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The variability of $\delta^{34}S$ and sulfur speciation in sediments of the Sulejów dam reservoir (Central Poland)

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ABSTRACT

The study was carried out on the Sulejów dam reservoir (Central Poland). Water and sediment samples were collected between February and October 2006. Sulfur compounds in the sediment were chemically extracted and subjected to isotopic analysis.

Large variability of SO_4^{2-} concentration in the water column (from 10.3 to 36.2 mg/dm^3) and the isotopic composition of sulfur ($\delta^{34}S$ from 2.1 to 5.4‰) was observed. The main identified sources of SO_4^{2-} were watercourses, surface runoff, and phosphorus fertilizers.

Both oxidized sulfur species (SO_4^{2-}) and its reduced forms were found in sediments. Particular sulfur forms were characterized by large variations in both, concentrations and the isotopic composition of sulfur. SO_4^{2-} in the sediment and in the water column had different genesis. Bacterial oxidation of organic sulfur and its binding in SO_4^{2-} were observed in the sediment. Under reducing conditions, oxidized and organic sulfur is converted to H_2S which reacted with Fe or other metallic ions leading to metal sulfide precipitation. Monosulfides were shown to have a very low concentration, ranging up to 0.07 mg/g of sediment. The transformation of elemental sulfur from sulfides through their chemical oxidation occurred in the sediment.

1. Introduction

The aim of this study was to better understand sulfur cycling in the Sulejów dam reservoir, especially to assess geochemical interactions between the water column and sediments in context of their periodical supply by organic matter coming from cyanobacterial bloom.

Sulfur cycling in aquatic sediments involves both reductive and oxidative processes (Jorgensen, 1988, 1990). In freshwater, sulfur occurs as SO_4^{2-} and organic compounds (David and Mitchell, 1985; Herlihy et al., 1988; Peiffer, 1988; Jędrysek, 2005). The main sources of sulfur are weathering of rocks within the catchment of a water body, oxidation of organic sulfur, burning of fossil fuels, and discharge of wastewater containing the sulfate (VI) ion (David and Mitchell, 1985; Herlihy et al., 1988; Cook and Kelly, 1992; Dornblaser et al., 1992). Sulfur compounds are transported into water, primarily through surface runoff or precipitation.

The SO_4^{2-} concentration in freshwater is relatively low compared to seawater (28 mM) and ranges from about 10 to more than 1000 μM (Jorgensen, 1988). Acidic lakes are characterized by low concentrations (<100 μM), while in the case of oligotrophic lakes SO_4^{2-} concentrations are at a level of <300 μM. On the other hand, meso- and eutrophic lakes are usually characterized by high concentrations (700–800 μM). Lakes with a large supply of mining water and wastewater can reach very high concentrations exceeding 1000 μM (Jorgensen, 1988, 1990). As microbial part of sulfur cycling, especially sulfate uptake and assimilation and sulfate dissimilative reduction are strongly connected to organic carbon and nitrogen availability (Davidian and Kopriva, 2010), we can expect in eutrophic waters, both: more dynamic sulfur turnover and more intensive sulfur removal from water column due to high rate of organic matter precipitation.

Observations of sulfur cycling in lakes were frequently neglected due to imprecise research methods that prevented accurate chemical analysis (Jorgensen, 1988, 1990; Bak and Pfennig, 1991).

The SO_4^{2-} ion supplied to a water undergoes numerous biogeochemical processes, which result in change of its concentration,

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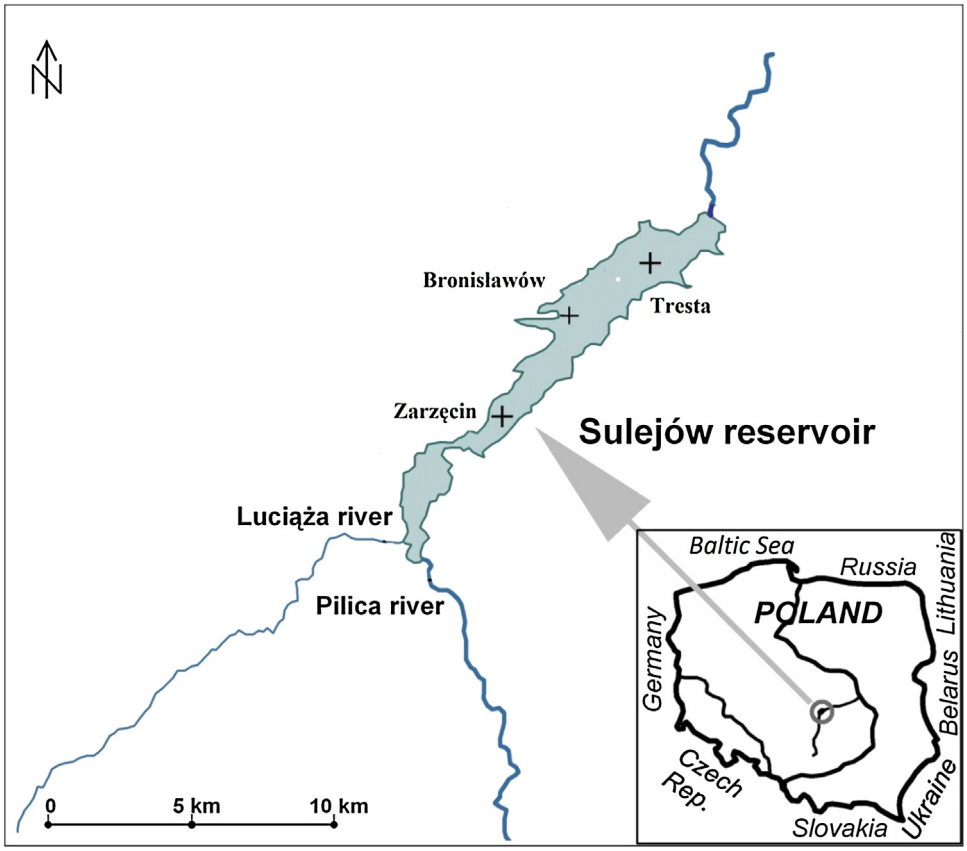


Fig. 1. Location of sampling points on the Sulejów Reservoir.

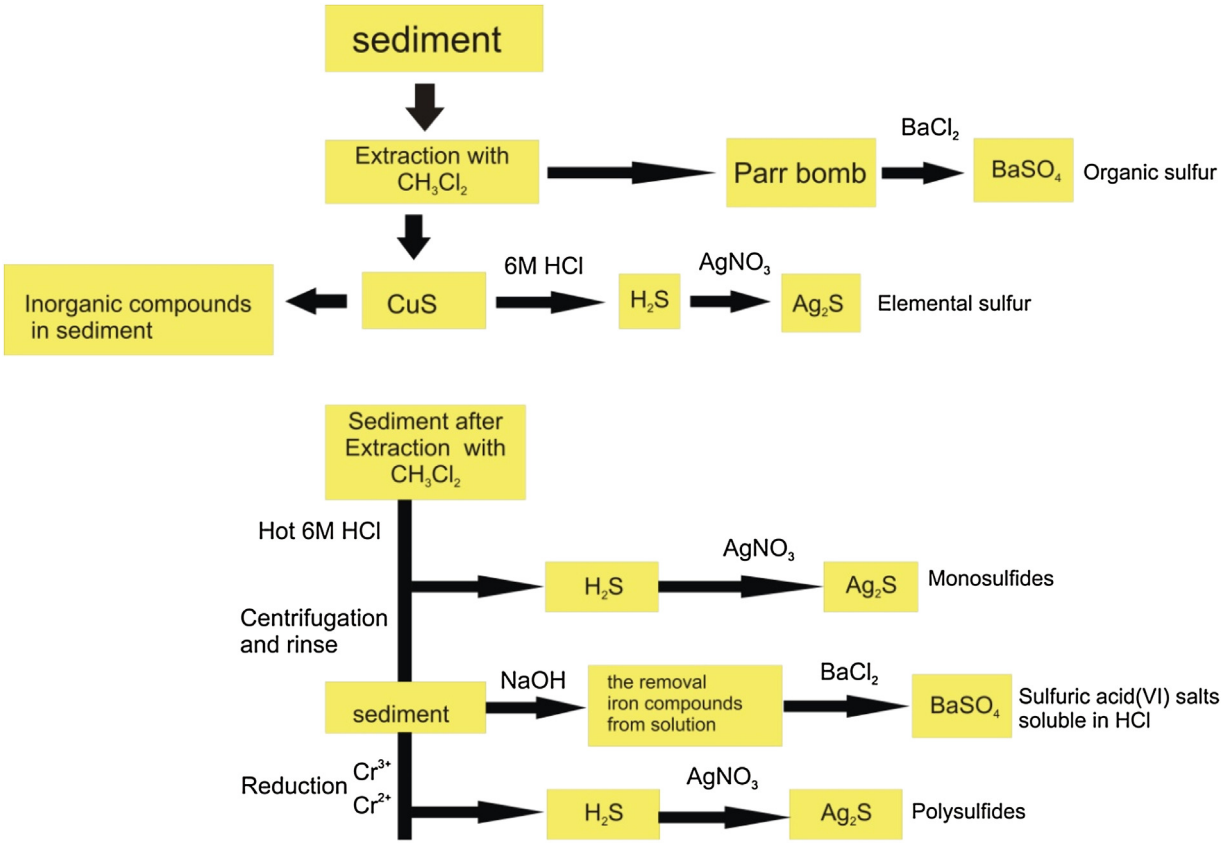


Fig. 2. Flow diagrams showing the chemical separation of particular forms of sediment sulfur.

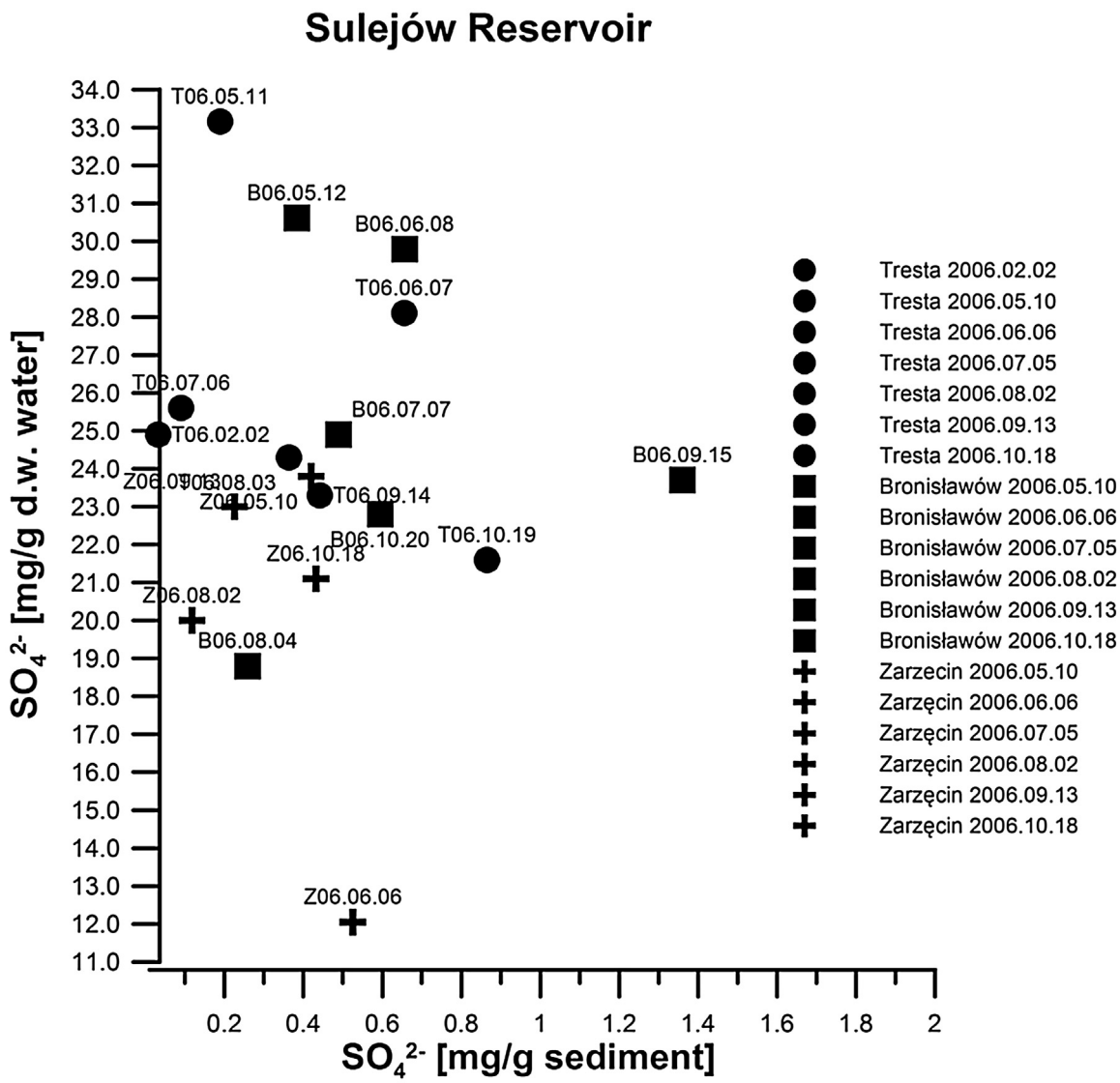
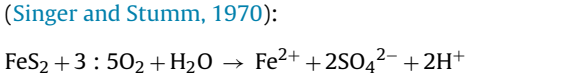


Fig. 3. A comparison of the concentration of sulfate (VI) ions in the sediment and the concentration of dissolved sulfate (VI) ions in the water column in the Sulejów reservoir.

both in the water and in the sediments. The SO_4^{2-} ion from the water column is assimilated by plankton organisms and incorporated into the cell structure. Under favorable conditions, SO_4^{2-} can be transported to the anaerobic zone where it is bacterially reduced to H_2S. Hydrogen sulfide can react with metals and be precipitated in the sediment as mono- and polysulfides under such conditions (Jorgensen, 1990). It was prooved that about 90% of reduced sulfur bound to monosulfides was transformed very quickly into pyrite (Davison et al., 1985; Rudd et al., 1986; Rickard, 1997). Only a small fraction of reduced sulfur (<10%) remains deposited in the sediment for a longer period of time (e.g. Bak and Pfennig, 1991; Rudd et al., 1986; Jorgensen, 1997; Berner and Westrich, 1985). Pyrite can be oxidized either by molecular O_2 or by Fe^{3+} ions acting as electron acceptors (Tichomirowa and Junghans, 2009). Accordingly, these reactions are commonly described by the following bulk reactions (Singer and Stumm, 1970):

$$FeS_2 + 3:5O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$



$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-}$$

The elemental sulfur formation mechanisms have not been fully identified to the date, but it seems that the most important process of S^0 formation is the oxidation of sulfides precipitated in sediments under conditions of low oxygen concentration. Moreover, iron and manganese oxides can act as important sulfide oxidants that facilitate the formation of elemental sulfur (Jorgensen, 1988).

SO_4^{2-} is a very stable ion that does not undergo isotopic exchange under aeration zone. The isotopic composition of sulfur in this compound is therefore determined only by the sources of its origin and redox reactions, which are predominantly controlled by the biosphere and which in consequence lead to changes in its concentration in the water column and in the sediment. These inputs are also balanced by the outputs such as sulfur removal by oxidation, pyrite precipitation, or reaction with organics. Thus, the $\delta^{34}S(SO_4^{2-})$ value is affected by the isotope mixing mass balance of SO_4^{2-} originating from different sources (Jędrysek, 1998, 2005; Clark and Fritz, 1997).

The process that modifies the isotopic composition of SO_4^{2-} to the greatest extent is bacterial SO_4^{2-} reduction, which causes SO_4^{2-} to be enriched in the heavy isotope of sulfur (^{34}S), because sulfate (VI) reducing bacteria preferentially break the bonds of light isotopes (Krause and Grinienko, 1991; Clark and Fritz, 1997). During sulfate reduction, the bacteria produce gaseous H_2S that has a $\delta^{34}S$ value at least 25‰ lower

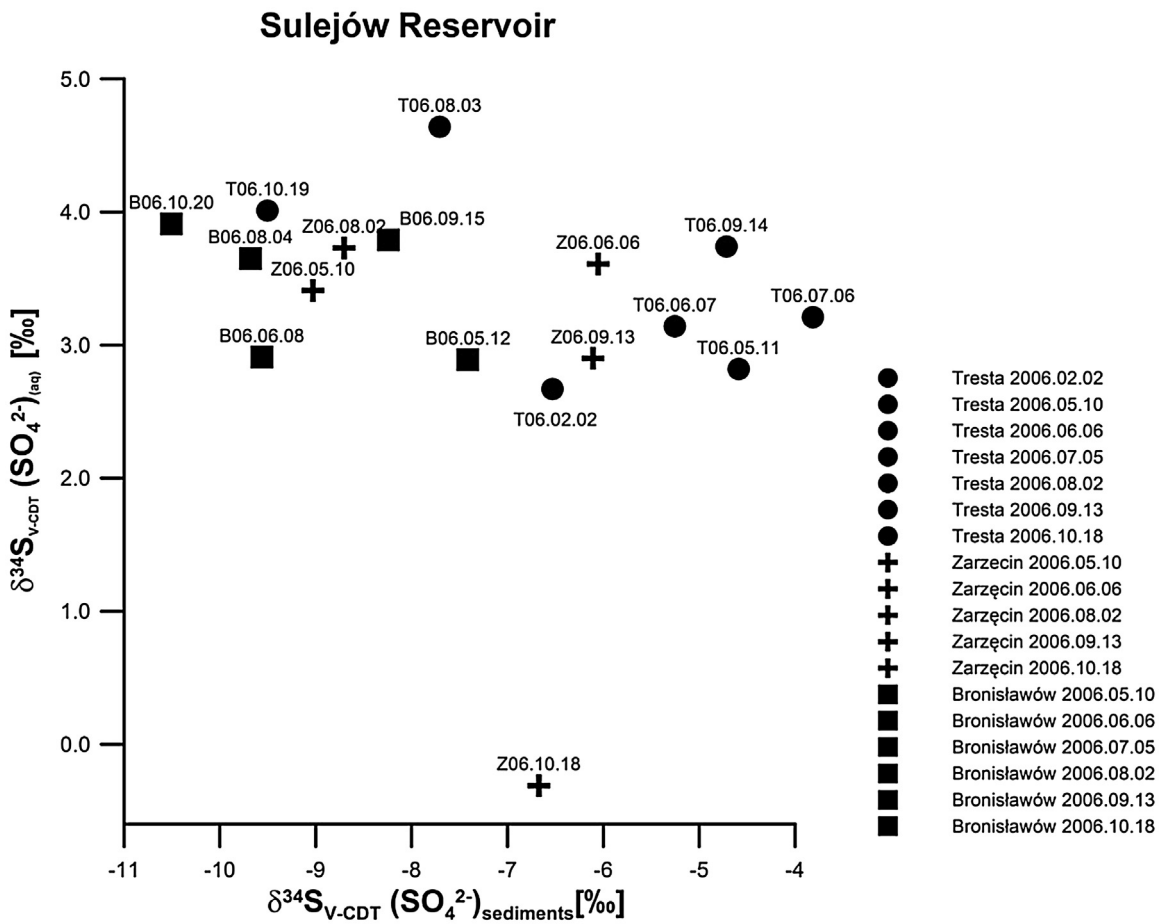


Fig. 4. A comparison of the isotopic composition of sulfur in the water-soluble sulfate (VI) ion from the sediment and the isotopic composition of sulfur in the sulfate ion dissolved in the water column.

than the sulfate source (Clark and Fritz, 1997). Consequently, the residual pool of sulfate becomes progressively enriched in ^{34}S. Experiments on sulfide oxidation with ferric iron show variable isotopic fractionation $\varepsilon_{SO4-FeS2}$ (Balci et al., 2007): $\varepsilon_{SO4-FeS2} = -0.7‰$; (Mazumdar et al., 2008): $\varepsilon_{SO4-FeS2} = -0.9‰$; (Thurston and Mandernack, 2010): $\varepsilon_{SO4-FeS2} = -3.7‰$; (Heidel and Tichomirowa, 2011): $\varepsilon_{SO4-FeS2} = -0.8‰$. Laboratory experiments reveal that there is no isotopic fractionation between coarse- and fine-grained sediments in which the experiment lasted more than 30 days. However, fractionation occurs in fine-grained sediments in which the experiment lasted less than 30 days (Tichomirowa and Junghans, 2009).

In freshwater sediments, organic sulfur occurs as esters, which are characterized by the enrichment in the heavy isotope of sulfur by 3.6‰ on average in relation to the sulfate ion dissolved in water, and in the form of carbon-bound sulfur, primarily in amino acids for which a low enrichment in the heavy isotope of sulfur, in the order of −l‰ relative to the sulfate ion from the water, was encountered (Kendall and McDonnell, 1998).

SO_4^{2-} is the dominant form utilized by plants, in particular in environments where the sulfate concentration is low. Sulfate uptake and assimilation by plants are repressed in negative feedback loop in a presence of reduced sulfur, including sulfide hydrogen. (Davidian and Kopriva, 2010). Therefore, H_2S may inhibit the uptake of sulfate (Brunold and Erismann, 1975). Bacterial sulfate uptake also may be affected by sulfate hydrogen, which cause reversible toxicity effect due to subsequent inhibition on cytochrome oxidase and other metalloenzymes (Guidotti, 1996). However different groups of bacteria respond to different levels of H_2S concentration, where sulfate reducing bacteria show the highest sensitivity (Mirzoyan and Schreier, 2014). In most cases, assimilatory sulfate reduction does not lead to significant fractionations; for aquatic plants, typical fractionations range from 0 to 3‰ (Nriagu et al., 1991). Sulfates (VI) produced by the oxidation of gaseous hydrogen sulfide are depleted in heavy isotopes and usually are characterized by negative values of $\delta^{34}S$, e.g. −11‰ (Toran and Harris, 1989).

2. Study area

Samples were collected from the Sulejów reservoir which was developed in the mid 1970′s in the middle section of the Pilica River (Fig. 1). Until 2003, it was the main water reservoir supplying drinking water to the city of Łódź. Furthermore, it is an important tourism and recreation site for the residents living in the nearby localities.

The Sulejów Reservoir is a shallow eutrophic waterbody with a high catchment area to reservoir area ratio (Tarczyńska, 1997). The catchment of this reservoir, with an area of 4.884 km^2, is used for agricultural purposes in more than 64%, whereas forests cover 26.90% (Ambrożewski, 1980). At the maximum impoundment level, the reservoir length is 17 km and its maximum width is 2 km, while its depth increases in the direction towards the dam from 1.5 to 11 m.

The reservoir is fed from the direct catchment, which comprises surface runoff from the adjacent areas and smaller watercourses flowing directly into the reservoir, and from the indirect catchment which includes the catchment of the upper and middle sections of the Pilica River and the catchment of the Luciąża River. In the total

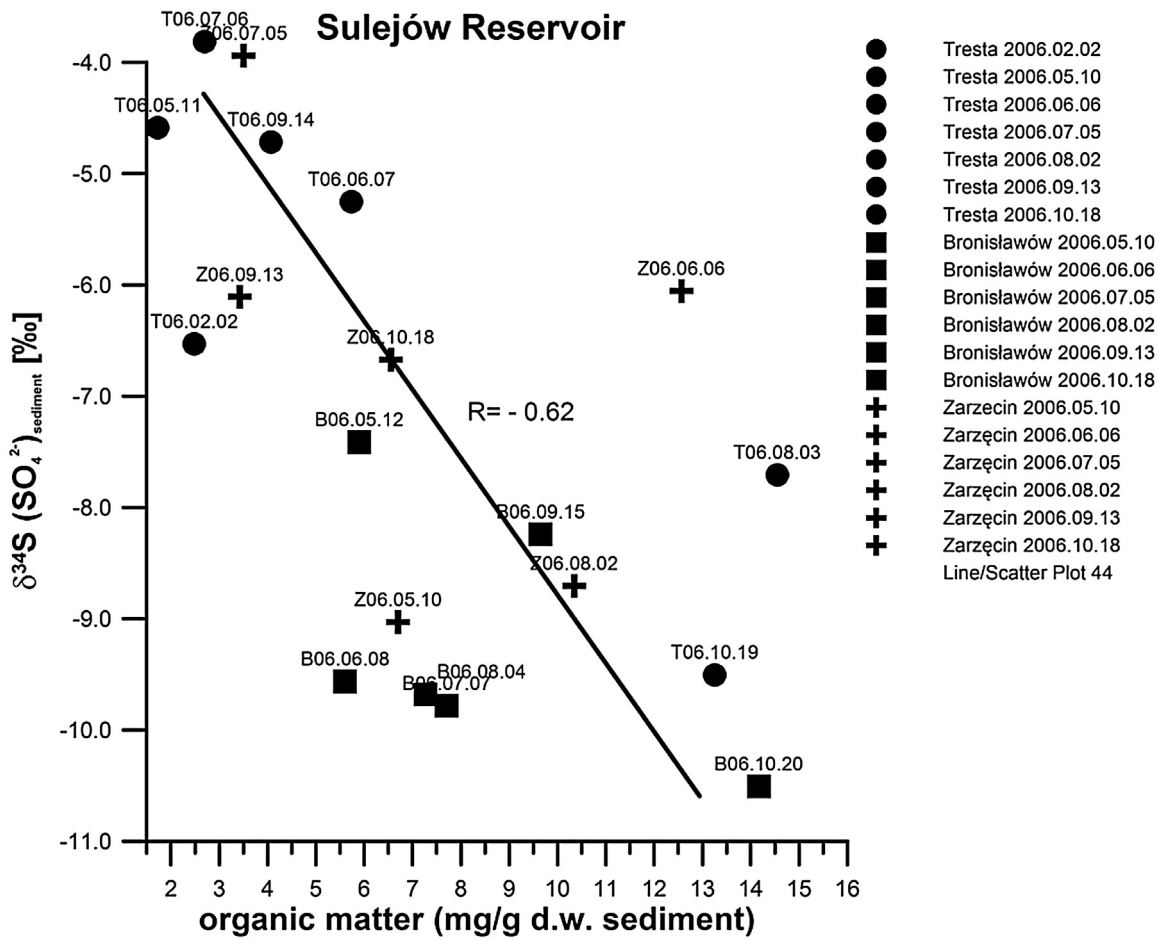


Fig. 5. A comparison of the organic matter content and the isotopic composition of the water-soluble sulfate (VI) ion in the sediment water.

water balance, the Pilica River has an 82% contribution to the water inflows into the reservoir, while Luciąża River about 14% (Wagner-Łotkowska, 2002).

During the summer period with relatively high temperatures and low activity of zooplankton, Cyanobacteria, which best develop in the lacustrine part, begin to predominate in the phytoplankton community (Izydorczyk, 2002). The largest cyanobacterial blooms are observed during summer flood waves when a significant amount of nutrients is supplied to the reservoir. At the same time, large amounts of suspensions and organic compounds are carried into this water; are quickly degraded by bacteria whose population are fast multiplied. (Wagner-Łotkowska, 2002; Trojanowska, 2004).

3. Sampling and analysis

Sediment samples were collected in 2006 in different seasons: winter (2nd February 2006), spring (10th May, 6th June 2006), summer (5th July, 8th August 2006), autumn (13th September, 18th October 2006). Samples were taken using Kajak type core sampler. Lacustrine sediment was collected from 3 sites within the reservoir area: Zarzęcin (riverine part), Bronisławów (central part), and Tresta (lacustrine part) (Fig. 1), in the form of the core with a thickness of 3 cm. The depths of the sampled sites is shown in Table 1. The sediment samples were frozen to prevent the oxidation of sulfides and bacterial degradation of organic compounds.

In the laboratory, the unfrozen sediment was homogenized and divided into two parts. One part was used to determine the quantitative content of organic matter, while the other part was used for chemical analysis of sulfur being at different levels of oxidation in the sediment (Mayer and Krouse, 2004).

As a result of the chemical analysis, the following forms of sulfur in the sediment were separated and analyzed in quantitative terms (Fig. 2):

1. water-soluble sulfuric (VI) acid salts;
2. elemental sulfur (S^0);
3. organic sulfur;
4. hydrochloric acid-degradable monosulfides;
5. polysulfides not readily degradable in hydrochloric acid (due to the methodology used, individual forms of polysulfides were not identified).

The analysis was performed based on the previously published studies on methods of separation of sulfur at various levels of oxidation found in lacustrine and marine sediments (e.g. Canfield et al., 1996; Hall et al., 1988; Rice et al., 1993; Zhabina and Volkov, 1978; Zaback and Pratt, 1992) using an extraction line designed by Drzewicki (2009).

3.1. SO_4^{2-} dissolved in water

To perform the quantitative and qualitative analysis of SO_4^{2-} dissolved in the water column, the sulfate(VI) ion was separately precipitated as $BaSO_4$. For this purpose, a sample of water was heated and acidified with 6 M hydrochloric acid up down to pH = 2. Next, the sample was filtered and 20 ml 10% of $BaCl_2$ at a concen-

Table 1
Concentration and $\delta^{34}S$ of sulfur speciation in the dam Sulejów.

	SO_4^{2-} (mg/g sediment)	$\delta^{34}S$ (SO_4^{2-})[‰]	Elemental S (mg/g sediment)	$\delta^{34}S$ (S^0) [‰]	Monosulphides (mg/g sediment)	Polysulphides (mg/g sediment)	$\delta^{34}S$ (Poly-sulphides) [‰]	Organic S (mg/g sediment)	$\delta^{34}S$ (Organic S) [‰]	C (organic matter [%]	Depth
2006.02.02											
Tresta	0.032	−6.50	0.05	−11.20	0.01	0.07	−10.70	0.24	−0.30	2.48	7.5
2006.05.10											
Zarzęcin	0.42	−9.00	0.06	−3.60	0.00	0.08	−7.15	0.32	−2.50	6.70	2.5
Tresta	0.19	−4.60	0.04	−3.90	0.00	0.07	−6.30	0.68	−1.60	1.73	7.5
Bronisławów	0.38	−7.40	0.11	−3.00	0.00	0.12	−7.20	0.56	−1.30	5.90	4.0
2006.06.06											
Zarzęcin	0.53	−6.00	0.62	−3.30	0.01	0.27	−5.50	0.54	−2.80	12.57	2.5
Tresta	0.66	−5.25	0.34	−3.70	0.00	0.32	−5.00	0.60	−1.40	5.74	7.5
Bronisławów	0.66	−9.55	0.41	−4.30	0.00	0.86	−5.90	0.80	−2.00	5.61	4.0
2006.07.05											
Zarzęcin	0.39	−3.90	0.03	−0.40	0.00	0.06	−4.20	0.39	0.60	3.50	2.5
Tresta	0.09	−3.80	0.03	−2.70	0.00	0.04	−4.40	0.12	−3.00	2.70	7.5
Bronisławów	0.49	−9.80	0.07	−5.40	0.01	0.38	−7.30	0.49	−2.50	7.71	4.0
2006.08.02											
Zarzęcin	0.12	−8.70	0.31	−4.10	0.01	0.36	−7.90	0.45	−1.30	10.35	2.5
Tresta	0.36	−7.71	0.33	−4.55	0.01	0.19	−10.50	0.66	−2.50	14.55	7.5
Bronisławów	0.26	−9.70	0.41	−9.35	0.00	0.48	−6.90	0.48	−2.10	7.27	4.0
2006.09.13											
Zarzęcin	0.23	−6.10	0.05	−2.10	0.00	0.04	−3.20	0.51	−3.50	3.43	2.5
Tresta	0.44	−4.70	0.05	−0.85	0.01	0.16	−2.90	0.72	−2.10	4.07	7.5
Bronisławów	1.36	−8.20	0.08	−1.70	0.01	0.38	−3.30	0.30	−2.60	9.65	4.0
2006.10.18											
Zarzęcin	0.43	−6.70	0.09	−9.57	0.03	0.37	−12.60	0.55	−1.20	6.55	2.5
Tresta	0.86	−9.50	0.38	−12.96	0.00	0.62	−11.90	0.60	−2.20	13.26	7.5
Bronisławów	0.59	−10.50	0.06	−7.90	0.07	0.81	−10.50	0.49	−2.00	14.17	4.0

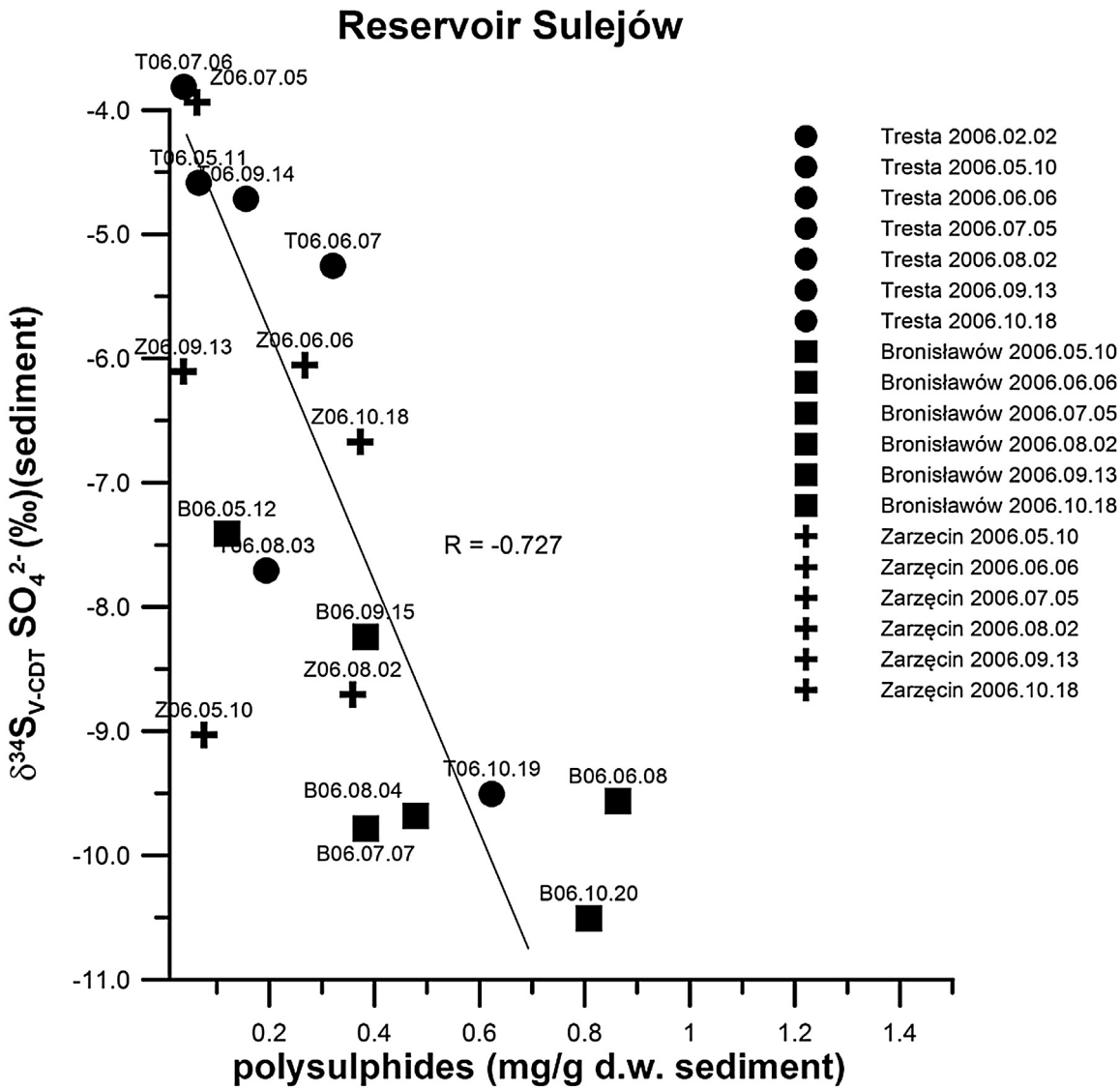


Fig. 6. A comparison of the isotopic compositions of sulfur in the water-soluble sulfate (VI) ion in the sediment water and the polysulfide concentration in the sediment.

tration of was added to precipitate sulphates. The precipitates were purified of chlorides by multiple washing and centrifugation steps.

3.2. Sedimentary SO_4^{2-}

The defrosted sample was initially centrifuged before being freeze dried. After drying, the sediment was weighed, submerged in distilled water and stirred using a magnetic stirrer for 5 h at 50 °C. This was designed to rinse out SO_4^{2-} which had sorbed on mineral grains and occurred in the interpore spaces (Hall et al., 1988). The SO_4^{2-} concentrations were expressed in mg/g sediment dry weight. It was further analyzed in the same way as water-dissolved SO_4^{2-}.

The remaining lacustrine sediment was freeze dried and used for further chemical analysis.

3.3. Extraction of elemental sulfur

To extract elemental and organic sulfur from the sediment, a modified standard Soxhlet apparatus was used (Rice et al., 1993). Spectrally pure CH_2Cl_2 was used to dissolve elemental and organic sulfur (Zaback and Pratt, 1992). A previously weighed and dried sample was placed in a glass thimble located in the middle part of the Soxhlet extractor. Sedimentary elemental and organic sulfur was dissolved and leached into the solution. The dissolved elemental sulfur precipitated on copper granules as CuS, whereas the organic sulfur remained in the CH_2Cl_2 solution. After completion of the extraction, the sediment was dried under a fume hood until the CH_2Cl_2 was completely evaporated. The CH_2Cl_2 solution was purified using filter paper and concentrated in the evaporator. The metallic copper was washed with fresh CH_2Cl_2, dried with a gaseous nitrogen stream, and used during the next analysis.

3.4. Extraction of organic sulfur

The solution of organic sulfur compounds obtained as a result of extraction with CH_2Cl_2 in stage I was concentrated and analyzed by the oxidation method in a Parr bomb apparatus (Mayer and Krouse, 2004). This process involved the explosive combustion of the sample in an atmosphere of pure oxygen under a pressure of 20 atm in the presence of water (ca. 20 ml). As a result of combustion, SO_2 is released and then oxidized to SO_4^{2-}. The obtained aqueous solution containing SO_4^{2-} was filtered and subsequently the SO_4^{2-} ions were precipitated to $BaSO_4$ using the $BaCl_2$ solution.

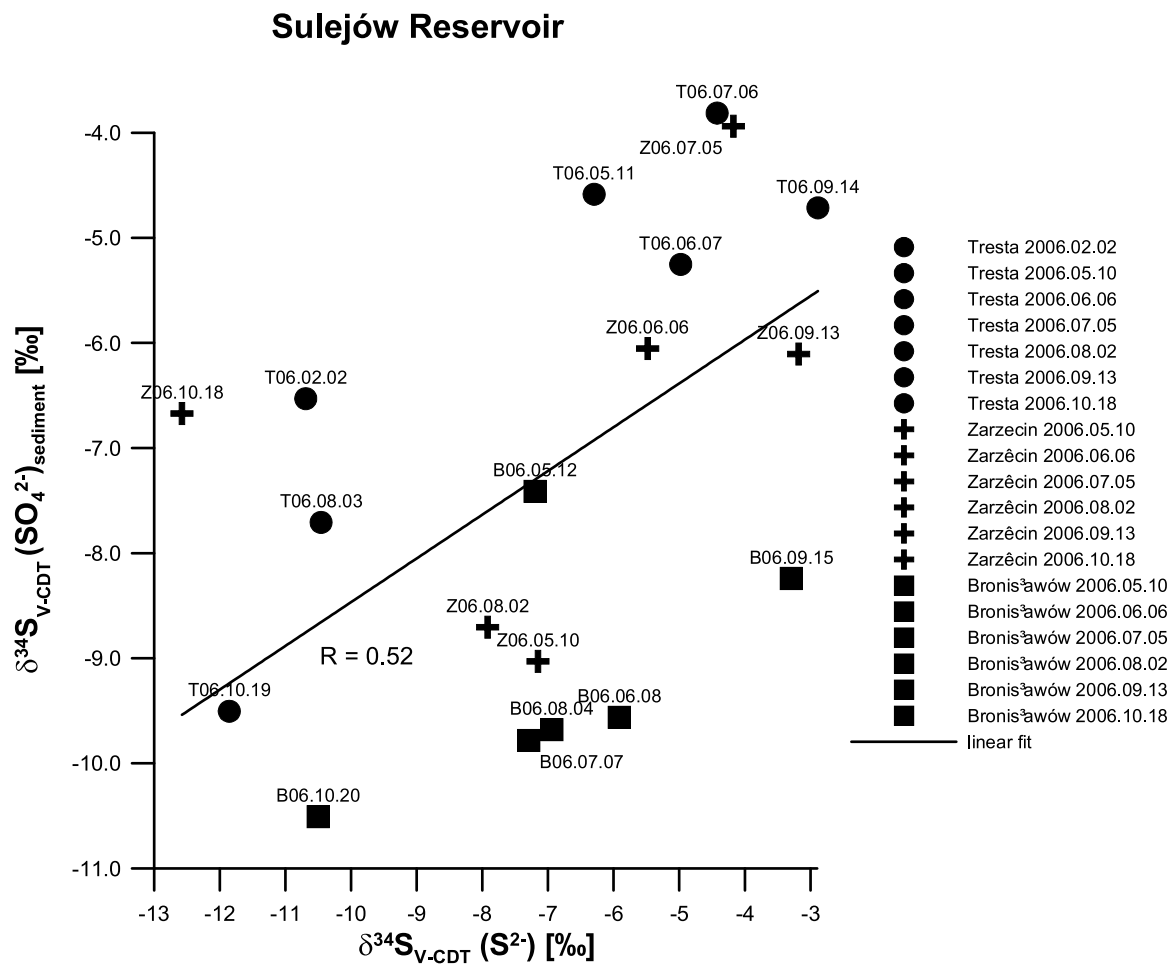


Fig. 7. A comparison of the isotopic composition of sulfur in the water-soluble sulfate (VI) ion in the sediment water and the isotopic composition of sulfur in sediment polysulfides.

3.5. Decomposition of monosulfides

Sediment digestion with a hot 6 M HCl solution in an atmosphere of nitrogen was used to decompose monosulfides (Hall et al., 1988). The analysis was performed using a glass apparatus. As a result of the reaction with HCl, the sulfur contained in the monosulfides was converted into H_2S. Heating the solution to a temperature of 50 °C accelerated the reactions of monosulfide decomposition to H_2S. Under the influence of the flow of nitrogen, the obtained H_2S was transported through a buffer with sodium citrate with a pH = 4 (to prevent the formation of AgCl) and supplied to a washer containing $AgNO_3$. In the reaction of H_2S with silver(I) ions, the S^- ion was precipitated as Ag_2S sediment.

3.6. Soluble salts of sulfuric acid (VI) in HCl

The suspension from the previous step was centrifuged, while the remaining sediment was washed with distilled water many times and centrifuged to wash out soluble SO_4^{2-} ions. The combined supernatants were filtered and the solution pH was increased to 4 by adding NaOH to remove potentially occurring iron compounds (III). Subsequently, the solution was centrifuged again, filtered and acidified with HCl. SO_4^{2-} was precipitated with $BaCl_2$. The centrifuged lacustrine sediment was dried and used for further analysis.

3.7. Decomposition of polysulfides

The decomposition of polysulfides was carried out in an identical apparatus as used with the monosulfides. A properly prepared solution of 1 M $CrCl_3 \cdot 6H_2O$ and 0.5 M HCl was used to break down the compounds. This solution was poured into a Jones reducer containing metallic zinc and Cr^{3+} was reduced to Cr^{2+}. After a bright blue color was obtained, the chromium(II) salt solution was poured into a flask with the sediment and heated. Similarly as in the case of monosulfides, the hydrogen sulfide produced as a result of the decomposition of polysulfides was transferred to the washer with $AgNO_3$ and after the reaction with silver(I) ions it precipitated as Ag_2S sediment.

3.8. Isotopic analysis

For S isotopic analyses, pure $BaSO_4$ and Ag_2S was combusted with catalysts at 950 °C (Yanagisawa and Sakai, 1983). The SO_2 produced was cryogenically purified in a vacuum preparation line (Mizutani and Oana, 1973). Isotopic analyses were carried out using MI-1305 mass spectrometer in the Mass Spectrometry Laboratory at the Maria Curie-Skłodowska University in Lublin. The $\delta^{34}S$ values are reported in reference to VCDT international standard and expressed in ‰. Analytical error was lower than 0.15‰. The extraction apparatus was calibrated using the standards for all the sulfur forms. The standards were analyzed in terms of the isotopic composition before the extraction and after the completion of the analysis.

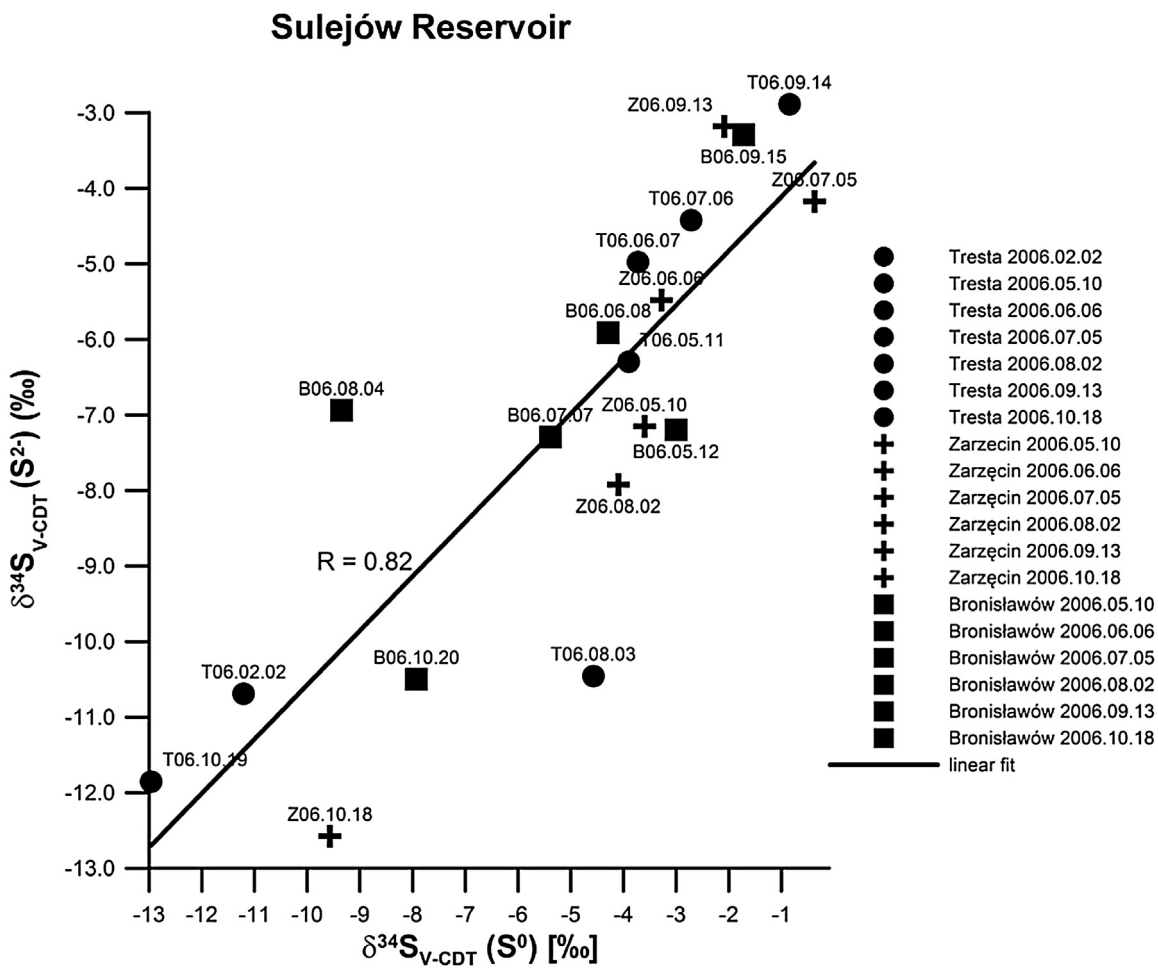


Fig. 8. A comparison of the isotopic composition of sulfur in elemental sulfur in the sediment and the isotopic composition of sulfur in sediment polysulfides.

4. Results

In the sediments both the oxidized (SO_4^{2-}) and reduced (organic sulfur, polysulfides, elementary sulfur) compounds have been obtained. The results of the analysis are shown in Table 1. The concentration of sulfates from water-soluble sediments varied from 0.03 to 1.36 mg/g (average value: 0.45 mg/g sediment) and isotopic composition of these sulfates varied from −10.5‰ to −3.8‰. The concentration of elementary sulfur varied from 0.30 to 0.60 mg/g sediment and $\delta^{34}S(S^0)$ value varied from −13.0 to −0.4‰. The concentration of polysulfides varied from 0.04 to 0.86 mg/g sediment, and $\delta^{34}S(S^{2-})$ varied from −12.6 to −2.9‰. The concentration of organic sulfur varied from 0.12 to 0.80 mg/g sediment, and $\delta^{34}S(S_{org})$ varied from −3.5‰ to 0.6‰.

An X-ray analysis did not confirm the presence of $CaSO_4$, Since the detection limit is 2% can be concluded that the gypsum content is less than this value.

5. Discussion

The study revealed significant variations both in the concentration of sulfur forms and in their isotopic composition. The investigated sediments contain both oxidized sulfur (SO_4^{2-}) and reduced forms (organic sulfur, polysulfides, and elemental sulfur). The high water content and sediment liquefaction cause sediment burial and mixing and hence probably the co-occurrence of oxidized and reduced forms. Average values of redox ranged from 190 to 250 mV. The obtained results do not show a significant correlation ($p > 0.05$) between the sediment concentrations of SO_4^{2-} and its $\delta^{34}S$ values, both for individual seasons and particular sampling sites (Figs. 3 and 4). A distinct depletion of SO_4^{2-} in the heavy isotope of sulfur, compared to water-column was observed in all sediment samples. Large variation in the composition of SO_4^{2-} in both environments indicates a different genesis of the sulfate (VI) ion deposited in the sediment and of that encountered in the water.

The samples collected from the water column exhibit low variability in the isotopic composition of $\delta^{34}S(SO_4^{2-})$, within a range from 2.6‰ to 4.6‰. The analysis of SO_4^{2-} from the sediment, on the other hand, revealed large variations in range from −10.5‰ to −3.8‰.

The main source of sulfate supplied to the sediments is organic sulfur contained in organic matter deposited at the bottom, which gradually undergoes bacterial decomposition. One of the most often mechanisms of microbial decomposition is enzymatic hydrolysis of organic compounds with sulfates liberation. For instance, the enzyme asrylsulfatase (EC 3.1.6.1.) catalyses irreversible hydrolysis of sulfate esters with liberation of sulfates. This enzyme is liberated by bacterial cells in response to lowering of sulfates concentration and usually is dependent on organic matter content (Hadas and Pinkas, 1997).

Products of bacterial activity, including sulfates coming from enzymatic hydrolysis, are isotopically light as bacteria preferentially utilize ^{32}S during mineralization of ester sulphates and carbon bonded sulphur (Schoenau and Bettany, 1989; Mayer et al., 1992; Burlingham et al., 2003). The acid hydrolysis of aryl sulphate monoesters has been shown to fractionate against ^{34}S by 15–18‰

(Burlingham et al., 2003). However the isotopic composition of sulfates is also dependent on the initial isotopic ratio of sulfur in organic matter. Therefore, the most depleted in ^{34}S sulfates were found with the highest organic matter concentration in sediments in October when at the end of vegetation period dead phytoplankton cells precipitates and supplies bacteria in fresh organic matter, which is favorably decomposed by bacteria and may stimulate microbial activity in sediments (Westrich and Berner, 1984; Arnon and Benner, 1996) (Fig. 5). Another similar event of increase of organic matter amount and parallel sulfates depletion in ^{34}S was noted in August, in each of sampling stations, after characteristic late summer braking down of the cyanobacterial bloom (Wojtal-Frankiewicz et al., 2015).

The bacterial oxidation of organic sulfur in the sediment leads to sulfur bonding into water-soluble SO_4^{2-} thereby with a decrease of organic matter content in the sediment, $\delta^{34}S(SO_4^{2-})$ in the sediment are shifted towards positive values. Bacteria preferentially reduced or oxidized ^{32}S from organic matter, thereby the remaining residuum was enriched in ^{34}S (Fig. 5). The sulfate ion formed subsequently became isotopically heavier, since the remaining organic matter became isotopically heavier. Therefore it is suspected that the most intensive aerobic and anaerobic bacterial sulfur transformation took place in Tresta station in spring and summer seasons.

Polysulfides were shown to be present in the sediment. The highest S^{2-} concentrations were observed in the deepest parts of the reservoir in Tresta, at the maximum up to 0.62 mg/g sediment, and in Bronisławów, up to 0.86 mg/g sediment. These areas are characterized by highest rate of organic matter production and deposition within the Sulejow Reservoir (Trojanowska and Izydorczyk, 2010), which might be responsible for local anoxic conditions that favor sulfides release. However, no significant correlations were found in S^{2-} concentrations between the sampled seasons.

The studies conducted by other authors (e.g. Bak and Pfennig, 1991; Rudd et al., 1986; Jorgensen, 1997; Berner and Westrich, 1985) have shown that only 10% of reduced sulfur remains in the sediment, while the rest undergoes successive biogeochemical transformations. The presence of polysulfides characterized by low values of $\delta^{34}S$ was found in all sediments analyzed (Table 1). A clear negative correlation ($R = -0.727$, $p = 0.001$) between the polysulfide concentration in the sediments and water-soluble $\delta^{34}S(SO_4^{2-})$ was observed (Fig. 6). During the oxidation of sulfides to SO_4^{2-}, their concentration in sediment decreases and $\delta^{34}S$ of the sulfate ion is shifted towards positive values. A positive correlation ($R^2 = 0.52$, $p = 0.027$) between the isotopic composition of $\delta^{34}S$ of polysulfides and $\delta^{34}S(SO_4^{2-})$ in the sediment were observed (Fig. 7). Oxidizing conditions and fine-grained sediment promoted oxidation of sulfides to sulfates. But variable isotopic fractionation occurred between SO_4^{2-} and the sulfide during the oxidation. Moreover, a part of SO_4^{2-} formed was found to be enriched in ^{34}S, but ^{34}S impoverishment was also found for a part of SO_4^{2-}.

The analysis of the sediments showed a very low concentration of monosulfides or even their absence (0.00–0.07 mg/g sediment). Such a low concentration made it impossible to complete an isotopic analysis allow interpretation of the transformation pathways of these compounds in the sediment. A probable reason for such low monosulfide concentrations in the sediment is the high solubility of these compounds and their quick transformation into polysulfides, mainly pyrite (Davison et al., 1985; Rudd et al., 1986; Rickard, 1997).

Another form of sulfur found in sediments is elemental sulfur. The most frequent process of elemental sulfur formation is chemical oxidation of sulfides (Holmer and Storkholm, 2001). Elemental sulfur, whose concentrations varied within a wide range between 0.03 and 0.62 mg/g sediment, was found to be present in all the sediment samples. A clear correlation was demonstrated between the isotopic composition of $\delta^{34}S(S^0)$ and the isotopic composition of $\delta^{34}S$ of polysulfides ($R = 0.823$, $p = 0.000$) (Fig. 8). With the enrichment of polysulfides in the heavy isotope of sulfur, the proportion of $\delta^{34}S$ in elemental sulfur also increases. Such a relationship indicates the formation of elemental sulfur from sulfides through their chemical oxidation. Elemental sulfur is characterized by higher $\delta^{34}S$ values than in the case of S from polysulfides, which suggests that during an oxidation reaction heavier isotopes are oxidized more readily. In the case of elemental sulfur, the enrichment in isotopically heavier sulfur, in relation to sulfides, ranged between 2.40 and 5.90‰ in individual samples.

6. Conclusions

The use of extraction and degradation of various sedimentary sulfur speciations allows us to trace the geochemical cycle of sulfur in the Sulejów reservoir and to draw the following conclusions:

a The isotopic composition of sedimentary SO_4^{2-} shows a clear enrichment in isotopically light sulfur relative to SO_4^{2-} dissolved in the water column.
b Bacterial hydrolysis of organic compounds in sediments was important source of sulfates.
c Polysulfides were shown to be present in the reservoir sediments, with their highest concentration observed in the deepest parts of the reservoir where the greatest organic matter accumulation occurs. This situation favors the occurrence of local anaerobic conditions. A clear correlation was shown between $\delta^{34}S(SO_4^{2-})_{sediment}$ and $\delta^{34}S(S^{2-})_{sediment}$. Sediment turbulences promote the oxidation of reduced species (primarily polysulfides) to sulfates. A fine-grained sediment additionally promotes this process.
d The process of oxidation of polysulfides to elemental sulfur occurred in the sediment. The produced elemental sulfur became isotopically heavier than the polysulfides.

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