Uncertainties in the determination of major ions, as reported by the laboratory, were in the range 5–10%. Bicarbonates were determined by the potentiometric titration method, and concentrations of NO_3^- were determined in the field using a Slandi LF portable spectrophotometer (SLANDI®, SLANDI sp. z o.o., Michalowice, Poland). The anion-cation charge balance method was followed to assess the accuracy of the chemical analyses: for all water samples, the charge balance was less than 5%. The chemical analyses were performed at the Institute of Environmental Protection, National Research Institute in Warsaw, Poland. Table 1 shows a compilation of the physicochemical data obtained for groundwater.

Water samples for the analysis of oxygen stable isotope and hydrogen composition were collected in 30 mL amber-glass bottles and tightly sealed. Routine mass spectrometric techniques were applied for the determination of the isotopic composition of water, namely an off-line technique of CO_2–H_2O equilibration [23,24] to determine $^{18}O/^{16}O$ ratios, and an off-line static batch water reduction on hot zinc to determine $^{2}H/^{1}H$ ratios [25–28]. The results were reported using δ notation with respect to the VSMOW international standard. Normalization of measured data was perform according to three international standards, namely: VSMOW ($\delta^2H = 0.0‰$, $\delta^{18}O = 0.0‰$), VSLAP ($\delta^2H = -427.5‰$, $\delta^{18}O = -55.50‰$), and GISP ($\delta^2H = -189.5‰$, $\delta^{18}O = -24.76‰$). The precision of the measurements was ±0.08‰ and ±0.9‰ for $\delta^{18}O$ and δ^2H, respectively. The precision of the isotopic measurements was calculated based on long-term measurements of international reference materials as well as our internal standard water. The analyses were performed at the Institute of Geological Sciences of the Polish Academy of Sciences (ING PAN) in Warsaw, Poland.

Water samples for the analysis of the stable isotopes of sulfur ($^{34}S/^{32}S$ ratio) and oxygen ($^{18}O/^{16}O$ ratio) of dissolved sulfates were collected in HDPE bottles with volumes of 1 or 2 L depending on SO_4^{2-} concentration, which was determined in the field using a Slandi LF portable spectrophotometer. Afterwards, the water samples were acidified to a pH of 2–3 and an appropriate amount of 10% BaCl solution was added in order to precipitate all dissolved sulfates as $BaSO_4$ [29]. A method based on the reduction of $BaSO_4$ with graphite to CO_2 was applied to determine the $^{18}O/^{16}O$ ratio of sulfates [30,31], while a method for the conversion of $BaSO_4$ to SO_2 at 850 °C was applied to determine the $^{34}S/^{32}S$ ratio [32]. The results of the analysis were reported using δ notation: $\delta^{18}O$ with respect to VSMOW and $\delta^{34}S$ with respect to VCDT. Normalization of measured data was perform according to international standards, namely: NBS-127 ($\delta^{34}S = +20.3‰$ VCDT, $\delta^{18}O = +9.3‰$ VSMOW) and IAEA-SO6 ($\delta^{34}S = -34.1‰$ VCDT, $\delta^{18}O = -11.35‰$ VSMOW). The precision of the measurements was ±0.1 ‰ for both $\delta^{18}O$ and $\delta^{34}S$. The analyses of the isotopic composition of sulfates were performed in the Laboratory of Mass Spectrometry at the Institute of Physics UMCS, Lublin, Poland. Table 2 shows a compilation of the isotopic data obtained for groundwater.

Table 1. Chemical composition of atmospheric precipitation and groundwater from piezometers in the Pożary research station. Rainwater is presented for depth 0.0 m. *nd*—not detected; *na*—not analyzed; *<0.5*—below detection limit.

Date	**D**	**T**	**pH**	**Eh**	**SC**	**Ca^{2+}**	**Mg^{2+}**	**Na^{+}**	**K^{+}**	**HCO_3^{-}**	**SO_4^{2-}**	**Cl^{-}**	**NO_3^{-}**	**$NH4^{+}$**	**TDS**
	(m)	**(°C)**	**(–)**	**(mV)**	**(uS/cm)**	**(mg/dm^3)**									
IX.2009	rain	10	5.87	328	52	3.9	0.4	1.4	2.1	8.6	6.1	3.3	0.6	2.3	28.7
	2.1	10.1	7.06	−28	741	124.0	21.2	11.2	1.2	441.9	54.0	37.6	*<0.5*	*na*	691.1
	3.3	10.8	6.66	31	512	93.0	7.2	8.7	1.7	172.0	62.0	58.3	*<0.5*	*na*	402.9
	4.75	10.5	6.68	23	484	102.0	12.2	9.6	0.2	241.0	63.0	19.5	*<0.5*	*na*	447.5
	8.35	9.4	6.74	25	750	138.0	8.4	9.7	1.0	322.0	105.0	40.8	*<0.5*	*na*	624.9
X.2009	rain	9.5	5.74	298	44	3.0	0.4	1.1	0.8	*nd*	11.5	4.0	0.9	2.0	23.7
	2.1	9.4	7.05	−14	758	125.0	20.6	12.5	2.7	431.8	55.1	35.5	*<0.5*	*na*	683.2
	3.3	9.5	6.83	35	521	96.7	11.6	8.9	1.7	222.8	68.0	49.5	*<0.5*	*na*	459.2
	4.75	9.5	6.71	26	489	104.6	12.1	9.1	0.2	244.0	65.0	20.3	*<0.5*	*na*	455.3
	8.35	8.9	6.97	23	702	116.0	12.7	9.8	0.8	326.0	82.0	40.5	*<0.5*	*na*	587.8
XI.2009	rain	10	5.65	278	45	4.1	0.5	1.0	0.4	*nd*	14.2	5.5	0.79	1.1	27.59
	2.1	10.7	7.16	5	752	122.7	23.2	14.9	3.4	416.2	60.4	50.5	*<0.5*	*na*	691.3
	3.3	9.2	6.83	26	528	109.0	9.2	11.6	1.3	199.6	87.2	60.5	*<0.5*	*na*	478.4
	4.75	9.6	6.73	14	499	98.9	8.5	9.4	0.2	221.5	62.1	28.0	*<0.5*	*na*	428.6
	8.35	9.3	6.93	24	708	135.5	12.3	4.3	0.6	349.7	80.0	43.2	*<0.5*	*na*	625.6
III.2010	rain	12	4.44	257	18	0.5	0.1	0.6	0.3	*nd*	2.1	3.5	0.67	1.0	8.77
	2.1	13.1	7.1	49	780	130.0	25.9	11.9	1.4	423.7	59.1	34.5	*<0.5*	*na*	686.5
	3.3	10.9	6.78	73	545	101.0	8.0	8.8	0.3	161.5	113.2	52.9	*<0.5*	*na*	445.7
	4.75	11.4	6.56	84	544	103.0	8.3	12.1	0.2	255.7	62.2	22.0	*<0.5*	*na*	463.5
	8.35	12.4	6.89	105	749	144.0	15.2	9.6	0.4	374.9	69.5	60.1	*<0.5*	*na*	673.7
VI.2010	rain	15	5.22	315	58	1.7	0.7	1.1	3.1	1.0	7.1	6.0	1.27	5.1	27.07
	2.1	15.3	7.09	60	776	129.0	27.5	15.2	0.9	430.9	53.3	33.3	*<0.5*	*na*	690.1
	3.3	15.3	6.95	106	560	104.0	8.1	11.5	0.2	186.0	94.2	36.4	*<0.5*	*na*	440.4
	4.75	14.5	6.65	131	591	111.0	9.1	11.5	0.3	277.0	58.2	29.7	*<0.5*	*na*	496.8
	8.35	15.8	6.79	100	795	149.0	15.9	13.0	0.3	392.0	51.8	39.3	*<0.5*	*na*	661.3
VII.2010	rain	16	5.59	292	35	1.3	0.2	0.5	1.3	1.1	4.7	4.0	0.60	1.8	15.5
	2.1	15.7	7.06	55	759	133.0	27.3	12.6	1.5	420.6	50.3	29.3	*<0.5*	*na*	674.6
	3.3	17.2	6.95	83	542	106.0	8.0	9.3	0.2	198.6	81.4	39.0	*<0.5*	*na*	442.5
	4.75	15.1	6.69	109	511	104.0	8.1	8.3	0.2	245.5	52.0	21.0	*<0.5*	*na*	439.1
	8.35	16.1	6.88	86	731	147.0	15.6	10.3	0.2	383.0	67.4	48.4	*<0.5*	*na*	671.9

Table 2. The isotopic composition of groundwater and dissolved sulfates in the Pożary aquifer at monitored depths throughout the observation period. *na*—not analyzed.

Date	**D**	**δ^{18}O H_2O**	**δ^{2}H H_2O**	**δ^{18}O SO_4**	**δ^{34}S SO_4**	**$SO_4{}^{2-}$**	**Date**	**D**	**δ^{18}O H_2O**	**δ^{2}H H_2O**	**δ^{18}O SO_4**	**δ^{34}S SO_4**	**$SO_4{}^{2-}$**
	(m)	**(‰) vs. VSMOW**			**(‰) vs. VCDT**	**(mg/dm^3)**		**(m)**	**(‰) vs. VSMOW**			**(‰) vs. VCDT**	**(mg/dm^3)**
VIII.2009	rain	−7.48	−55.4	*na*	*na*	2.3	II.2010	snow	−18.29	−148.0	13.2	8.8	3.65
	2.1	−8.48	−67.0	13.0	15.8	49.0		2.1	−9.11	−73.7	15.4	19.6	72.0
	3.3	−8.57	−66.5	7.7	4.8	110.0		3.3	−8.45	−68.1	7.8	3.4	115.0
	4.75	−7.96	−66.4	13.5	12.8	61.0		4.75	−7.56	−65.4	15.5	12.8	80.0
	8.35	−7.58	−67.4	10.3	7.9	78.0		8.35	−7.85	−67.7	13.5	12.1	74.0
IX.2009	rain	−8.92	−70.4	*Na*	*na*	6.10	III.2010	rain	−12.04	−91.0	*na*	*na*	2.1
	2.1	−9	−67.2	15.7	19.5	54.0		2.1	−9.08	−73.3	15.4	19.8	59.1
	3.3	−8.45	−65.7	11.0	8.3	62.0		3.3	−8.33	−68.8	6.3	1.4	113.2
	4.75	−8.75	−66.8	15.7	13.1	63.0		4.75	−7.64	−65.0	14.5	13.8	62.2
	8.35	−8.2	−63.4	13.5	6.4	105.0		8.35	−7.7	−66.4	12.8	12.1	69.5
X.2009	rain	−14.75	−93.0	*Na*	*na*	11.5	IV.2010	rain	−10.42	−77.8	*na*	*na*	*na*
	2.1	−8.93	−66.1	15.8	20.9	55.1		2.1	−9.12	−73.0	15.5	19.2	68.0
	3.3	−8.26	−62.6	9.3	6.8	68.0		3.3	−7.84	−69.7	5.1	−2.6	140.0
	4.75	−8.64	−64.6	16.8	15.7	65.0		4.75	−7.47	−64.9	15.6	13.9	80.0
	8.35	−8.4	−65.1	11.5	8.7	82.0		8.35	−6.76	−61.1	14.5	12.3	73.0
XI.2009	rain	−11.03	−87.9	*na*	*na*	14.2	V.2010	rain	−9.1	−68.1	*na*	*na*	2.1
	2.1	−9	−73.0	15.3	19.7	60.4		2.1	−9.03	−73.9	15.0	18.8	70.0
	3.3	−8.29	−68.1	7.7	3.5	87.2		3.3	−7.95	−67.8	6.3	−0.4	115.0
	4.75	−8.6	−70.3	15.8	13.9	62.1		4.75	−7.58	−66.1	15.7	14.6	80.0
	8.35	−8.47	−70.1	12.2	8.7	80.0		8.35	−6.58	−60.1	15.0	13.7	68.0
XII.2009	snow	−15.6	−128.0	9.1	4.3	2.3	VI.2010	rain	−5.64	−40.2	9.8	6.0	7.1
	2.1	*na*	*na*	*na*	*na*	*na*		2.1	−9.11	−65.3	14.4	17.6	53.3
	3.3	*na*	*na*	*na*	*na*	*na*		3.3	−7.93	−58.9	5.9	1.4	94.2
	4.75	*na*	*na*	*na*	*na*	*na*		4.75	−7.98	−61.2	14.6	14.5	58.2
	8.35	*na*	*na*	*na*	*na*	*na*		8.35	−6.94	−55.6	12.99	11.5	51.8
I.2010	snow	−15.67	−124.9	*na*	*na*	1.7	VII.2010	rain	−8.17	−63.5	*na*	*na*	4.7
	2.1	*na*	*na*	*na*	*na*	*na*		2.1	−9.17	−65.7	15.1	16.6	50.3
	3.3	*na*	*na*	*na*	*na*	*na*		3.3	−8.16	−61.1	13.9	10.1	81.4
	4.75	*na*	*na*	*na*	*na*	*na*		4.75	−8.88	−65.3	15.1	15.9	52
	8.35	*na*	*na*	*na*	*na*	*na*		8.35	−7.47	−58.5	12.4	9.7	67.4

The PHREEQC software provided by the USGS (version 2.13.2 with the minteq.dat thermodynamic database), was used to calculate saturation indices (SIs) for selected minerals.

Together with groundwater, rainwater samples were collected and analyzed in order to determine the chemical and isotopic composition of atmospheric precipitation, which is the major input (recharge) component in the studied groundwater system. Rainwater samples were obtained from the meteorological station of Integrated Monitoring of the Natural Environment of Kampinos National Park (52°17′10′′ N, 20°27′17′′ E), located about 2 km west of the Pożary research station. A standard Hellmann's rain gauge was used to collect and measure atmospheric precipitation. Monthly cumulative rainwater was collected in separate polyethylene bottles with volumes of 1–2 L (one for each month), which were stored in a refrigerator at a temperature of 4 °C and subjected to the same set of chemical and isotopic analyses together with groundwater obtained from the piezometers. Physicochemical parameters of the rainwater were measured in the field during each water collection.

Tables 1 and 2 show data obtained for the rainwater samples. In order to present the entire vertical profile of the chemical and isotopic composition of atmospheric precipitation and groundwater, the data for rainwater are presented for a depth of 0.0 m in plots of Section 4.

4. Results

Chemical analyses of groundwater and rainwater were made six times during an entire monitoring period. The results are presented in Table 1.

Variations of groundwater temperature, pH, ORP, and EC at different depths are presented in Figure 2. The groundwater temperature in the Pożary aquifer varied between 8.9 and 17.2 °C, depending on the seasonal ambient air temperature (Figure 2). The pH of the groundwater ranged from 6.56 to 7.16, indicating slightly acidic and neutral conditions. Taking into account the vertical profile, the lowest pH values in the range of 4.44–5.87 are characteristic of atmospheric precipitation (i.e., rain and snow). In groundwater, the pH is higher than that of precipitation, and clearly varies with depth: It was highest in the upper part of the aquifer (pH > 7.0) and then decreased, reaching the lowest values in the middle part, before again reaching higher values in the deeper part (Figure 2). The EC of groundwater ranged from 484 to 780 μS/cm, and varied with depth, repeating the trend characteristic for pH.

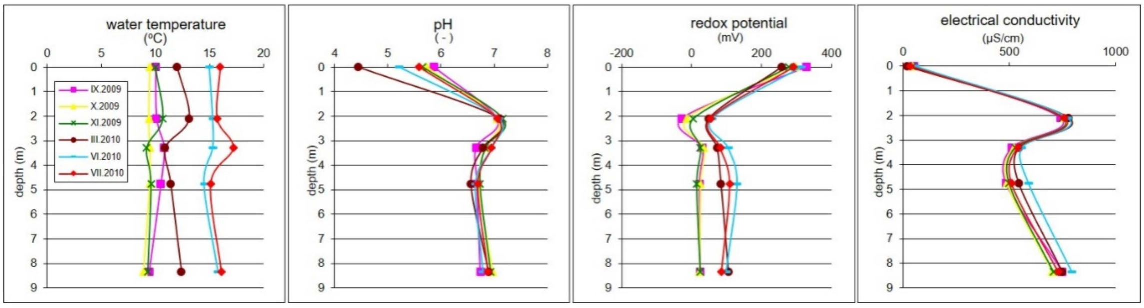

Figure 2. Seasonal variations of physicochemical parameters of groundwater in the Pożary aquifer vertical profile. The values for rainwater are shown at depth 0.0 m.

The ORP varied between −28 and +109 mV, depending on the season and sampling depth. The lowest values occurred at 2.10 m bgs, indicating slightly reducing conditions (from −28 to 60 mV), probably due to the influence of the microbial decomposition of organic matter in the peat layer. In the deeper parts of the aquifer, positive values of redox potential were observed (from 14 to 109 mV), indicating a mildly reducing environment.

The hydrogeochemical type of the water in the aquifer changes with depth as a result of the variation in the concentration of major anions (Figures 3 and 4). In the upper part of the aquifer, water of HCO_3-Ca type dominates. In the middle part, at a depth of 3.3 m, the concentrations of the major anions change abruptly: The content of HCO_3^- reaches the minimum, the contents of SO_4^{2-} and Cl^-

reach the maximum, and the hydrogeochemical type of the water evolves into HCO_3-Cl-SO_4-Ca or HCO_3-SO_4-Cl-Ca. In the deeper parts of the aquifer, the concentration of HCO_3^- gradually increases, whereas the contents of SO_4^{2-} and Cl^- decrease abruptly at a depth of 4.75 m before beginning to rise again with depth; from a depth of 4.75 m, water of the HCO_3-SO_4-Ca type dominates (Figures 3 and 4). On the other hand, at a depth of 3.3 m, the concentrations of major cations (Ca^{2+}, Mg^{2+}, and Na^+) usually exhibit the lowest values, which remain stable or rise slightly in deeper parts of the aquifer. A comparison of archival and actual data of the chemical composition of groundwater shows similar trends of evolution with depth (Figure 3).

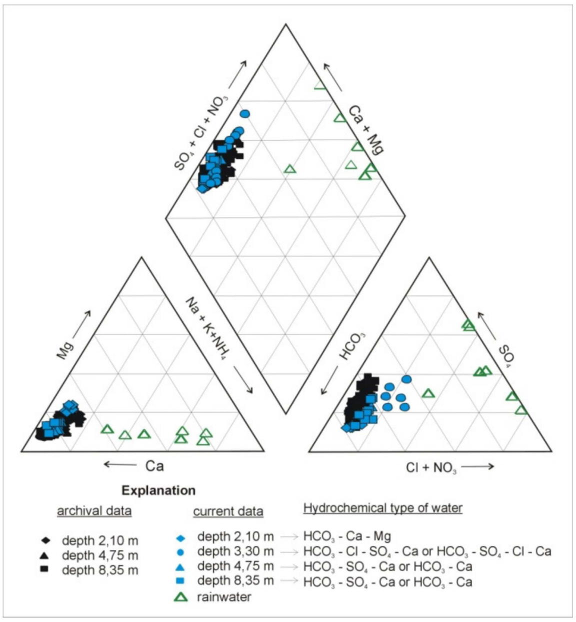

Figure 3. Piper diagram showing chemical composition of groundwater in vertical profile of the Pożary aquifer. Rain water are plotted for reference. Archival records refer to groundwater monitoring period from June 1999 to December 2001 [15,33].

The variation in the stable isotope compositions of groundwater ($\delta^{18}O$ and δ^2H) and dissolved sulfates ($\delta^{34}S$ and $\delta^{18}O$) with depth in the aquifer are summarized in Table 2 and Figure 4.

Typically, the oxygen and hydrogen isotopic composition of groundwater generally reflects the mean weighted annual composition of precipitation. In our case of a shallow unconfined aquifer with a relatively thin unsaturated zone (i.e., about 0.5 m in thickness) composed of a peat layer, the large seasonal variations of the O and H isotopic composition of precipitation are considerably attenuated in the upper part of the saturated zone. For example, the variation coefficient of $\delta^{18}O$ in the precipitation (rain and snow) reached about 35%; while at a depth of 2.1 m, seasonal variations were attenuated to about 2% (Figure 4). The isotopic composition of dissolved sulfates in atmospheric precipitation was measured three times: Two times in rain water, with each value representing rain water collected over a few months (due to a relatively low concentration of dissolved sulfates and the small amount of water available after each month), and one time in snow in December.

The obtained values of isotopic composition (Table 2) are typical for the fallout in rural areas (e.g., [12]). The isotopic composition of SO_4^{2-} dissolved in groundwater ranged from −2.6 to +20.9‰ and from +5.1 to +16.8‰ for $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$, respectively. As can be seen from Figure 4, both $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ demonstrate significant variation along the depth profile. Generally, the observed vertical variation trend of the isotopic composition of SO_4^{2-} is reversed compared to that of SO_4^{2-} concentration. Sulfates were most depleted in ^{34}S and ^{18}O at a depth of 3.30 m in almost all of the observation period (Figure 4). At a depth of 3.30 m, the values of $\delta^{34}S_{SO4}$ gradually decreased from

September 2009 to April 2010, before increasing from April 2010 to July 2010. For $\delta^{18}O_{SO4}$, a seasonal trend similar to that of $\delta^{34}S_{SO4}$ was observed.

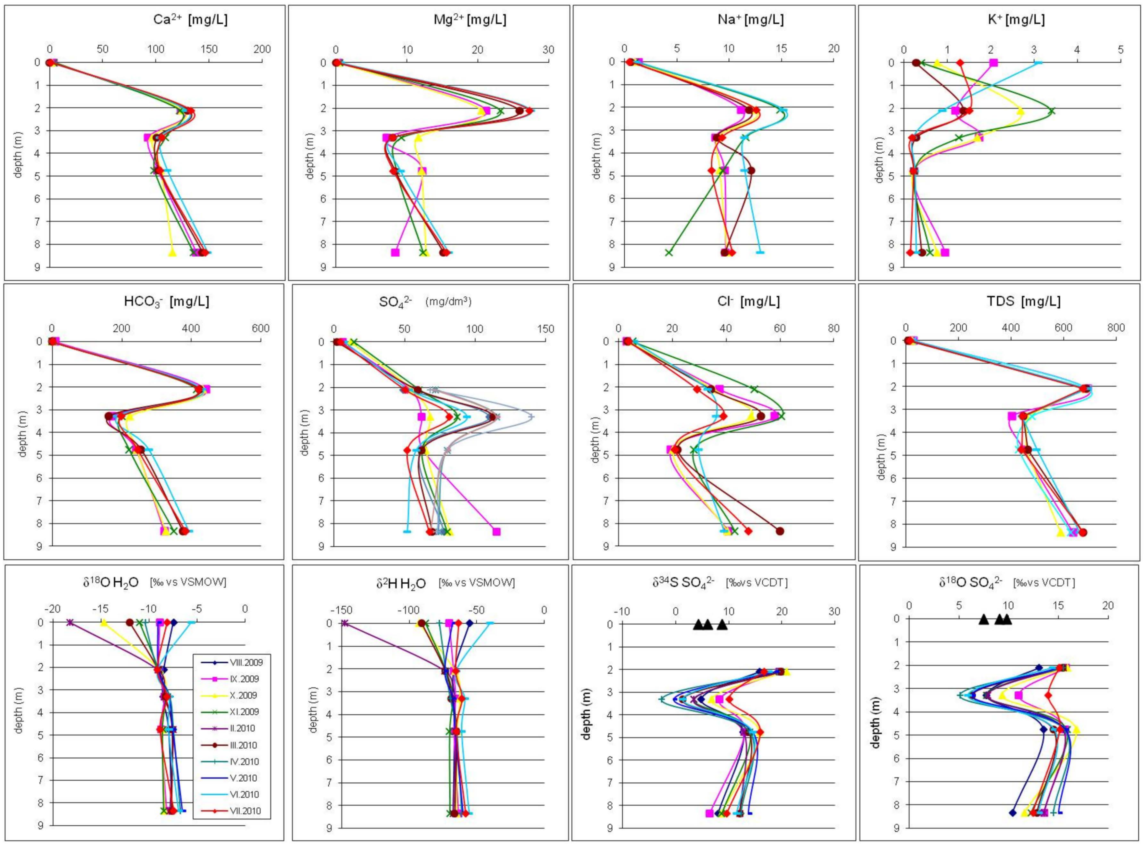

Figure 4. Seasonal variations of chemical and isotopic composition of groundwater in the Pożary aquifer with depth. The values for rainwater are shown at depth 0.0 m. For more explanations see the text.

5. Discussion

The chemical composition of subsurface water is always a complex function of many variables, e.g., the composition of recharge, the mineralogy and composition of the geological environment, and the hydrogeological and hydraulic settings. One of the main factors affecting groundwater chemistry is the presence of organic matter. The mineralization (oxidation) of organic matter in soil and aquifer environments always implies a series of redox reactions which control the distribution of major species dissolved in groundwater, with the organic matter being the major reductant [2–7].

As long as free oxygen is available in the saturated zone, the simplified reaction of organic matter oxidation can be written as follows:

$$CH_2O + O_2 \rightarrow CO_2 + H_2O \quad (1)$$

During this process, firstly carbon is released as CO_2. Depending on the reactivity and composition of organic matter, a combination of organic NO_3^- and HPO_4^{2-} can also be released to groundwater. The concentrations of NO_3^- and HPO_4^{2-} have not been studied in detail in the aquifer of the Pożary research station. However, clear evidence of organic matter decomposition in the aquifer vertical profile was shown by Porowska and Leśniak [15]—namely, an increase in CO_2 partial pressure and DIC content with a carbon isotopic composition typical of organic origin (reported $\delta^{13}C$ from −17 to −25‰ vs. PDB), an increase in organic carbon concentration (DOC), and a decrease in oxygen content (DO, reported concentrations range from 0.48–1.62 mg/dm^3). An additional consequence of the increase in CO_2 concentration in the upper part of the aquifer is an increase in the weathering capacity of groundwater and the induction of carbonate mineral dissolution, which may result, for example, in an increase in Ca and Mg concentrations (see Figure 4).

Water saturation promotes anoxic conditions in soil, vadose zone, or an aquifer. When molecular oxygen is not available (i.e., when it has been used up), the oxidation of organic matter continues and terminal electron acceptors other than O_2 are utilized. Depending on redox potential, pH, and availability of electron acceptors, the following microbial reduction processes can occur after O_2 depletion (i.e. the sequential reduction chain—a series of reactions which represent successively lower Eh levels): Nitrate, manganese, iron, sulfate, and finally CO_2 [7]. The reduction of NO_3^- by organic matter (denitrification) is a bacterially catalyzed process, it starts the sequential reduction chain in the aquifer, and can be written as an overall reaction (after [3]):

$$5CH_2O + 4NO_3^- \rightarrow 2N_2 + 4HCO_3^- + CO_2 + 3H_2O \tag{2}$$

Denitrification predominantly proceeds to the final product of N_2 [8,34–37]. An additional consequence of this process is the increase of HCO_3^- concentration and pH values (e.g., see the upper part of the profile up to 2.1 m in Figures 2 and 4). Different forms of nitrogen in shallow groundwater in wetlands and peat bogs of the Kampinos National Park were studied by Krogulec and Jóźwiak [38]. They typically reported very low concentrations of NO_3^- (from 0 mg/dm^3 to a maximum of 5.3 mg/dm^3) as a result of denitrification. Our research corroborates their conclusions: The concentration of NO_3^- in the groundwater of the Pożary aquifer was below 0.5 mg/dm^3 (see Table 1). Taking into account the aquifer profile below the peat layer, the transition between the denitrification zone and the sulfate reduction zone most likely occurs in the depth range from 2–4 m bgs: Here, the sulfate concentration starts to decrease and the HCO_3^- concentration starts to rise with depth (Figure 3).

The geochemical modeling of sulfur speciation (based on PHREEQC software) shows that sulfate is the main species of sulfur in the groundwater studied. The groundwater sulfates may be derived from various sources, such as atmospheric, pedospheric, lithospheric, and anthropogenic. In shallow aquifers in peatland areas, the sources of sulfate are usually pyrite, gypsum, biogenic sulfur compounds contained in the peat (mostly lithospheric sources), and atmospheric deposition [3,5,6,9,39,40].

However, the concentration, as well as the sulfur and oxygen isotopic composition, of sulfates in groundwater are controlled not only by sulfate sources but also by subsequent biotic and abiotic processes in the aquifer, including hydraulic conditions (e.g., groundwater mixing, fluctuation of ground water level, lateral flow). Hence, four processes may potentially control the distribution and isotope signatures of dissolved sulfate in the Pożary aquifer: (1) Bacterial (dissimilatory) sulfate reduction; (2) the formation and oxidation of reduced inorganic sulfur (RIS); (3) the dissolution of evaporitic sulfates (mainly gypsum); and (4) the mixing of sulfate from different sources. All of these processes result in specific patterns of the concentration and isotopic composition of dissolved SO_4^{2-}, and in favorable hydrogeological settings can be identified by geochemical and isotopic techniques.

5.1. Sulfate Sources in Groundwater Studied

The sources of sulfate in groundwater can have a wide range of $\delta^{34}S$ values. Usually, the local source of sulfate in groundwater is estimated using the relationship between $\delta^{34}S$ and the concentration of dissolved sulfate [12,41–43]. Plotting the $\delta^{34}S$ values of groundwater sulfate versus the inverse of sulfate concentration ($1/[SO_4^{2-}]$) for all water samples yielded a straight line with a correlation factor (R^2) of 0.6 and a y-axis intercept of −7.9‰ (Figure 5A).

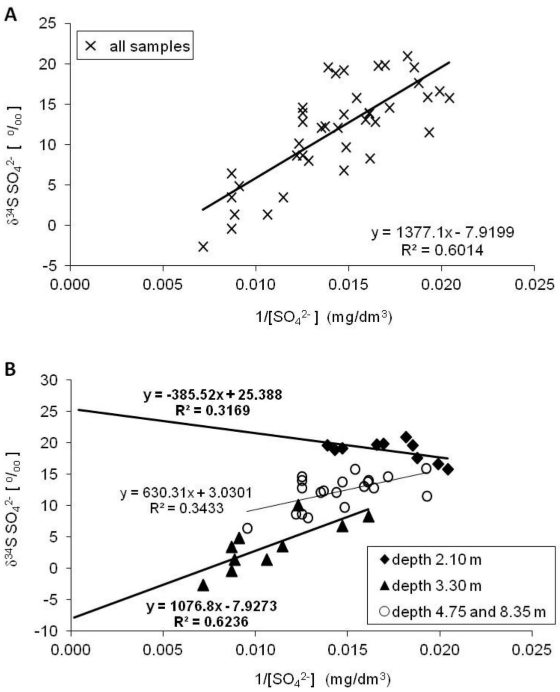

Figure 5. The δ^{34}S values and concentrations of dissolved sulfates in groundwater profile of the Pożary aquifer. For more explanations see the text.

The slope of the line *s* equals

$$s = C_R \times (\delta^{34}\mathrm{S_R} - \delta^{34}\mathrm{S_I}) \tag{3}$$

where C_R refers to the concentration of the remaining (i.e., measured) sulfate, and δ_R and δ_I refer to the sulfur isotopic composition of the remaining (i.e., measured) and initial (i.e., source) sulfate, respectively. The *y*-axis intercept represents δ_I.

The *y*-axis intercept indicates the sulfur isotopic composition of the potential source of groundwater sulfates. The value of −7.9‰ strongly suggests that the RIS compounds are the dominant lithogenic source responsible for increasing the sulfate concentration in the groundwater of the Pożary aquifer. However, a more detailed picture of the sulfate sources can be obtained by taking into account the entire observation period and the variation of sulfate concentration and sulfur isotopic composition separately in the monitored respective depths of the aquifer (Figure 5B).

The most extreme relationships were observed for groundwater sulfates at depths of 2.1 and 3.3 m. The *y*-axis intercept for sulfates at the depth closest to the peat layer yielded a $\delta^{34}\mathrm{S_I}$ value of +25.4‰, which suggests that the dominant source of dissolved sulfate may be connected with the dissolution of evaporitic sulfates (mainly gypsum) and/or sulfates undergoing bacterial reduction in the peat and aquifer. However, sulfates with different sources may be present at a depth of 2.1 m depending on the season—i.e., mainly depending on the position of the groundwater level, which fluctuates as a result of local climatic conditions, namely precipitation volume, thawing of snow cover, local infiltration or runoff to rivers, etc. When the groundwater level decreases, more of the peat is exposed to air and undergoes decomposition, and more sulfates of evaporitic and biogenic (i.e., the oxidation of organic compounds) origin accumulates in the peat. Rainfall facilitates the dissolution of sulfates (e.g., gypsum) and their transfer to the aquifer. During times of high groundwater level caused by heavy rains in autumn and snow thawing in spring, a peat layer occurs within the saturation zone, and a considerable admixture of additional sulfates with an atmospheric origin or related to gypsum dissolution or dissolution (oxidation) or RIS compounds can reach groundwater, increasing the sulfate concentration in the water in the aquifer below the peat layer [44–46]. At a depth of 3.3 m, the *y*-axis intercept yielded a $\delta^{34}\mathrm{S_I}$ value of −7.9‰, the same as the average for all water samples (Figure 5B).

This strongly suggests that the oxidation of RIS, the most likely being pyrite, is responsible for the increase in SO_4^{2-} concentration in this part of the aquifer profile.

The *y*-axis intercept for sulfates at depths of 4.75 and 8.3 m (which are taken together, as the isotopic composition of sulfates at these depths is quite similar) yielded a $\delta^{34}S_I$ value of +3.0‰. Values of $\delta^{34}S_I$ below +10‰ suggest that the dominant source of dissolved sulfates might be connected with atmospheric sulfates. Indeed, at the Pożary research station, the $\delta^{34}S$ values of sulfates dissolved in rainwater and snow were found to be between +4.25 and +8.79‰ (Table 2). On the other hand, depending on the season and the intensity of the lateral flow of water and direct infiltration, the $\delta^{34}S$ of dissolved sulfates in deeper parts of the aquifer may be a result of the mixing of sulfates from different sources and overlapping biogeochemical processes. At least, the contribution of atmospheric sulfates and sulfates derived from the dissolution of gypsum and pyrite should be taken into account, as well as common processes such as the bacterial reduction of sulfates and the oxidation of sulfides. Anthropogenic sources of sulfur in the groundwater, such as fertilizers, manure, and sewage, are negligible, due to the fact that the Pożary research station is located within the Special Protection Area of the Kampinos National Park, relatively far from arable lands and urban areas.

5.1.1. Atmospheric Sulfates

The sulfur geochemistry of any groundwater in unconfined aquifer is initially controlled by the recharge environment, i.e., atmospheric inputs, namely the sulfate content in snow and rain and the extent of evaporation in the study region. The hydrogen and oxygen isotopic composition of the groundwater indicate a meteoric origin: δ^2H and $\delta^{18}O$ values were located along the Global Meteoric Water Line (GMWL), which is typical for the meteoric recharge of the modern hydrological cycle with some seasonal variation and rainfall effects (Figure 6). There was a loss of seasonal variation of the isotopic composition of groundwater during infiltration through the unsaturated zone (Figure 4): At the piezometer depth of around 2.1 m, the seasonal variation of δ^2H and $\delta^{18}O$ was attenuated to less than 5% of that observed in the precipitation. The sulfur isotopic composition of atmospheric sulfate ($\delta^{34}S_{SO4}$) is usually controlled by emissions from fossil fuel combustion and the biological release of S-bearing compounds, which gives $\delta^{34}S$ values that usually range from slightly negative to about +10‰ CDT [12,42].

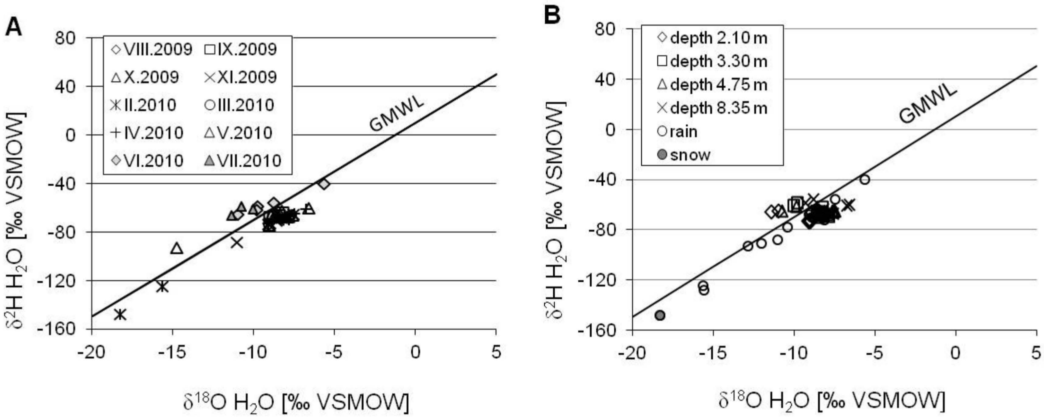

Figure 6. The δ^2H vs. $\delta^{18}O$ relationship in groundwater of the Pożary aquifer. Differentiation of isotopic composition is shown for sampling seasons (**A**) and depth profile (**B**). Global Meteoric Water Line (GMWL) after [47]: $\delta^2H = 8.13 \times \delta^{18}O + 10.8$.

On the other hand, the oxygen isotope composition of freshwater sulfates ($\delta^{18}O_{SO4}$) may be controlled by the oxygen isotope composition of water ($\delta^{18}O_{H2O}$) and dissolved oxygen ($\delta^{18}O_{DO}$). DO comes from the dissolution of atmospheric oxygen which is enriched in heavy isotopes: Values of $\delta^{18}O_{DO}$ are usually around +23.5‰ VSMOW [48,49]. The range of $\delta^{18}O_{SO4}$ for atmospheric deposition in Central Europe varies between +7 and +17‰ VSMOW [41,50], while at the Pożary research station,

$\delta^{18}O_{SO4}$ values in rain and snow were found to be between +9.0 and +13.2‰ VSMOW (based on four measurements, see Table 2). The formation of sulfates in shallow oxygen-rich underground environments produces higher values of $\delta^{18}O_{SO4}$. In the Pożary sandy aquifer, the high $\delta^{18}O$ values of groundwater sulfates (from +10.34 to +16.75‰, except at a depth of 3.30 m) imply that atmospherically derived oxygen may be an important constituent of the total sulfate pool. However, depending on the additional biogeochemical processes which affect the isotopic composition of sulfates, the contribution of atmospheric oxygen to groundwater SO_4^{2-} may vary widely [44,51]. For example, at a depth of 3.30 m, the increase in the SO_4^{2-} concentration is connected with a decrease in the $\delta^{18}O_{SO4}$ and $\delta^{34}S_{SO4}$ values, which strongly suggests that sulfate concentrations are controlled by other processes than only the simple mixing of atmospheric input. Moreover, the groundwater collected from different depths in the studied aquifer revealed a relatively high SO_4^{2-} concentration (from ~52 to 140 mg/dm^3) compared to rain water or snow, whose SO_4^{2-} concentrations range from ~0.1 to 5 mg/dm^3 according to Porowska (2003) [52] and from 1.65 to 14.2 mg/dm^3 according to our measurements. This suggests that, on the scale of the whole aquifer profile, the contribution of sulfates originating directly from atmospheric precipitation may be rather minor, and considerable variations in SO_4^{2-} concentrations and its isotopic composition are controlled by additional sulfate sources and overlapping biogeochemical processes.

5.1.2. Dissolution of Gypsum

Sulfates in the analyzed groundwater may also be derived from soluble minerals such as gypsum ($CaSO_4 \cdot 2H_2O$ or anhydrite $CaSO_4$), which is a common sulfate mineral in freshwater peatland. Similar to pyrite, gypsum is mostly authigenic, and may constitute a considerable source of sulfate dissolved in groundwater affected by peatland [53]. Saturation indices calculated based on our data show undersaturation with respect to gypsum, and the potential dissolution of gypsum along the whole vertical profile of the aquifer, regardless of the hydrogeochemical conditions (Figure 7).

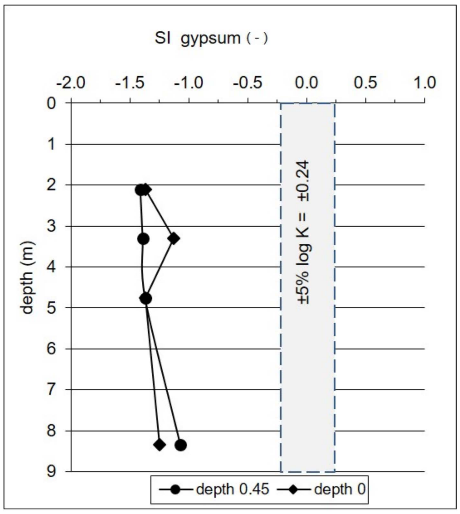

Figure 7. Saturation indices (SI) with respect to gypsum calculated for chemical composition of water in two extreme positions of the groundwater level, namely: −0.45 m bgs in November 2009, and 0.0 m bgs (i.e., the groundwater level reaches the ground surface, the peat bed is fully saturated) in April 2010.

The dissolution of gypsum causes an increase in the sulfate concentration in groundwater, and occurs without measurable isotope fractionation, i.e., dissolved sulfates retain the original isotopic composition of gypsum [40,54–56]. Sulfates in the groundwater of the upper part of the Pożary aquifer—which have high $\delta^{34}S$ and $\delta^{18}O$ values of around +20‰ and +16.7 ‰, respectively (Tab. 1), and have predicted $\delta^{34}S$ values of the source sulfate as high as +25‰ (Figure 5)—may originate from the dissolution of gypsum formed in the peat layer [12].

5.1.3. Mineralization of Carbon-Bonded Sulfur (C-S) Compounds

A large proportion of the sulfates in the studied aquifer might originate from the decomposition of peat during times of low water table. Similar trends were observed in [45,46]. Sulfur compounds may be retained in the peat as both (i) organic forms and (ii) reduced inorganic forms (RIS), depending on the oxygen availability [4]. Several studies have suggested that H_2S, formed as an end product of the dissimilatory sulfate reduction (see reaction in Equation 6) can react rapidly with organic matter, producing carbon-bonded sulfur (C–S) (e.g., [57]). The C–S can be further degraded to biogenic compounds such as CH_3SH (i.e., methanethiol as a volatile form), $(CH_3)_2S$ (i.e., dimethylsulfide as a liquid form), and H_2S gas, which can escape from the soil or can be oxidized back to $SO_4{}^{2-}$. In the rainy season, when the groundwater table rises, the sulfates accumulated in the peat are more easily dissolved and transferred into groundwater below the peat layer, thus increasing their concentration. Evidence for the decomposition of organic matter in the Pożary aquifer profile was clearly shown by Porowska and Leśniak [15]. The availability of organic matter and the presence of H_2S (giving a characteristic "rotten egg" odor) from a possible dissimilatory sulfate reduction suggests that C–S compounds can form in the studied peat and groundwater. Their further mineralization and transformation may additionally affect the concentration and isotope signature of sulfates dissolved in groundwater. Processes such as the decay and oxidation of organic compounds do not change the $\delta^{34}S_{SO4}$ significantly [44]. However, C–S compounds were not analyzed in this study, and their role in formation of groundwater sulfates needs to be further studied.

5.2. Precipitation/Oxidation of Reduced Inorganic Sulfur (RIS)

Numerous studies have shown that pyrite (FeS_2) is a commonly occurring species of RIS in freshwater peatlands, while greigite (Fe_3S_4) and mackinawite ($FeS_{0.9}$) are minor components of the RIS pool [1,5,6,57,58]. Two genetic types of pyrite have been identified in peat bogs, namely syngenetic and epigenetic [6,59–61]. Syngenetic pyrite is formed in anoxic environments during bacterial sulfate reduction ($S_{sulfate} \rightarrow S_{pyrite}$), mainly as framboidal pyrite and more rarely as euhedral pyrite. Epigenetic pyrite is produced during the humification of peat, when sulfur from sulphobacteria and carbon from plant respiration bond and are reduced to sulfidic sulfur ($S_{organic} \rightarrow S_{pyrite}$). Berner and Raiswell [62] suggested a greigite (Fe_3S_4) precursor for framboidal pyrite (FeS_2) and amorphous FeS and a mackinawite precursor for euhedral pyrite. Framboidal pyrite (i.e., mostly syngenetic) is clearly the most abundant species of RIS in peat deposits, and was found, for example, in peatland of the Lubartowska Upland, Western Poland [53]. Moreover, Jóźwiak [63] indicated the possibility of the precipitation of pyrite from the groundwater of selected peatland of the Kampinos National Park. According to Berner and Raiswell [62], at the Pożary research station, hydrogeochemical conditions in the aquifer are favorable to the formation of framboidal as well as euhedral pyrite. SIs calculated based on our data show supersaturation with respect to pyrite and the potential possibility of its formation along the entire profile of the aquifer (Figure 8). On the other hand, the negative values of SIs for greigite and mackinawite show that these compounds are not stable and undergo dissolution.

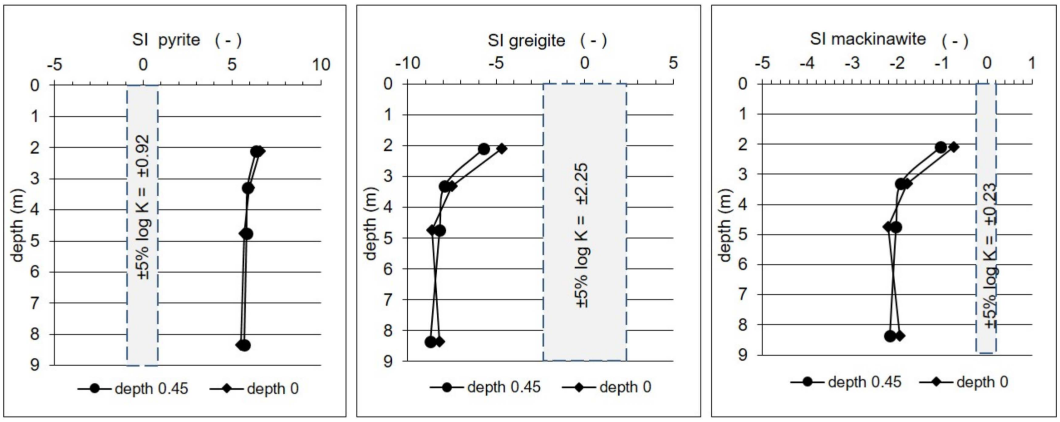

Figure 8. Saturation indices (SI) with respect to pyrite, greigite, and mackinawite. Calculations were made for chemical composition of water in two extreme positions of groundwater level, i.e., −0.45 m bgs in November 2009, and 0.0 m bgs (i.e., the groundwater level reaches the ground surface, the peat bed is fully saturated) in April 2010.

Peatlands are very heterogeneous environments in which SO_4^{2-} reduction and S^{2-} oxidation often coexist [5]. Even if hydrogeochemical conditions temporarily cause an environment which favors sulfate reduction, the short-term products of this reduction, such as pyrite or labile organic sulfur, can be either oxidized or mineralized. In the case of the Pożary sandy aquifer, which is overlain by a peat layer, the formation of RIS (i.e., pyrite) might be connected firstly with the sulfate reduction processes in the peat as well as in the aquifer itself in an anoxic environment. Sulfate reduction results in the formation of sulfides (i.e., H_2S and/or HS^-, depending on the pH), which react with Fe-oxides and form FeS_2, usually in a two-step process [3]:

$$2FeOOH + 3HS^- \rightarrow 2FeS + S^o + H_2O + 3OH^- \quad (4)$$

$$FeS + S^o \rightarrow FeS_2 \quad (5)$$

In the first step, part of the sulfide reduces Fe(III) and produces S^o, while the remainder of the dissolved sulfide precipitates as FeS, which is much less stable than pyrite but forms kinetically very quickly due to the sluggish precipitation of FeS_2. In the second step, FeS transforms to FeS_2, which is an oxidation reaction. The precipitation of pyrite lowers the concentration of sulfide in groundwater. Depending on the environmental conditions, sulfide minerals produced during bacterial sulfate reduction can have $\delta^{34}S$ values which are more than 50% lower than those of the initial sulfate; commonly found $\delta^{34}S$ values for RIS in sedimentary rocks vary between −30 and +5‰ CDT [40]. These sulfur compounds are often finely dispersed in sediments, and under oxidizing conditions they may become a significant source of groundwater sulfates. The oxidation of pyrite or aqueous sulfides is a very common process in surface or near-surface environments and peatlands [11,64]. The process can be bacterially mediated or abiotic [64,65]. Exemplary reactions can be written as follows:

$$FeS_2 + 3\frac{1}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (6)$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (7)$$

The participating aerobic oxidizers, such as *Thiobacillus*, prefer low pH, the presence of organic matter, and warm temperature [66]. The oxidation of sulfides to SO_4^{2-} generally results in minimal isotopic fractionation, essentially retaining the original isotopic composition of the sulfide minerals [67]. During times of low water table, pyrite can be oxidized, causing an increase in sulfur load with water infiltration into the saturation zone and the aquifer. Even a small drop in the water table is sufficient to promote the oxidation of reduced forms of sulfur [67].

5.3. Bacterial Dissimilatory Sulfate Reduction

Microbial sulfate reduction by organic matter is one of the most important processes responsible for the sulfur cycle in hydrogeological environments. Dissimilatory sulfate reduction is an energy-gaining respiratory process conducted by a specific group of anaerobic prokaryotic bacteria (the genus *Desulfovibrio* and others) through chemical reactions in which organic carbon is oxidized while sulfates are reduced as they serve as terminal electron acceptors [2]. Such a redox reaction can be written as follows:

$$2CH_2O + SO_4^{2-} \rightarrow 2HCO_3^{-} + H_2S \quad (8)$$

where CH_2O represents a generic form of organic matter with the oxidation state of a carbohydrate. The end-product H_2S gas dominates at low and moderate pH (below 7.0), while at high pH, HS^- and S^{2-} dominate, and concentration is limited only by the solubility of sulfide minerals [3,28]. The geochemical conditions within the studied Pożary aquifer are favorable for bacterial dissimilatory sulfate reduction and H_2S formation. The dissolved organic carbon occurs in the peat and groundwater and provides the source of organic matter for the sulfate reduction process [15]. The surplus of organic carbon promotes the sulfate reduction and stability of the precipitated reduced sulfur compounds [9,68]. The redox potential is favorable for SO_4^{2-} reduction within the whole aquifer profile. In the near-surface zone, the ongoing reduction of SO_4^{2-} can be recognized by the presence of a characteristic "rotten egg" odor of dissolved H_2S, and additionally by the decrease of the organic carbon concentration in the groundwater profile [15], the decrease of the SO_4^{2-} content and the increase of the HCO_3^- content, as well as an increase in pH in comparison to deeper parts of the aquifer.

Typically, bacterial sulfate reduction affects the concentration of dissolved sulfates and is characterized by considerable isotopic fractionation of sulfur and oxygen e.g., [69–72]. As the process proceeds, the heavy sulfur and oxygen isotopes gradually accumulate in the residual sulfate reservoir, i.e., the residual aqueous sulfates are enriched in ^{34}S and ^{18}O isotopes relative to the original SO_4^{2-} due to the preferential consumption of lighter isotopes (^{32}S-O bonds need less energy to break) by bacteria [54,73]. This results in a positive linear (or near-linear) correlation between the $\delta^{34}S$ and $\delta^{18}O$ values of the residual sulfates in the analyzed groundwater (Figure 9A). Additionally, the increase of the $\delta^{34}S$ and $\delta^{18}O$ values of the dissolved sulfates with decreasing SO_4^{2-} concentrations also corroborates the bacterial sulfate reduction process in the groundwater [40,55]. The linear relationship between the $\delta^{34}S$ values and the SO_4^{2-} concentration for all samples from the entire observation period yielded an R^2 value of 0.67 (Figure 9B).

On the other hand, the positive trend between the $\delta^{34}S$ and $\delta^{18}O$ values for all samples yielded an R^2 value of 0.83; the slope of the regression line was 1.68, which falls within the typical range for natural systems of 1.4 to 3.5 [74]. Theoretically, the slope of the $\delta^{34}S$ vs. $\delta^{18}O$ plot represents the ratio of the enrichment factors for sulfur (ε_{34S}) and oxygen (ε_{18O}) during bacterial sulfate reduction. In most groundwater environments (i.e., conditions typical for a closed system, no contact with considerable amounts of sulfate minerals which could replenish their loss), such enrichment in ^{34}S and ^{18}O in the residual sulfate usually follows a Rayleigh fractionation model. The Rayleigh model is an exponential function that, in this case, describes the progressive partitioning of ^{34}S and ^{18}O into the remaining sulfates as the initial sulfate concentrations decrease during the reduction process:

$$\delta^{34}S_R = \delta^{34}S_I + \varepsilon \times \ln f \quad (9)$$

$$\delta^{18}O_R = \delta^{18}O_I + \varepsilon \times \ln f \quad (10)$$

where the subscripts R and I refer to the respective isotope ratios in the remaining (i.e., residual) and initial concentrations of sulfate, ε is the enrichment factor for sulfur and oxygen, and f is the fraction of residual sulfate: $f = [SO_4^{2-}]_R/[SO_4^{2-}]_I$.

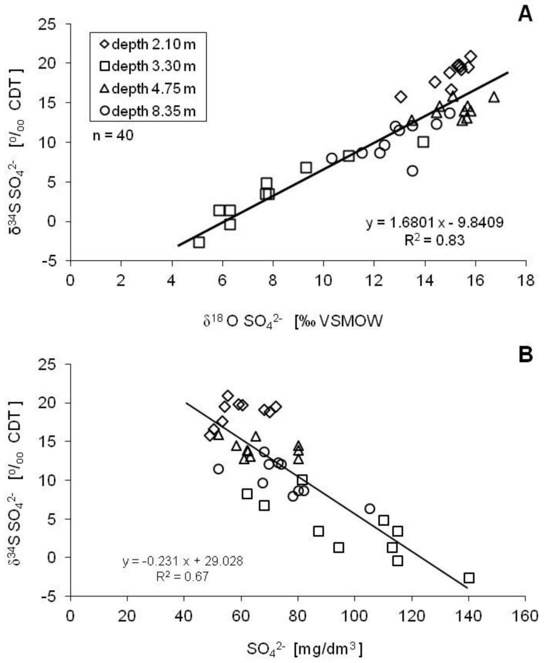

Figure 9. Trends of the δ^{34}S and δ^{18}O values for residual sulfates in groundwater of the Pożary aquifer. Linear correlations strongly suggest the occurrence of the bacterial sulfate reduction.

The relationships between the fraction (*f*) of the residual sulfate and the δ^{34}S and δ^{18}O values of all groundwater samples from the aquifer of the Pożary research station are shown in Figure 10. In order to calculate the fraction of residual sulfate, the highest measured sulfate concentration in the groundwater was assumed as the initial value, i.e., 140 mg/dm^3, at a depth of 3.3 m.

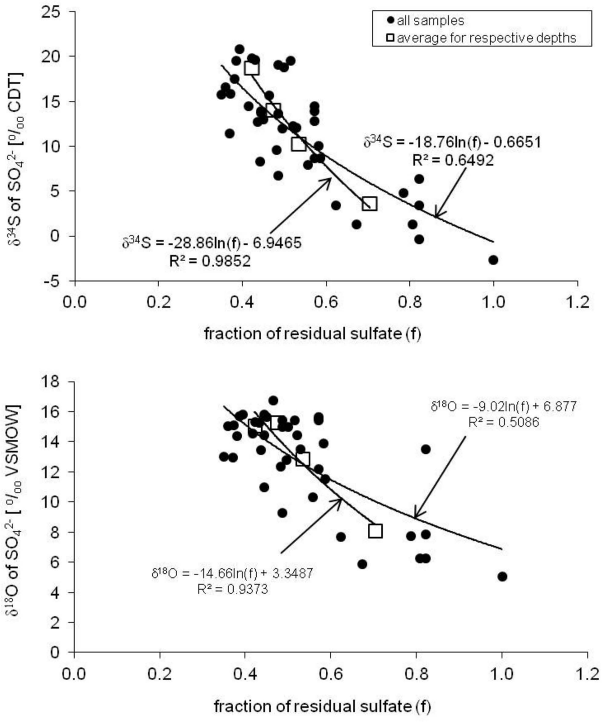

Figure 10. Relationship between the fraction (*f*) of the residual sulfate and its δ^{34}S and δ^{18}O values in groundwater samples from the aquifer of the Pożary research station. Note: fraction *f* was calculated for modeling purpose.

Based on these relationships, the enrichment factors (ε) for sulfur and oxygen were estimated to be −18.8‰ and −9.0‰, respectively (Figure 10). On the other hand, the logarithmic regressions for the mean values (from the entire observation period) of sulfate concentrations and isotopic compositions at particular depths yielded much better correlation factors (R^2), higher than 0.9. The estimated enrichment factors for sulfur and oxygen were −28.9‰ and −14.7‰, respectively (Figure 10). The estimated values of the enrichment factors yield $\varepsilon_{34S}/\varepsilon_{18O}$ ratios of about 2.0, which is in quite good agreement with the obtained slope of the δ^{34}S vs δ^{18}O enrichment around 1.7 (Figure 9).

The isotopic fractionation during bacterial sulfate reduction, as well as the enrichment factors and the reduction rates, are governed by local environmental and geochemical conditions under which the bacteria function [12,40,75]. The relationships between the fraction of the residual sulfates (f) and the sulfates' δ^{34}S values in groundwater in the aquifer profile calculated for different seasons reveal that the enrichment factors (ε) vary in a wide range, from about −36.3 to −13.0‰. Such variation confirms that local climatic, environmental, and hydrogeological conditions have a strong impact on the bacterial sulfate reduction process in the peat and in the aquifer, and the final isotopic composition of the residual sulfates found in the studied groundwater. It can be seen that the highest absolute values of the enrichment factors (ε) are connected with seasons of decreasing vegetation activity (i.e., late autumn, winter, and early spring), lower ambient air temperature, and high levels of the groundwater table (up to the ground surface). The observed values of the seasonal sulfur isotope enrichment factors for bacterial sulfate reduction in the Pożary aquifer are within the typical range of ε_{34S} reported in the literature for aquifers and wetland peat, that is, from −60‰ to −2.6‰ [41,76–79].

A general summary of the sulfate sources in groundwater of the unconfined Pożary aquifer deduced from distribution of dissolved sulfates and their O and S isotopic compositions is shown in Figure 11.

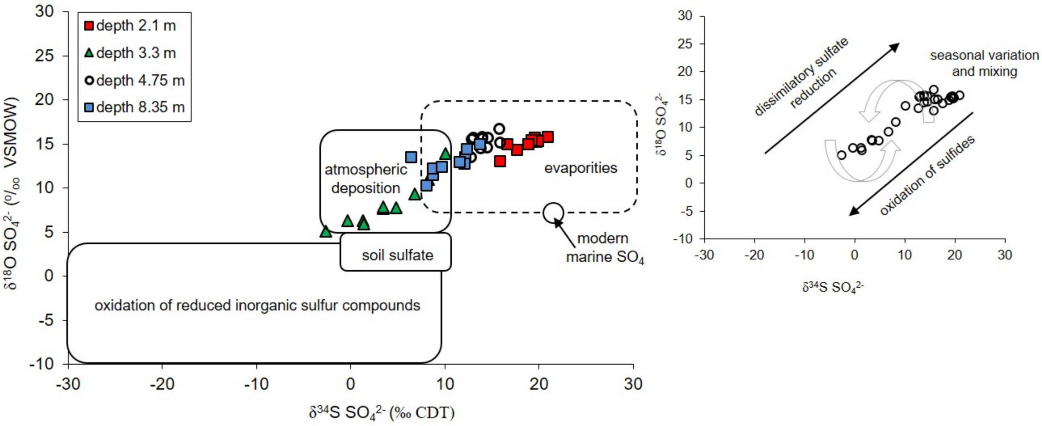

Figure 11. The δ^{34}S versus δ^{18}O of dissolved SO_4^{2-} in groundwater of unconfined sandy aquifer against the background of typical sulfate sources and trends of biogeochemical processes.

There are three sources of sulfates that are most likely in the studied groundwater. The sulfates connected with atmospheric deposition (i.e., rain and snowmelt) reach the aquifer by direct infiltration though the peat layer and vadose zone and/or by lateral groundwater inflow from an adjacent area. The second source of sulfates is connected with sulfate flax from the peat layer. These sulfates are enriched in heavy oxygen ^{18}O and sulfur ^{34}S isotopes which is typical for dissolution of evaporitic sulfates (most likely gypsum formed in the peat) or for residual sulfates formed during dissimilatory sulfate reduction in the peat bed. The third source of sulfates is connected with oxidation of reduced inorganic sulfur compounds (i.e., first of all the precipitation/dissolution of pyrite, the dissolution of greigite and mackinawite) in the aquifer.

The bacterial sulfate reduction seems to be the most important biogeochemical process affecting the concentration and the isotopic composition of sulfates dissolved in groundwater across entire profile of the Pożary aquifer. However, the bacterial sulfate reduction as a single process cannot fully explain the distribution of SO_4^{2-} concentration and its isotopic composition in the groundwater profile. The imposition of other processes such as precipitation of sulfide minerals, sulfide oxidation/re-oxidation, groundwater lateral inflow and mixing, must also occur in the studied aquifer.

6. Conclusions

The results of this study show that the peat layer above the unconfined sandy aquifer of the Pożary research station controls the occurrence, origin, and seasonal variation of sulfates and physiochemical composition of groundwater.

The peat layer is firstly the source of organic matter to groundwater in the aquifer. The mineralization of organic matter in the peat and in the aquifer affects in the first place the distribution and concentration of nitrates, sulfates, and carbon species according to the sequential reduction chain.

Two main factors control the concentration and isotopic composition of the SO_4^{2-} dissolved in the groundwater of the studied aquifer, namely, (i) different sources of sulfates, and (ii) the imposition of biogeochemical processes taking place in the peat layer and in the aquifer.

Detailed analysis of the isotopic composition of aqueous sulfates and the distribution of SO_4^{2-} concentrations across the aquifer profile during the entire observation period revealed three main sources of sulfates in the studied groundwater:

(a) The atmospheric deposition—sulfates which are introduce to the aquifer with the recharge water such as rain and snowmelt. Their initial values of $\delta^{34}S_{SO4}$ in the area of the Pożary research station documented for rain and snow varied from +4.3 to +8.8‰ with concentrations ranging from 1.7 to 14.2 mg/dm^3. Such isotopic composition is typical for sulfate of anthropogenic origin in atmospheric precipitation in industrialized regions of the northern hemisphere with $\delta^{34}S$ values ranging from −3 to +9‰. The atmospheric sulfates reach the aquifer by direct infiltration of recharging water though the peat layer and vadose zone and by lateral groundwater inflow from an adjacent areas, where the aquifer is not cover by peat.

(b) The evaporitic sulfate minerals (lithogenic source)—sulfates enriched in heavy ^{18}O and ^{34}S isotopes with $\delta^{34}S_{SO4}$ ranging from +15.8 to +20.9‰ and $\delta^{18}O_{SO4}$ from +13.0 to +15.8‰. Such isotopic composition is typical for sulfates originating most likely from the dissolution of evaporitic gypsum which may be formed in the peat layer or in the aquifer's vadose zone during seasons with low groundwater level. Sulfates of such isotopic composition were observed exclusively in the most upper part of the aquifer profile (monitoring depth of 2.1 m) which is the closest to the overlying peat bed. It is very likely that the source of sulfates is connected with sulfate flax from the peat layer. Calculated initial value of the dominant source of dissolved sulfate at the depth of 2.1 m yielded a $\delta^{34}S_I$ value of +25.4‰, which also strongly suggests the influence of sulfates originating from bacterial sulfate reduction.

(c) The reduced inorganic sulfur compound (RIS; lithogenic source)—sulfates depleted in heavy ^{18}O and ^{34}S isotopes with $\delta^{34}S_{SO4}$ ranging from −2.6 to +10.1‰ and $\delta^{18}O_{SO4}$—from +5.10 to +13.9‰. Sulfates of such isotopic composition were observed in the aquifer exclusively in monitoring depth of 3.3 m. Depletion in heavy isotopes is connected with increasing SO_4^{2-} concentration: Usually increased from about 1.5–2 times (depending on the season) in relation to the uppermost part of the aquifer profile. The source of these sulfates is connected with oxidation/re-oxidation of reduced inorganic sulfur compounds in the aquifer i.e., first of all with the dissolution/precipitation of pyrite, the dissolution of greigite and mackinawite. Calculated initial value of the dominant source of dissolved sulfate at the depth of 3.3 m yielded a $\delta^{34}S_I$ value of −7.9‰ which corroborates that the oxidation of RIS is responsible for the increase in SO_4^{2-} concentration in this part of the aquifer profile.

The observed linear trend of $\delta^{34}S$ vs $\delta^{18}O$ for aqueous sulfates can be attributed to (i) bacterial (dissimilatory) sulfate reduction, (ii) a mixing process in the aquifer, and/or (iii) the precipitation of sulfide minerals. Bacterial sulfate reduction is the most important biogeochemical process affecting the concentration and isotopic evolution of sulfates dissolved in groundwater in the Pożary aquifer.

The sulfur isotope enrichment factor (ε_{34S}—expresses the partitioning magnitude of the ^{34}S isotopes into the residual sulfates during bacterial sulfate reduction undergoing the Rayleigh fractionation model) calculated for each monitoring season revealed wide variation range from about −36.3 to −13.0‰. Such variation of ε_{34S} corroborates that local climatic, environmental, and hydrogeological conditions have a strong impact on the bacterial sulfate reduction rate in the peat and in the aquifer, and on the final isotopic composition of the residual sulfates found in the studied groundwater. The highest absolute values of the enrichment factor ε_{34S} are connected with seasons of decreasing vegetation activity (i.e., late autumn, winter, and early spring), lower ambient air temperature, and high levels of the groundwater table up to the ground surface (i.e., full saturation of the peat layer).

The bacterial sulfate reduction as a single process cannot fully explain the distribution of SO_4^{2-} concentrations and the isotopic compositions of sulfur in the groundwater profile. The imposition of sulfide oxidation/re-oxidation, as well as groundwater mixing processes, must also be taken into account in the studied aquifer.

The biotic and abiotic transformations of sulfur compounds in the studied aquifer are interconnected with other geochemical processes through their common substrates or products. Bacterial sulfate reduction in groundwater profile results in change of isotopic signature of recharge water, a decrease of redox potential (Eh), slight decrease of pH, decrease of SO_4^{2-}, increase of HCO_3^- (alkalinity), and precipitation of sulfide minerals. On the other hand, the imposition of the RIS oxidation causes the increase of water pH, the increase of SO_4^{2-} concentration, and the decreases of alkalinity. The influence of this competitive processes of sulfur species transformations are reflected by the complex variations of the physicochemical parameters of groundwater and the concentration of chemical compounds across the aquifer profile. The monthly monitoring of the aquifer vertical profile allowed us to identify the zones where these different processes are dominant.

There are two issues that need further studies from the perspective of our experience gained during this research, namely, (i) the seasonal monitoring of the sulfate content and its isotopic composition inside the peat layer, and (ii) the identification and analysis of the main forms of the carbon-bonded sulfur compounds (C–S) in order to evaluate their influence on the formation of aqueous sulfates and sulfide minerals in groundwater in contacts with peatlands.

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