NATURAL AND ANTHROPOGENIC ORIGIN SULPHATE IN AN MOUNTAINOUS GROUNDWATER SYSTEM: S AND O ISOTOPE EVIDENCES

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Abstract. Concentration of sulphate, $\delta^{34}S(SO_4^{2-})$, $\delta^{18}O(SO_4^{2-})$ and $\delta^{18}O(H_2O)$ values, in surface waters and groundwaters from crystalline rocks in mountainous Rudawy Janowickie Massif (RJ) in SW Poland, have been analysed. The RJ is located close to the area of the biggest anthropogenic emission source of sulphur compounds in Europe called the "Black Triangle". The lowest concentration of sulphate ions dissolved in water (13 mg/l) were found in groundwaters at the highest altitude (750m asl). In the course of groundwater downward infiltration (hydraulic gradient) the concentration of sulphate ions increased with decreasing altitude. The highest concentrations of SO_4^{2-} (100 mg/l in springs at metamorphic rocks and 60 mg/l in springs at granites) were observed at the foothills (altitudes 410 and 580 m asl, respectively). Likewise, the sulphur and oxygen isotope composition of sulphate ions showed systematic increasing trends with respect to the altitude decrease (from 3.45 to 11.05‰ and from −6.53 to 10.03‰, respectively).

Three main sources of sulphate for the surface-water/groundwater systems in RJ have been isotopically discriminated. The high $\delta^{34}S$-$\delta^{18}O$ sulphate showed waters from precipitation and peat bogs. The lower $\delta^{34}S$—$\delta^{18}O$ sulphate originated due to decomposition of organic matter. The lowest $\delta^{34}S$—$\delta^{18}O$ sulphates formed due to microbial (*Thiobacillus ferrooxidans*) pyrite oxidation within the pyrite-deposit weathering zone. The highest contribution of anthropogenic sulphate have been observed at the top-hills and during low water levels at lower altitudes. The contribution of biogenic and geogenic sulphate relatively increased with the increasing distance (time?) of the water flow through rocks or/and increasing water level in springs.

The isotope, hydrochemical and hydrogeological observations confirmed a negligible role of anthropogenic sulphur in the groundwaters analysed. This suggests significant improvement in the natural environment in the Western parts of Sudety Mountains.

Keywords: sulphate, water, sulphur, oxygen, stable isotopes, contamination

1. Introduction

The sulphur supplied from anthropogenic sources, especially acid rain, may strongly modify the aquatic environments and consequently geochemical sulphur cycle. This process concerns mainly industrial areas where energy is gained from fossil fuel burning. The Black Triangle (SE Germany, NW Czech Republic, SW Poland) is

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one of the biggest area in Europe with anthropogenic emission of sulphur compounds (etc. Jędrysek, 2000). The sulphur pollution in the atmosphere effects the perturbation of biological processes in the forest area, especially in higher altitudes of mountain regions situated near the Black Triangle (Baron and Sobik, 1995; Jędrysek *et al.*, 2002).

Our study area is located in the RJ mountains (the Western Sudety) in SW Poland, about 70 km to E from the main sulphur emitters in the Black Triangle. In this area, in 1980's and 1990's near all sulphate ions in surface waters and groundwaters originated from the acid rain precipitation (Ciężkowski *et al.*, 1986; Kryza *et al.*, 1994, 1995; Dobrzyński, 1997; Macioszczyk, 1987). However, since 1990 the concentration of SO_2 in the atmosphere rapidly decreased from 48 to 9 mg/m^3 in 2000 (Wrocław Regional Inspectorate of Environmental Protection, 2001). Therefore, significant decrease in SO_4^{2-} ion concentration in the surface waters and groundwaters of the RJ massif is expected.

In this paper we present seasonal variations in SO_4^{2-} concentration, spring discharge and water levels from 1999 to 2002. Moreover, the sulphur and oxygen isotope analysis of sulphate ions dissolved in surface waters and groundwaters have been analysed (December 2001 and February 2002).

Main goals of this work were (1) to observe the sulphur and oxygen isotopic variations in the sulphate dissolved in water, (2) to determine the natural sulphur contribution (geogenic and biogenic origin) regarding the residence time of the water, (3) to estimate the present contamination of surface waters and groundwaters with anthropogenic sulphur.

2. Field Site

The RJ massif is a small mountain ridge 15 km long, with maximum elevation 935.8 m asl. It is in a central part of Sudety Mountains (SW Poland). The RJ Mountains are high-grade of metamorphic rocks massif in the east (Teisseyre, 1973; Mazur, 1993) and granite in the west (Mierzejewski, 1985, 1990). The metamorphic rocks of RJ is a fragment of south-east cover of granite rocks of Karkonosze Mountains granite. Crystalline dolomites, meta-volcanic rocks, skarns (Narębski, 1968; Narębski and Teisseyre, 1971), granites, gneisses, mica-schist (Smulikowski, 1952; Lis, 1970) are the most common rocks of RJ, however the silica-rich rocks are dominant. The meta-volcanic chlorite-micas shits are relatively abundant in pyrite (Jaskólski, 1964) (in a region of Wieściszowice village), which show intensive oxidation (Parafiniuk and Dobrzyński, 1995; Prafiniuk, 1996).

In the RJ the largest pool of surface water is the Purple Pond located in an abandoned pyrite mine near Wieściszowice village (Figure 1, Table I). The surface waters of the RJ are draining through streams and finally tribute to the Bóbr river (a left tributary of Odra river). The dominating form of groundwater drainage in RJ is a spring discharge, however, an important form of drainage is also an inflow

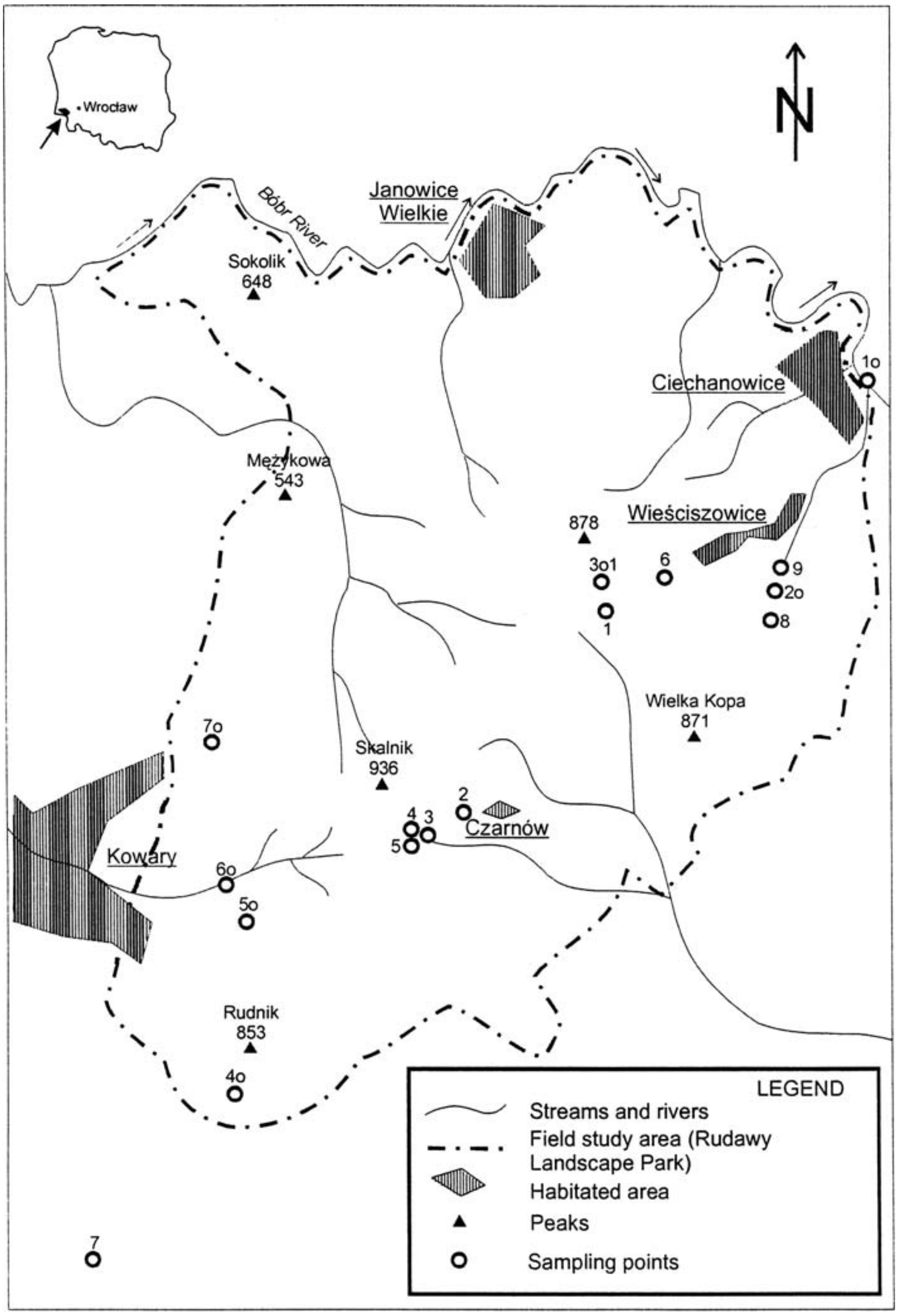

Figure 1. A map of sampling points of water in the Rudawy Janowickie massif.

TABLE I

Sulphate ion concentration, isotope composition of sulphates and waters, (springs/streams/pond) observed on December 2001 and February 2002 in the Rudawy Janowickie massif

Characteristic of observation point	Sample points	alt. a.s.l. [m]	Sulphates (SO_4^{2-})						Water (H_2O)								
			Concentration [mg/1]		$\delta^{34}S_{CDT}$[‰]		$\delta^{18}O_{SMOW}$[‰]		$\delta^{18}O_{SMOW}$[‰]		$\Delta^{18}O_{SMOW}(SO_4^{2-} - H_2O)$[‰]		$\Delta^{34}S_{CDT}(SO_4^2)$	$\Delta^{18}O_{SMOW}(SO_4^2)$	$\Delta^{18}O_{SMOW}(H_2O)$	Spring/stream discharge [l/s]	
			December 5th, 2001	February 21th, 2002	December 5th, 2001	February 21th, 2002	December 5th, 2001	February 21th, 2002	December 5th, 2001	February 21th, 2002	December 5th, 2001	February 21th, 2002	Dec.-Febr. [‰]	Dec.-Febr. [‰]	Dec.-Febr. [‰]	December 5th, 2001	February 21th, 2002
Precipitation	1	760	6,50	4.00	6,08	n.a.	8,74	n.a.	−12,98	n.a.	21,72	n.a.	n.a	n.a	n.a	n.a	n.a
	2	750	1,70	1.31	n.a	n.a	n.a	n.a	−14,07	−13,28	n.a.	n.a.	n.a.	n.a.	−0,79	n.a	n.a
Refluxes from	3	750	22,50	23.46	11,05	7.81	10,03	7,54	−10,03	−9,58	20,06	17,12	3,24	2,49	−0,45	n.a.	n.a.
Peat-bogs	4	750	20,30	21,06	9.89	5,69	9.10	−9,40	−9,84	−9.67	18,94	19,07	4,20	−0,30	−0,17	n.a.	n.a.
	5	800	n.a.	20.89	n.a.	6.90	n.a.	7,55	n.a.	−9,76	n.a.	17,31	n.a.	n.a.	n.a.	n.a.	n.a.
Bóbr River	1o	410	38,10	31.02	7,77	6.23	7,64	6,12	−9,60	−10,78	17,24	16,90	1,54	1,52	1,18	n.a.	n.a.
Streams	6o	510	31,00	30.27	7,74	6.05	6,14	6,42	−10,22	−9,22	16,36	15,64	1,69	−0,28	−1,00	25	14
	6	625	6.50	23.07	n.a.	3.55	n.a.	4,82	n.a.	−9,98	n.a.	14,80	n.a.	n.a.	n.a.	n.a.	n.a.
Springs																	
Metam.	3ol	760	26.30	25.19	7,08	7.23	6,25	5,79	−11,49	−8,53	17,74	14,32	−0,15	0,46	−2,96	2,17	1.5
rocks	4o	680	29.40	28.02	6,57	5.96	5,85	7,30	−10,42	−10,38	16,27	17,68	0,61	−1,45	−0,04	0,098	0.61
	7	950	n.a.	20.00	n.a.	5.68	n.a.	5,17	n.a.	−10,94	n.a.	16,11	n.a.	n.a.	n.a.	n.a.	n.a.
Granites	5o	580	38.40	38.35	5,86	5.11	4,99	7,52	−11,07	−9,75	16,06	17,27	0,75	−2,53	−1,32	0,210	0,182
	7o	580	36.90	38.40	6,46	6.11	5,10	5,21	−10,18	−10,03	15,28	15,24	0,35	−0,11	−0,15	0,074	0,085
Pyrite oxidation zone																	
Spring	2o	500	107.76	102.50	5,04	3.71	−2,09	−2,14	10,46	−9,89	8,37	7,75	1,33	0,05	−0,57	0,055	0,0018
“Purple Pond”	8	550	1284.22	1450.78	4,30	3.45	−6,53	−5,50	−10,59	−10,21	4,06	4,71	0,85	−1,03	−0,38	n.a.	n.a.
Stream from “Purple Pond”	9	450	n.a.	377.51	n.a.	3.26	n.a.	−4,97	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
N			12	16	11	14	11	14	12	14	11	13	10	10	11		
Minimum			1.7	1.3	4,3	3.3	− 6,5	−5,5	−14,1	−13,3	4,1	4,7	−0,2	− 2,5	−3,0		
Mean			136.9	139.7	7,1	5.5	5,0	4,3	−10,9	−10,1	15,6	14,9	1,4	−0,1	0,6		
Median			30.2	26.6	6,6	5.8	6,1	6,0	−10,4	−9,9	16,4	16,1	1,1	−0,2	−0,4		
Maximum			1284.2	1450.8	11,1	7.8	10,0	9,4	−9,6	−8,5	21,7	19,1	4,2	2,5	1,2		

n.a. – no analysed.

of groundwaters through stream-bed. The groundwaters of the RJ occur within fractured crystalline rocks and sedimentary cover deposited on this crystalline rocks. Three aquifers can be discriminated by Marszałek (1996): (1): the shallowest zone of pore waters (sedimentary cover), (2) a deeper zone of pore and fissure waters (in fractured and porous rocks) and (3) the deepest zone of fissure waters occurring in deep tectonic dislocations and fractures. The presented paper reports sulphate concentration and S–O isotope ratio in waters occurred in the zones (1) and (2).

3. Methods

3.1. SAMPLING

Ten stations for hydrogeological and hydrochemical observations have been selected on the basis of hydrogeological and hydrochemical mapping (Jezierski, 2002). In these points, during 26 months (from October 21, 1999 to December 21, 2001), seasonal changes of springs and stream discharge value and sulphate ion concentrations were measured (Table II). Moreover SO_4^{2-} concentrations were analysed in precipitations (points 1, 2 in the Table I and Figure 1), refluxes from peat-bog (point 3; Table I, Figure 1) and surface water from "Purple Pond" (located in dormant mine of pyrite – point 8; Table I, Figure 1). The number of sulphate analyses has been shown in Table III.

3.2. CHEMICAL ANALYSIS

Concentration of total sulphur was analysed using ICP (Inductive Coupled Plasma) spectrometry ARL Model 3410 in the Faculty of Chemistry at the University of Wrocław. The values of total sulphur concentration were recalculated to concentration of sulphate ions because practically only that chemical form of sulphur in this water was present (Jezierski and Szynkiewicz, 2002). Measurements of spring and stream discharges were carried out using volumetric method discriminated by Pazdro and Kozerski (1990).

TABLE II

Number of sulphate concentration analyses from the action of hydrogeological and hydrochemical mapping

Lithology	Hydrological characteristic of sampling points	Number of SO_4^{2-} concentration analyses
Granite	Surface water	3
	Spring	25
Metamorphic rocks	Surface water	6
	Spring	14

TABLE III

Number of sulphate concentration analyses in the points of stationary hydrogeological and hydrochemical observations

Sampling stations	Number of $SO_4{}^{2-}$ concentration analyses carried out
1o	25
2o	28
3o1	25
4o	29
5o	26
6o	26
7o	26
3	9
1,2	13
8	4

3.3. ISOTOPE ANALYSIS

The samples of water and snow were collected on December 5th, 2001 and February 21th, 2002. Immediately after sampling the water was frozen for 24 hours. Afterwards it was boiled, and $BaCl_2 + HCl$ were added to precipitate a barium sulphate. The precipitate was washed with redistilled water to remove chlorine ions and dried in 130 °C. The sulphur from barium sulphate was converted to SO_2 gas during combustion with V_2O_5 in 900 °C (Yanagishawa and Sakai, 1983). The oxygen from $SO_4{}^{2-}$ was converted to CO_2 gas during reaction with graphite in 1400 °C (Mizutaini and Rafter, 1973). Isotope equilibration between CO_2 and H_2O used to determine the oxygen isotope composition of water. The sulphur and oxygen isotope composition were measured in Finigan Mat CH7 mass spectrometry with a modified detection system. The sulphur and oxygen isotope ratios of sulphate and water have been expressed as a δ^{34}S value relative to CDT and δ^{18}O value relative to V-SMOW, respectively.

4. Results

4.1. CHEMICAL COMPOSITION

The lowest concentrations of sulphate ions in waters from the RJ were found in groundwaters sampled of the highest altitudes – about 13 mg/l (both in the water from the granite and metamorphic rocks). The concentration of sulphate ions in

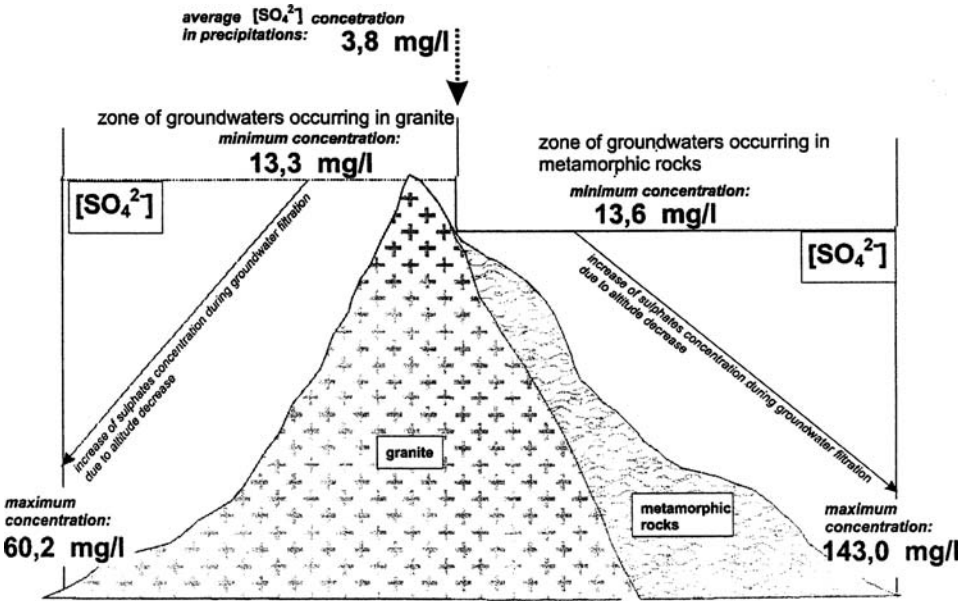

Figure 2. The scheme showing groundwaters geological relations between the granite and metamorphic rocks in the study area.

groundwaters is growing downward up to 100 mg/l in the springs located in metamorphic rocks and to 60 mg/l in springs located in granites (Figure 2).

The highest concentration of sulphate ions is observed in groundwaters and surface waters in the region of Wieściszowice village (in spring 2o ($\max[(\mathrm{SO}_4^{2-})] = 122, 5$ mg/l); in stream flowing from the “Purple Pond” $[(\mathrm{SO}_4^{2-})] = 685, 0$ mg/l) and in the “Purple Pond” $[(\mathrm{SO}_4^{2-})] = 2377, 8$ mg/l).

Statistical parameters concerning concentration of sulphate in the water analysed (Figure 3) show:

1. similar amplitudes of variations and concentrations of sulphate (25–75 percentile) in the surface waters and springs from both metamorphic rocks and granites(sampling points lo, 3o1, 4o, 5o, 6o, 7o, 3),
2. the lowermost concentration of sulphate has been found in meteoric waters (25–75 percentile),
3. the highest variations in concentration of sulphate and the highest concentration of sulphate (25–75 percentile) have been found in waters from the pyrite oxidation zone (sampling point 2o).

4.2. ISOTOPIC COMPOSITION

The sulphur isotope composition of sulphate ions reveal the ranges of δ^{34}S values from 4.3 to 11.05% in December 2001 and from 3.45 to 7.81 ‰ in February 2002

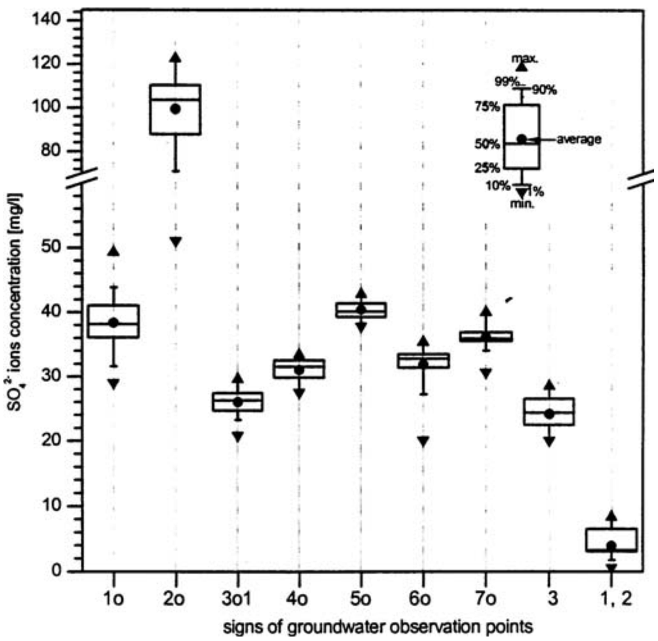

Figure 3. Statistical parameters of seasonal variations in concentration of sulphate ions in waters from Rudawy Janowicke.

(Table I). In each case (Figure 4) the lowest values of $\delta^{34}S$ characterize the water from "Purple Pond", where the intensive bacterial process of pyrite weathering exists ($\delta^{34}S$ from 3.45 to 4.30‰). The highest values of $\delta^{34}S(SO_4^{2-})$ was in the stream water flowing out from the peat-bog. In general, in December the sulphate is enriched in ^{34}S relative to that in February. The difference of $\delta^{34}S$ values between December and February ($\Delta^{34}S(SO_4^{2-})_{Dec-Feb}$ value) ranges from −0.15 to 4.20‰ (Table I, Figure 5A). The highest $\Delta^{34}S(SO_4^{2-})_{Dec-Feb}$ values are observed in the surface waters and the peat-bog outflows.

The $\delta^{18}O(SO_4^{2-})$ value ranges from −6.53 to 10.03‰ in December and from −6.07 to 7.54‰ in February (Table I, Figure 6). The $\delta^{18}O(SO_4^{2-})_{Dec-Feb}$ values are in the range from −2.53 to 2.49‰ (Table I, Figure 5B). In each case the lowest values of $\delta^{18}O(SO_4^{2-})$ characterize the water from the Purple Pond (from −6.53 to −5.17‰). The highest values of $\delta^{18}O(SO_4^{2-})$ are noted in the surface waters flowing out from the peat-bogs (from 7,54 to 10,03‰).

The oxygen isotope composition in water shows narrower variations as compared to that in sulphate ions (Table I). In general, all water samples collected in December are ^{18}O-depleted as compared to the water sampled in February, namely, the $\delta^{18}O(H_2O)$ value varies from -14.07 to $-9.60\%_0$ in December and from -11.04 to $-8.53\%_0$ in February (Table I). The $\Delta^{18}O(H_2O)_{Dec-Feb}$ varies from -2.96 to $1.18\%_0$ (Table I,Figure 5C) and shows similar ranges to that in the

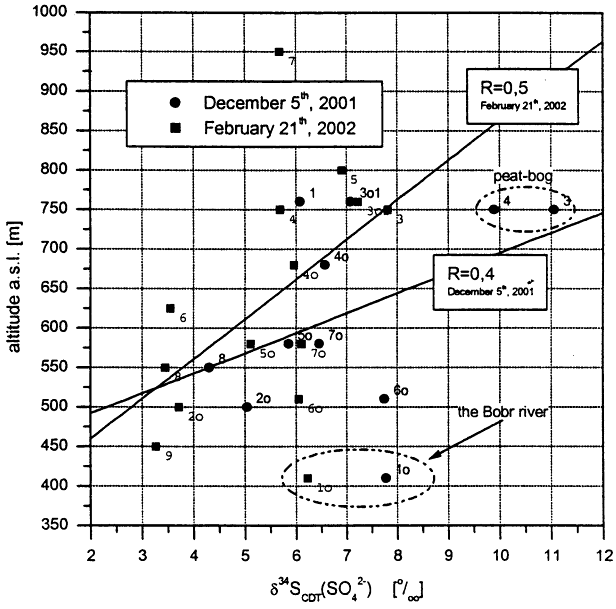

Figure 4. The variation of $\delta^{34}S(SO_4^{2-})$ value with altitude in waters from Rudawy Janowickie (December 2001 and February 2002).

$\Delta^{18}O(SO_4{}^{2-})_{Dec-Feb}$ value (Table I, Figure 5B). The $\Delta^{18}O(SO_4{}^{2-} - H_2O)$ values show two different ranges from 4.04 to 4.14 ‰ and from 15.24 to 21.72‰ (Table I, Figure 8AB).

General trends can be observed as a function of altitude decline: an increase of SO_4^{2-} concentration (Figure 7) and $\Delta^{18}O(SO_4{}^{2-} - H_2O)$ value in December 2001 (Figure 8A) and February 2002 (Figure 8B) and a decrease in $\Delta^{34}S(SO_4{}^{2-})$ and $\Delta^{18}O(SO_4{}^{2-})$ values (Figure 4, 6). The $\Delta^{18}O(SO_4{}^{2-})_{Dec.Feb}$ value ($R = -0.76$; Figure 5B) and $\Delta^{18}O(H_2O)_{Dec.Feb}$ value ($R = -0.71$; Figure 5C) show negative linear correlations with the altitude.

5. Discussion

5.1. SPATIAL VARIATION IN SO_4^{2-} CONCENTRATION

Evaporation is an important factor controlling concentration of ions dissolved in water in the environment. It is especially important in the recharge zone at the highest part of the mountains where the surface waters and groundwaters are initially poorly mineralized. The evaporation is the initial process of chemical evolution of meteoric waters especially with respect to an increase the concentration of dissolved compounds including sulphates. Hydrochemical modelling showed that

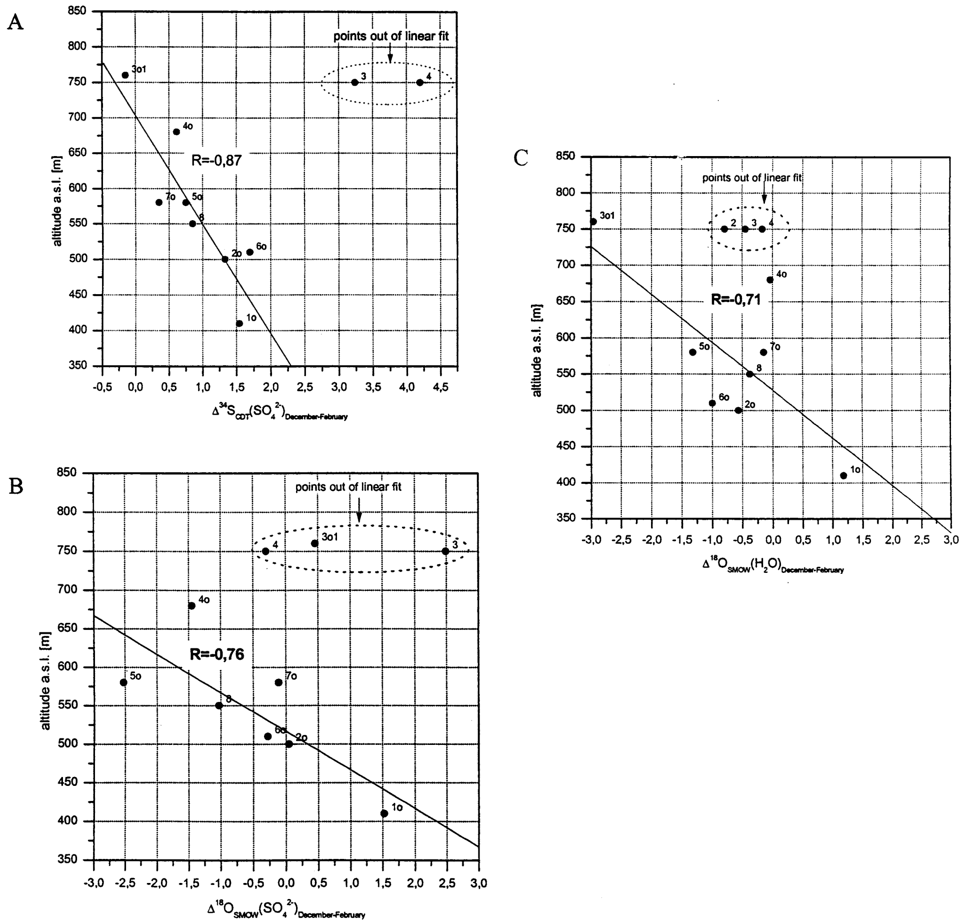

Figure 5. Changes of: A) $^{*}\Delta^{34}S_{CDT}(SO_4{}^{2-})_{\text{December–February}}$, B) $\Delta^{18}O_{SMOW}(SO_4{}^{2-})_{\text{December–February}}$, C) $\Delta^{18}O_{SMOW}(SO_4{}^{2-})_{\text{December–February}}$ values with altitude in waters from Rudawy Janowicke. $^{*}\Delta^{34}S_{CDT}(SO_4{}^{2-})_{\text{December–February}} = \delta^{34}S_{CDT}(SO_4^{2-})_{\text{December}} - \delta^{34}S_{CDT}(SO_4^{2-})_{\text{February}}$.

evaporation of water in the RJ results up to 17% increase in concentration of SO_4^{2-} (Jezierski, 2002).

5.2. Sources of sulphur

The sulphur and oxygen isotope composition may indicate the origin of sulphate. This is partly due to high stability of SO_4^{2-} molecule which makes it recalcitrant to isotope exchange with other sulphur and oxygen compounds. In natural condition, the half-time of oxygen isotope exchange between SO_4^{2-} and water takes 10^4–10^5 (Lloyd, 1968) or 10^7 years (Chiba and Sakai, 1985).

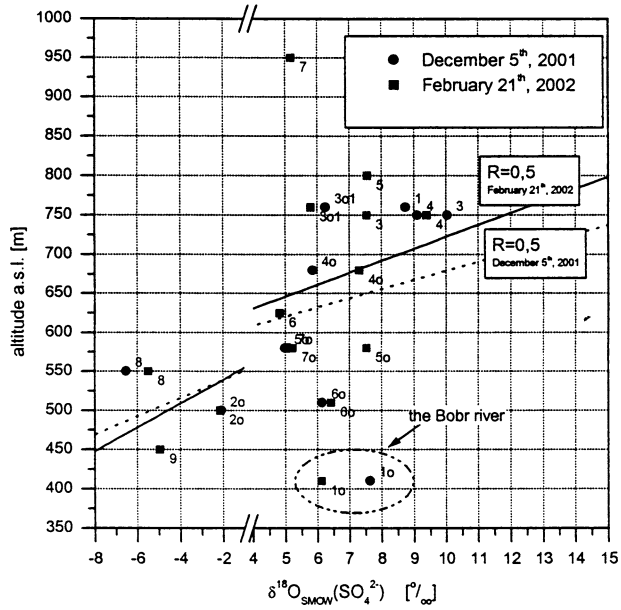

Figure 6. The variations of $\delta^{18}O(SO_4^{2-})$ value with altitude in waters from Rudawy Janowicke (December 2001 and February 2002).

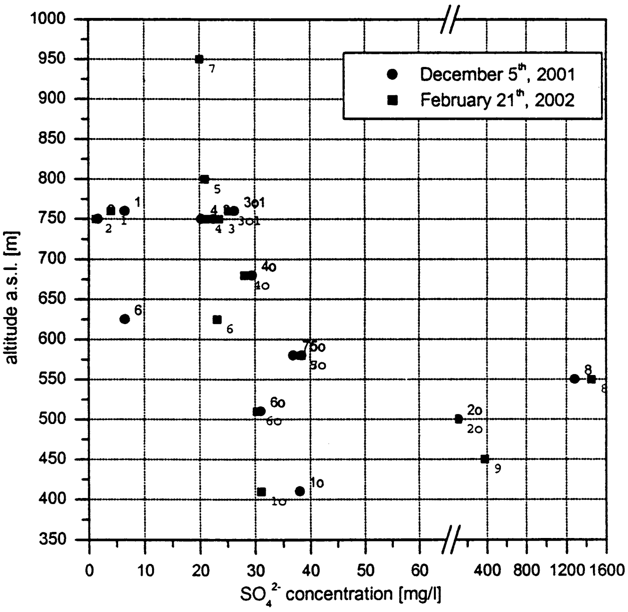

Figure 7. The variations of sulphate concentration with altitude in waters from Rudawy Janowickie (December 2001 and February 2002).

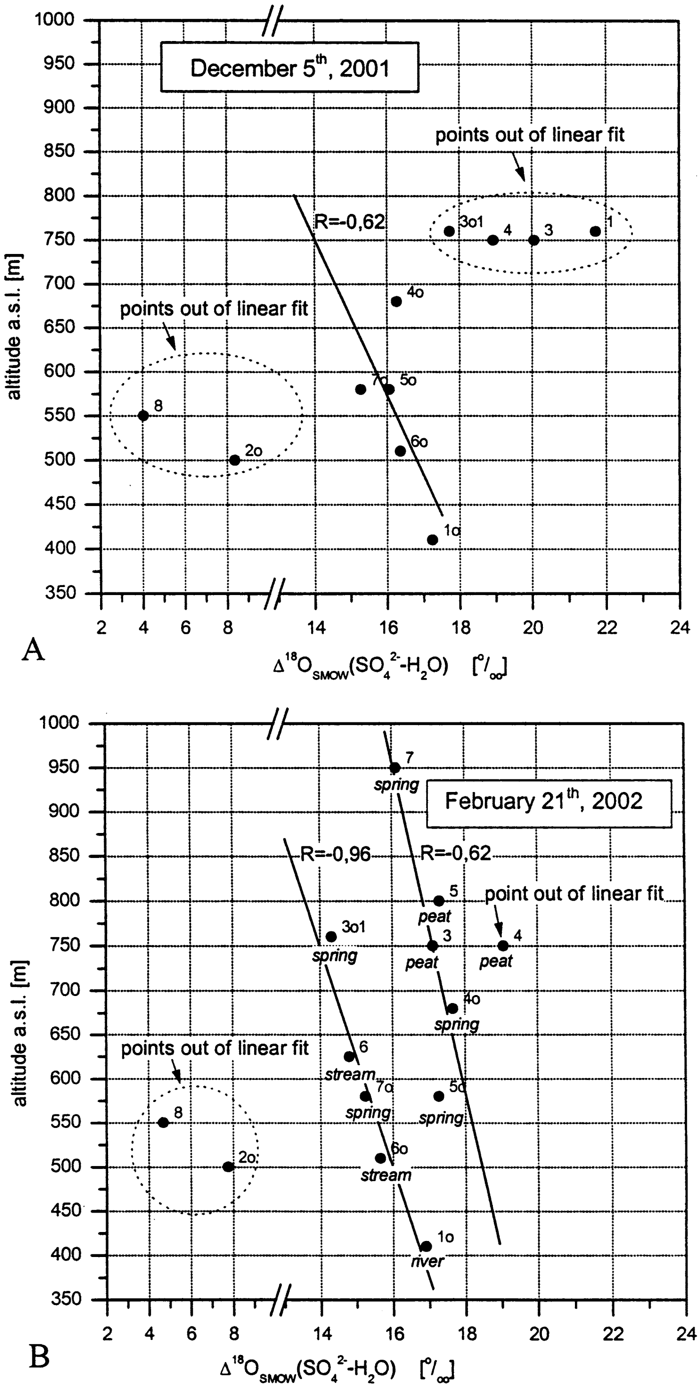

Figure 8. The variations of $\Delta^{18}O(SO_4^{2-}\text{-}H_2O)$ value with altitude in waters from Rudawy Janowickie: A) December 2001 and B) February 2002.

Accordingly, the sulphur and oxygen isotope composition of sulphate ions in the surface waters and groundwaters of RJ may keep information on origin and formation processes of that SO_4^{2-}. Three sources of sulphate are dominant in this region: (1) anthropogenic origin - sulphur compounds from atmospheric pollutions; (2) geogenic origin - sulphate formed mainly due to decomposition and oxidation of sulphur-bearing minerals in crystalline rocks and (3) biological origin – from decomposition and mineralization of organic matter contained in forest soils and peat-bogs. The picture is complicated due to mixing of waters, containing sulphur from anthropogenic, geogenic and biogenic sources, or locally due kinetic isotope fractionation controlled by biological processes (e.g. peat-bogs areas).

5.2.1. *Anthropogenic Sulphur*

$\delta^{34}S$ and $\delta^{18}O$ values for sulphate of anthropogenic origin range from 0 to 10 ‰ and from 5 to 20 ‰, respectively (Longinelli and Cortecci, 1970; Krouse and Grinenko, 1991; Hoefs, 1997; Jędrysek, 2000).

The attempts for sulphur and oxygen isotope analysis in sulphate ions from meteoric precipitation were made for samples from one of the highest point in RJ (altitude 800 m a s l, see Table I). In each sampling action the concentration of sulphate in precipitation was too low (from 1.31 to 6.50 mg/l) to analyse $\delta^{34}S$ and $\delta^{18}O$ values (the collected samples were too small). Nevertheless, in February 2002 the $\delta^{34}S$ and $\delta^{18}O$ values were measured showing 6.08 and 8.74‰, respectively (Table I). They are typical for anthropogenic sulphates and exhibit similar $\delta^{34}S$ and $\delta^{18}O$ values of sulphate measured in precipitation at neighbouring area of Karkonosze Mountains (Jędrysek *et al.*, 2002). The low concentration of Cl ions (0.88 and 0.79 mg/l) and low $\delta^{34}S(SO_4^{2-})$ rather excludes significant contribution of oceanic aerosol in the atmospheric SO_4^{2-}.

About two years monitoring of SO_4^{2-} concentration ($\%SO_4^{2-}$) have been carried out in 10 sampling stations (springs, streams or ponds). The number of sampling actions in the respective sampling points has been shown in Table III. It has been found that the $\%SO_4^{2-}$ varied in narrow ranges and the highest $\%SO_4^{2-}$ to the lowest $\%SO_4^{2-}$ ratio in each sampling point varied from 1.1 to 2.4 with average 1.5 (Table IV). This variation is probably resulted from seasonal changes in the magnitude of recharge of the groundwaters.

From the concentration ratios (Table IV) may be calculated that the concentration of sulphate in precipitation ranges from 1.31 to 9.75 mg/l. However, this values are distinctly lower than that observed in surface waters and groundwaters (Table I). Therefore, it may be concluded that the contribution of anthropogenic sulphate is negligible. Besides, an increase in concentration of sulphate (Figures 2, 7) and decrease in $\delta^{34}S(SO_4^{2-})$ and $\delta^{18}S(SO_4^{2-})$ values (Figures 4 and 6) with decreasing altitude suggest enrichment in sulphate ions from other sources (isotopic lighter) during water downward flow. Thus, the atmospheric precipitation of the anthro-

TABLE IV

The ratio of maximal to minimal concentration of sulphates in groundwaters measured in the same sampling points (SO_4^{2-} max /$SO_4{}^{2-}$ min) in the RJ between 21.10.1999 and 21.12.2001

Sampling stations	Number of measurements carried out	$\frac{\max}{\min}SO_4{}^{2-}$ concentration
2o	28	2.4
3o1	25	1.4
4o	29	1.2
5o	26	1.1
7o	26	1.3
3	9	1.4
		Average = 1.5

pogenic sulphate is only one among some other more important sources of sulphate in the RJ.

5.2.2. *Geogenic Sulphur – The Purple Pond*

Locally, the sulphates analysed are strongly enriched in the light isotopes, what may result from oxidation of sulphide minerals, especially pyrite from the RJ mica-schist rocks near Wieściszowice village (550 m a.s.l). This process definitely takes place in the water called Purple Pond (Figure 1) where pyrite was exploited in XIX and at the beginning of XX century. The pond has been formed in the place of the abandoned mine and the surface waters and groundwaters became strongly mineralised with sulphate ions (up to 1500 mg/l, Table I – point 8).

The $\delta^{34}S$ value of sulphates in the Purple Pond ranges from 3.45 to 4.30‰ (Table I) and it is slightly higher as compared to $\delta^{34}S$ of sulphides in mica-schists (from 1.0 to 2.2 ‰) analysed by Parafiniuk (1996). It is well known that sulphate, formed due to oxidation of pyrite, is slightly enriched in ^{34}S isotope as compared to that in the parental pyrite, and the sulphur isotope fractionation results from microbial oxidation (Nakai and Jensen, 1964; Kaplan and Rittenberg, 1964). Parafiniuk (1991, 1996) and Parafiniuk and Dobrzyński (1995) documented that sulphates in the Purple Pond are formed due to intensive pyrite oxidation by *Thiobacillus ferrooxidans*, i.e. the bacteria which oxidise Fe^{2+} to Fe^{3+}. The bacterial oxidation is about six orders faster as compared to an inorganic (abiotic) oxidation (Lacey and Lawson, 1970; Singer and Stumm, 1969; Nordstrom, 1977). Therefore, regardless high concentration of O_2 dissolved in the surface water at the Purple Pond ($\sim$7 mg/l) the role of abiotic oxidation due to O_2 activity is negligible (Parafiniuk, 1996).

The pH value of the water in the Purple Pond is 3.5 and shows little annual variations (Jezierski, 2002). Two pathways of pyrite oxidation are observed under acid condition: (i) no Fe mediated and (ii) Fe mediated. The first pathway is accelerated by dissolved oxygen and 87.5% of oxygen in the sulphate molecule is derived from dissolved oxygen. The remaining 12.5% of oxygen comes from water. The second pathway is mediated by ferric iron where 100% of oxygen is derived from water (Garrels and Thompson, 1960; Smith *et al.*, 1968). The atmospheric oxygen is strongly enriched in ^{18}O isotope (δ^{18}O $= +23.0$‰, Kroopnick and Craig, 1972; $+23.8$‰ Horibe; *et al.*, 1973) as compared to surface waters in the Purple Pond (δ^{18}O value was -10.59‰ on December 2001, and -10.21‰ on February 2002, Table I). Unfortunately, we do not know α fractionation factors in the O_2-SO_4^{2-} and H_2O-SO_4^{2-} systems, and moreover the bacterial processes are usually accompanied by kinetic fractionation. Nevertheless, the atmospheric oxygen is probably enough ^{18}O-enriched, as compared to the water in the system studied, to distinguish fairly well the role of these two oxidation pathways. Namely, it is expected that sulphate formed due to pyrite oxidation by dissolved oxygen is enriched in ^{18}O isotopes as compared to sulphate originated due to ferric iron oxidation. The δ^{18}O value of sulphate in the Purple Pond ranges from -6.53 to -5.50 ‰ and it is close to the oxygen isotope composition of water (Table I). The difference between δ^{18}O of sulphate and water ($\Delta^{18}O(SO_4^{2-}$–$H_2O)$) ranges from 4.06 to 4.71 ‰. Our data are apparently consistent with Parafiniuk (1996) who states that the oxidation of pyrite in the Purple Pond are mainly controlled by ferric iron oxidation what is also stimulated and accelerated by *Thiobacillus ferrooxidans.* This apparently contradicts to the experimental data presented by Taylor *et al.* (1984) who states that oxidation of pyrite in the presence of *Thiobacillus ferrooxidans* and in the aerobic condition is controlled by dissolved oxygen, and $\Delta^{18}O(SO_4^{2-}$-$H_2O)$ value is high and may reach up to 18 ‰ in well-aerated waters. The low $\Delta^{18}O(SO_4^{2-}$–$H_2O)$ value in the Purple Pond may suggest that sulphate is of deep-water origin where the water is O_2-depleted. However oxidation of pyrite by *Thiobacillus ferrooxidans* proceeds also at the surface and the pond water collects the soluble weathering products, removed by precipitation water from the pit walls of the abandoned mine (Parafiniuk 1996).

Sulphates from the Purple Pond showed the lowest values of δ^{34}S (from 4.30 to 3.26‰) and δ^{18}O (from -5.17 to -6.53‰) in the region under study, while the concentration of sulphate in the Purple Pond is the highest. Therefore contamination of groundwaters and surface waters with the water from the Purple Pond may help to trace the water regime studied. This effect is observed in a spring located near Wieściszowice village (point 2o) which is about 50 m (vertical) below the Purple Pond where the concentration of sulphate is one order higher (up to 380 mg/l) than that in the other water springs just above the Purple Pond (the average concentration of sulphate is about 30 mg/l).

5.2.3. *Biogenic Sulphate*

The biogeochemical sulphur cycle is complex and it is widely controlled by red-ox processes and accompanied by isotope effects. Decomposition of organic matter, especially in the oxidized environments, may result in isotopically depleted sulphate. On the other hand, in a deficit oxygen in the environment, the microbial sulphate reduction enriches the residual sulphate in ^{34}S and ^{18}O isotopes (*e.g.* Krouse *et al.*, 1970, Fritz *et al.*, 1989; Trembaczowski, 1990).

Forests and peat-bogs are considered to be the main pools of biogenic sulfur compunds in the RJ Mts. About 70% of the RJ is covered by coniferous forests. Spruce trees contribute about 90% of that forest stands and *Piceatum montanum* is the most common spruce of spruce species. Besides beech and java appear occasional in some places (Staff *et al.*, 1998). Peat-bog areas show a significant accumulation of organic matter. The spruce monoculture and SO_2 anthropogenic impact contributed the ecological disaster at the beginning of eighties (Baron and Sobik, 1995).

A large difference between sulphates concentration in waters outflowing from a small mountain peat-bogs near Czarnów (750 m a.s.l.) (up to 21.8 mg/l) and in the precipitation (up to 6.50 mg/l) has been observed (Table I). Thus, the peat-bog can be locally important source of sulphate. We suspect that signifficant amount of ^{34}S- and ^{18}O-enriched sulphates contributes to the groundwaters and streams in the RJ at lower than 750 m a.s.l levels. Namely, the sulphur and oxygen isotope composition of sulphate, dissolved in the water outflowing directly from the peat-bog, shows the highest $\delta^{34}S$ and $\delta^{18}O$ values (Table I) found in the area under study, both in December 2001 and February 2002.

The isotope composition of sulphur in organic matter from soil and spruce needles in RJ show the similar values as these in the adjacent Karkonosze Mountains (Jędrysek *et al.*, 2002). Sulfur isotope ratios in organic matter from soil of conifer and deciduous forest, marsh sediment in RJ were 4.08, 4.90, 3.13 respectively. However, they are higher as compared to peat ($\delta^{34}S = -5.87$ ‰). Exept of peat (strong redox processes), well correspond to lower range of $\delta^{34}S$ values of sulphate dissloved in surface waters and groundwaters in the region under study (Table I, Figure IV).

Two sources of biogenic sulphur in RJ massif can be discriminated due to stable isotope analysis: (1) ^{34}S and ^{18}O enriched sulphate from peat-bogs, and (2) ^{34}S depleted sulphate, from decomposition and oxidation of organic matter in the soil. It is not possible at present to quantitatively estimate the ratio between these sulphur sources. Nevertheless, from $\delta^{34}S(SO_4^{2-})$ values, one may conclude that decomposition of organic matter is an important source of sulphate in the region under study.

5.3. SEASONAL CHANGES

5.3.1. *Chemical Composition – Seasonal Dillution*

Seasonal variations in the precipitation directly influence on groundwater recharge and concentration of sulphate ions in the groundwater. Rain waters and snow-melting waters are slightly-mineralised, thus concentration of sulphate ions

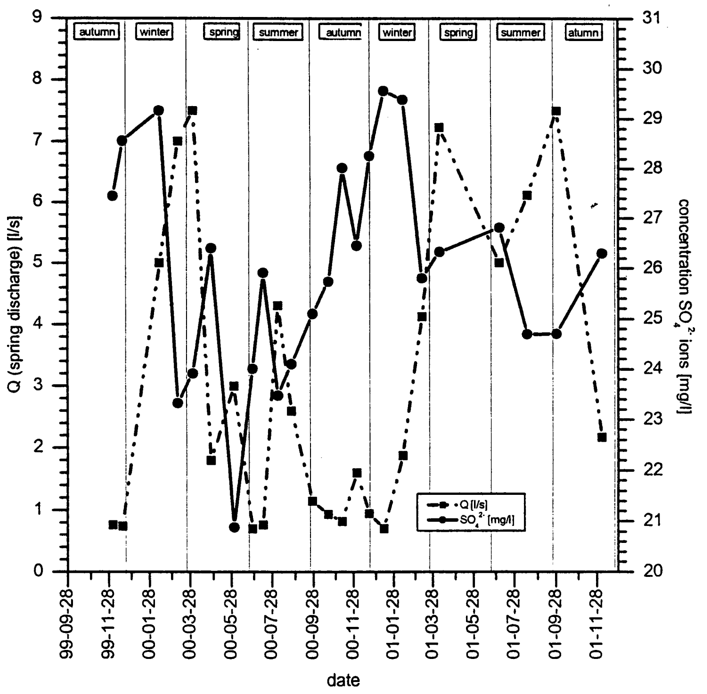

Figure 9. Seasonal variations in concentration of sulphate in waters from Rudawy Janowickie (October 21, 1999 to December 21, 2001).

decrease in groundwaters due to dilution by meteoric water. The ratio of the maximal to the minimal concentration of sulphates in groundwaters (SO_4^{2-}max/SO_4^{2-}min) of the RJ between 21.10.1999–21.12.2001 varied from 1.1–2.4 (with the average 1.5) (Table IV) with no altitudinal trends. The widest variation in the sulphate concentration in groundwaters and streams are revealed in periods of high precipitations and snow-melting periods (Figure 9) when fast runoff from the weathering zone is observed. During hydrological droughts, when springs and streams discharges were stable, little variation in concentrations of sulphate has been observed (Jezierski, 2002, Figure 9).

A simple analysis of seasonal variations in the concentration of SO_4^{2-} do not allow to estimate the role of dilution and dissolving at sulphate through washing out the SO_4^{2-} from the weathering zone. This, apparently can be done by means of $\delta^{34}S$ and $\delta^{18}O$ analysis of sulphate.

5.3.2. *Isotopic Composition and the Origin of* SO_4^{2-}

It is expected that the seasonal dilution by rain waters or snow-melting waters should result in seasonal variations in isotope composition of sulphate due to the contribution of anthropogenic SO_4^{2-} (acid rain) and biogenic and geogenic sulphate washed out from the soil and rocks, respectively. The biological and geogenic sulphate in the RJ shows low $\delta^{34}S$ values varying from 1.0 (pyrite, Parafiniuk, 1996) to 4.9 ‰ (Table I, organic matter -see chapter 5.2.3), respectively. We suspect that the low values of $\delta^{34}S(SO_4^{2-})$ on February 2002, when the water level was high (Table I) resulted from the observed wash out of sulphate from the soil and rocks. On the other hand, a contribution of anthropogenic sulphate moves $\delta^{34}S(SO_4^{2-})$ toward higher values. This has been noticed in December 2001 when low water level corresponds to concentration of sulphate in the atmospheric precipitation. Nevertheless it seems that generally, low concentration of sulphate in precipitation (Table I) makes the anthropogenic sulphate of secondary importance, especially when compare to peat-bogs, which probably deliver more sulphate to groundwaters than precipitation does.

The positive and negative correlations have been observed in the altitude-SO_4^{2-} concentration (Figure 7), altitude-$\delta^{34}S(SO_4^{2-})$ (Figure 4) and altitude-$\delta^{18}O(SO_4^{2-})$ (Figure 6) systems. The highest $\Delta^{34}S(SO_4^{2-})_{\mathrm{Dec-Feb}}$ values (1.54 i 1.96‰) was noted for groundwaters and surface waters located at lower altitudes (Figure 5A). It is probably resulted from a cumultive character of the drainage by surface waters (especially Bóbr river) and increasing downward mixing in the sulphate from precipitation, surface run-off, eluates from soil and peats, and inflow of groundwaters from various levels.

Distinct negative correlations in the altitude$-\Delta^{18}O(SO_4^{2-})_{\mathrm{Dec-Feb}}$ ($R = -0.76$, Figure 5B) and altitude$-\Delta^{18}O(H_2O)_{\mathrm{Dec-Feb}}$ ($R = -0.71$, Figure 5C) show a strong relation between $\Delta^{18}O$ of sulphate and water and with altitude-$\Delta^{18}O(SO_4^{2-}\text{-}H_2O)$ system, both in December 2001 and February 2002 (Figure 8AB). The oxygen isotope composition of water analysed shows clear altitudinal effect (Jezierski, 2002). This effect is well known and widely documented (e.g. Vogel *et al.*, 1975; Payne and Yurtsever, 1974; Stahl *et al.*, 1974; Sigenthaler and Oeschger, 1980). In our opinion, the differences in isotope composition of water collected in December 2001 and February 2002 may mainly result from the seasonal variations of air temperature but influence of temperature to oxygen isotope composition of sulphate is rather unclear and the lower $\Delta^{18}O(SO_4^{2-}\text{-}H_2O)$ values at higher altitudes may be resulted from other factors. Except of $\Delta^{18}O(SO_4^{2-}\text{-}H_2O)$ value in the Purple Pond, the $\Delta^{18}O(SO_4^{2-}\text{-}H_2O)$ values in surface waters and groundwaters, are very high and varying from 15.28 to 20.06 ‰ on December 2001 and from 15.24 to 19.07 ‰ on February 2002 (Figure 8AB). It may suggest the similar origin of oxygen (H_2O and O_2) in the sulphate from surface waters and groundwaters. The $\delta^{18}O(SO_4^{2-})$ value correlates slightly with altitude variation ($R = 0.50$, Figure 6) and the observed increase of $\Delta^{18}O(SO_4^{2-}\text{-}H_2O)$ value correlates with altitude decrease (Figure 8AB). These may be resulted from: (i) altitude $\delta^{18}O(H_2O)$-effect, (ii) increasing oxygenation, thus the role of O_2 in the SO_4^{2-} particles should be considered or/and (iii) mixing of waters of different origin during downward flow.

6. Conclusions

1. Three main, isotopically diverse, sources of sulphate in the surface waters and groundwaters have been detected. The high δ^{34}S and δ^{18}O values show sulphates from precipitation and the peat-bog area. The lower δ^{34}S and δ^{18}O sulphates originated from decomposition of organic matter. The lowest δ^{34}S and δ^{18}O values are in sulphate formed in the pyrite weathering zone, where pyrite is oxidized by *Thiobacillus ferrooxidans* bacteria.
2. Precipitation is not important source of sulphate ion in the surface waters and groundwaters of the RJ. We suggest that sulphate of biogenic and geogenic origin is dominant in these systems.
3. Isotopic variation in sulphate ions in the surface and groundwaters probably results mainly from mixing of biogenic and geogenic sulphate, or locally from isotopic fractionation controlled by biological processes (especially in the peat-bog area).
4. Atmospheric sulphur compounds of anthropogenic origin are of secondary importance in the RJ waters. This evidence significant improvement of natural enironment in the Western Sudety Mountains.

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