

Sulphur and Oxygen Isotopes Behaviour in Sulphates of Atmospheric Groundwater System Observations and Model

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Comparison of sulphate concentrations in groundwaters and atmospheric precipitation suggests that about 30 % of groundwater sulphate may be of atmospheric origin. Another source of sulphate ion is the oxidation of sulphur compounds by microorganisms in the soil or in the aquifer. The sulphates of atmospheric and biogenic origin are mixed in the soil and subsequently the mixture gets into the groundwater. The $\delta^{34}\text{S}$ data suggest, that $\delta^{34}\text{S}$ of biogenic sulphates is the same as that of atmospheric sulphates. Processes such as: the assimilation of sulphates by plants, their decay and oxidation of organic compounds do not change the $\delta^{34}\text{S}$ significantly. Significant differences between $\delta^{18}\text{O}$ values of sulphates of atmospheric and biogenic origin, which are created by microbiological sulphur-oxidizing processes, may be useful for interpretation of the processes in the groundwater system.

Introduction

A major problem in groundwater studies is the determination of the origin of sulphates. This paper presents oxygen and sulphur isotope compositions in groundwater sulphates and tries to explain its variations. In order to study oxygen and sulphur isotopic compositions 36 samples of the groundwater sulphates have been collected from several regions of Poland (Roztocze, Lublin Upland, and Kaczawskie Mountains). None of the studied groundwaters contained dissolved evaporates. Moreover 38 samples of atmospheric precipitation in Lublin have been collected to study the seasonal variations of sulphur and oxygen isotope composition and concentration of sulphate.

Analytical Procedures

The sulphate ion has been precipitated as BaSO_4 by the pouring of the sample of water into a bottle containing a few milliliters of BaCl_2 solution acidified with HCl . In this way the influence of any microbiological activity on the collected sulphate samples has been excluded. Then, pure BaSO_4 was reduced with graphite at 1000°C , by the Mizutani (1971) method, to obtain CO_2 for $\delta^{18}\text{O}$ analysis, or with NaPO_3 at 850°C , by Hałas and Wołacewicz (1981) method, to obtain SO_2 for $\delta^{34}\text{S}$ analysis. Measurements of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values were performed with a modified MI-1305 mass spectrometer (Hałas 1979, Hałas and Skorzyński 1980). Every sample was prepared twice and the measurements were repeated. Each of the δ -data presented in tables is mean value of four independent measurements with precision of 0.1 permil.

Description of the Study Area

The samples came from the Lublin Upland, most of Bystra and Ciemięga drainage basins and the Roztocze regions (SE Poland). The geological profile of the studied area is shown in Fig. 1.

Underground waters of Lublin Upland are retained mainly in pores and crevices of Cretaceous limestones, likewise some groundwater layers are in Quaternary sands. The infiltrating waters are retained by irregularly developed layers of clay-rich limestones, found in different horizons (Michalczyk and Wojciechowski 1981). Some layers are developed as soft marl and chalk, whereas others are hard rock. The depth of water table in this area is from 20 to 40 m (deep groundwaters). Other types of groundwaters are shallower groundwaters, which occur in Pleistocene sands. The depth of water table of these waters is 2 to 8 m (Michalczyk *et al.* 1984).

The water mobility is possible mainly through the system of crevices, formed by vertical and horizontal fractures, which cut rock layers. The water movement through the crevices system is about ten times greater than through the pores. Water conduction ability of rock layers changes irregularly, much more perpendicularly than horizontally. In strongly cracked rocks water moves mainly horizontally, across system of crevices, vertical movement of water occurs in weakly permeable layers.

The depth of Cretaceous aquifers may vary, from a few (on the valley-sides region), to several tens metres. Tertiary groundwaters contact with Cretaceous. Shallow local aquifers may occur in Quaternary sediments. Their affluence depends strongly on atmospheric precipitation. These groundwaters may slowly infiltrate to deeper layers. Part of these groundwaters flows out through little springs. The

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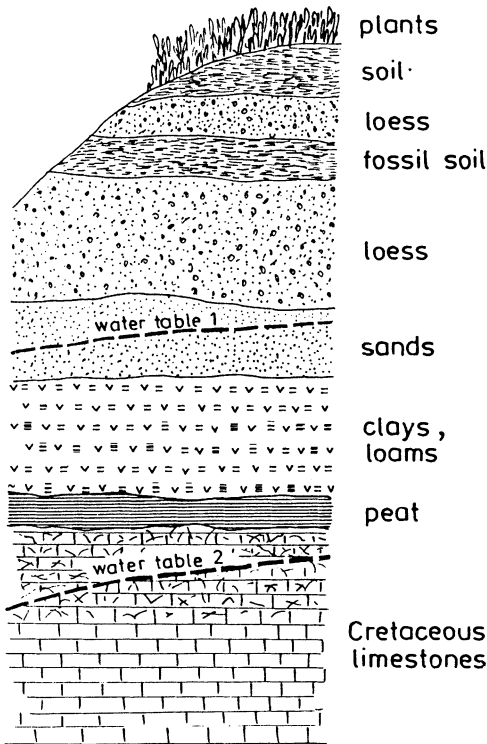


Fig. 1.
Hydrological situation of study area, there are two water levels, shallow groundwater – in Quaternary sands and loess and deeper groundwater, retained in Cretaceous limestones.

depth of water table in Quaternary layers is from a few to twenty m, while in the same areas in Cretaceous layers it is from 30 to 60 m below. These groundwaters flow out through the very efficient springs.

About 40% of the precipitation is observed during summer months. Mean amount of precipitated waters which has been observed on NW region (Kazimierz and Puławy) was from 418 to 895 mm, average 550-600 mm (Sadurska 1980, Michalczyk *at al.* 1984). A great amount of waters, about 450 mm return to the atmosphere by plant transpiration (Michalczyk and Wojciechowski 1981).

Seasonal variations of water tables have been observed from 1951-1980 (Michalczyk *at al.* 1984, Michalczyk 1986). For most cases fast increases and slow decreases have been observed. The water inflows have been observed mainly once a year. In the shallow wells water tables varied more often, but the amplitude has not been high. The variations have been smaller for deeper groundwaters, for most of them the increases have been observed only during springs. The highest states of water tables have been observed most often in April, March, November, May and October. The lowest states – during October, November, September, December and January. For most of Cretaceous groundwaters minimum states have been observed from October to March (Michalczyk *at al.* 1984, Michalczyk 1986).

Table 1 - $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values and concentration of sulphates in the groundwaters of Roztocze, Bystra and Ciemiega valleys, and Kaczawskie Mts.

OCEAN ATL. (STANDARD): $\delta^{34}\text{S} = +20.06\%$, $\delta^{18}\text{O} = +9.91\%$

No of sample and location	$\delta^{34}\text{S}_{\text{CDT}}\%$	$\delta^{18}\text{O}_{\text{SMOW}}\%$	$[\text{SO}_4^{2-}] \text{ mg/l}$
Roztocze groundwaters			
1. Janów Lubelski	+5.26	-	4
2. Siembidy	+4.29	+5.91	60
3. Horyniec	+1.38	+7.79	4
4. Horyniec	+2.29	+2.13	24
5. Płazów	+1.84	+2.69	15
6. Cieszanów	+4.36	+4.13	58
7. Lukawica	-4.87	+4.85	22
8. Rebizanty	-7.50	+1.51	17
9. Susiec	-3.16	+1.48	27
10. Nowiny Sopockie	-3.60	+1.53	30
11. Nowiny Horynieckie	-8.92	-0.73	31
Bystra river valley groundwaters			
12. Lopatki (well)	+8.86	+13.44	19
13. Lopatki	+2.77	+4.83	74
14. Stok	+0.87	+6.47	18
15. Stok	+1.06	+3.91	19
16. Stok	+2.43	+3.69	14
17. Celejów	-9.74	+4.87	21
18. Celejów	-13.14	+3.74	27
19. Nałęczów	-6.00	+3.76	39
20. Wąwolnica	-16.43	-0.64	30
21. Wierzchoniów	-19.09	+2.50	17
22. Charz	-20.32	+2.83	32
23. Charz	-5.23	+10.20	} samples of soil sulphates
	-	+4.77	
24. Wierzchoniów	-	+11.82	
25. Rzeczyca	-14.29	-1.02	39
26. Rzeczyca	+1.73	-0.75	29
27. Witoszyn	-19.68	-1.36	44
28. Bystra river	-13.41	+1.90	29
Ciemiega river valley groundwaters			
29. Dys	-5.32	+5.69	7
30. Baszki	-10.08	+4.67	17
31. Pliszczyn	-15.70	+3.20	12
Kaczawskie Mountains groundwaters			
32. Bolków	+3.30	+2.96	10
33. Bolków	-	+2.77	12
34. Bolków	+2.12	+3.14	25
35. Wojcieszów Miłek	+4.16	+4.46	31
36. Wojcieszów Wojcieszowianka	+3.61	+3.71	25
37. Swieradów Górne	-	+7.01	12
38. Lipa	+2.93	+3.24	70

Results

The results are shown in the Table 1. The $\delta^{34}\text{S}$ values of these sulphates signify large variations, from -20.30 to $+8.86\%$, while the variations of $\delta^{18}\text{O}$ are smaller, from -1.36 to $+13.44\%$. The groundwaters in this study may be divided into three groups according to $\delta^{34}\text{S}$:

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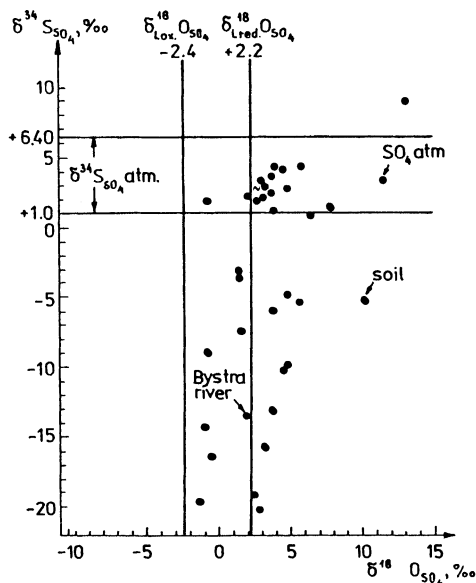


Fig. 2. Relationship between $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values of groundwater sulphates. It also shows the range of atmospheric sulphates $\delta^{34}\text{S}$ variation and the range of calculated values of $\delta^{18}\text{O}$ of sulphates formed by oxidizing processes.

- I those which have the most negative $\delta^{34}\text{S}$ values,
- II those which have positive $\delta^{34}\text{S}$ values, and
- III those with intermediate values of $\delta^{34}\text{S}$.

The $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of these sulphates are similar to values which Schwarcz and Cortecchi (1974) have observed in springs and streams from Italian Alps and Apennines. In Fig. 2 we may see the relationship between $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values of these sulphate samples though it is not distinct correlation.

Seasonal Variations

In order to study seasonal variations six springs in Bystra valley were chosen and their sulphate ion was analyzed on isotopic composition. The results are presented in the Tables 2-4 and in Figs. 3-5.

Table 2 - Seasonal variations of concentration of spring-water sulphates (in mg/l) in the Bystra river valley.

location	1982 Dec	1983 Mar	June	Aug	Dec	1984Feb
Stok	14.0	22.6	14.3	22.9	12.5	16.8
Nalęczów	39.0	29.2	-	55.7	35	43.8
Celejów	27.0	22.1	22.3	22.6	21.5	24.3
Charz	32.0	40.6	44.2	48.6	44	35.4
Wąwolnica	30.0	31.6	37.0	37	35	-
Wierzchniów	17.0	27.6	23.9	25.4	29	31.5

Table 3 – Seasonal variations of $\delta^{18}\text{O}$ values of spring-water sulphates in the Bystra river valley.

location	1982 Dec	1983 Mar	June	Aug	Dec	1984Feb
Stok	+3.69	+3.76	+5.97	+3.95	+5.74	+3.50
Nałęczów	+3.76	+2.70	-	+4.07	+5.00	+2.96
Celejów	+3.47	+2.85	+4.68	+3.74	+4.89	+3.24
Charz	+2.83	+1.30	+3.03	+1.18	+3.28	+1.92
Wąwolnica	-0.64	-2.47	+1.35	-1.70	-0.12	-0.71
Wierzchniów	+2.50	+1.05	+2.81	+0.44	+2.00	+0.78

Table 4 – Seasonal variations of $\delta^{34}\text{S}$ values of spring-water sulphates in the Bystra river valley.

location	1982 Dec	1983 Mar	June	Aug	Dec	1984Feb
Stok	+2.43	-0.22	+1.04	-	+0.57	+1.26
Nałęczów	-6.00	-7.63	-	-	-8.03	-
Celejów	-13.14	-11.76	-14.80	-13.36	-13.59	-13.63
Charz	-20.32	-16.84	-15.52	-17.98	-17.30	-17.86
Wąwolnica	-16.43	-20.57	-27.73	-17.93	-18.70	-
Wierzchniów	-19.09	-18.67	-17.87	-14.90	-18.53	-19.15

Atlantic Ocean (standard): $\delta^{34}\text{S} = +20.06\%$, $\delta^{18}\text{O} = +9.91\%$

Table 5 – Seasonal variation of $\delta^{34}\text{S}$, $\delta^{18}\text{O}$ and concentration of sulphates in Stok and Wawolnica groundwaters from 1986 to 1988.

	Stok			Wąwolnica		
	$[\text{SO}_4^-]$ mg/l	$\delta^{18}\text{O}$ SMOW (%)	$\delta^{34}\text{S}$ CDT (%)	$[\text{SO}_4^-]$ mg/l	$\delta^{18}\text{O}$ SMOW (%)	$\delta^{34}\text{S}$ CDT (%)
1986						
February				44	+2.64	-20.49
March				66	+2.52	-16.75
April				44	+2.97	-22.11
June				25	-0.04	-20.62
August				33	-0.46	-22.03
October				-	-0.48	-22.12
November				36	-0.38	-24.43
December				38	-0.53	-24.57
1987						
February	15	+4.87	-1.33	35	-0.77	-23.89
March	17	+6.29	-1.35	37	+1.33	-18.78
April	19	+4.16	-1.27	41	+0.05	-23.36
May	18	+4.11	-0.96	38	+0.26	-21.96
July	14	+3.40	-1.82	33	-0.61	-23.00
September	12	+3.68	-2.98	34	-0.25	-23.55
December	11.3	+3.10	+3.79	25	-1.21	-22.70
1988						
January	14.4	+3.12	-1.32	31	-1.10	-21.79
March	15	+2.82	-1.37	44	-0.21	-18.71
May	11	+2.70	-1.41	45	-0.80	-18.44

Atlantic Ocean (standard): $\delta^{34}\text{S} = +20.06\%$, $\delta^{18}\text{O} = +9.91\%$

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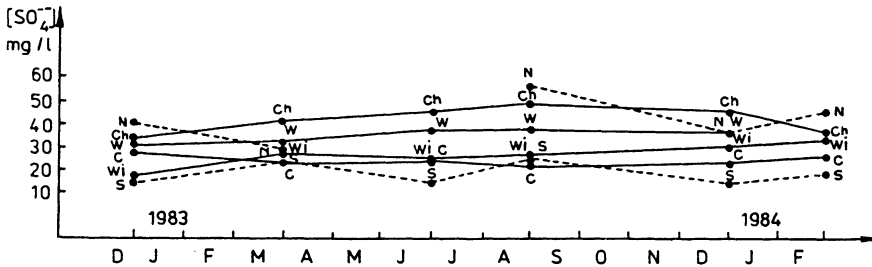


Fig. 3. The variations of sulphate ion concentration, values of six springs in the Bystra river valley.

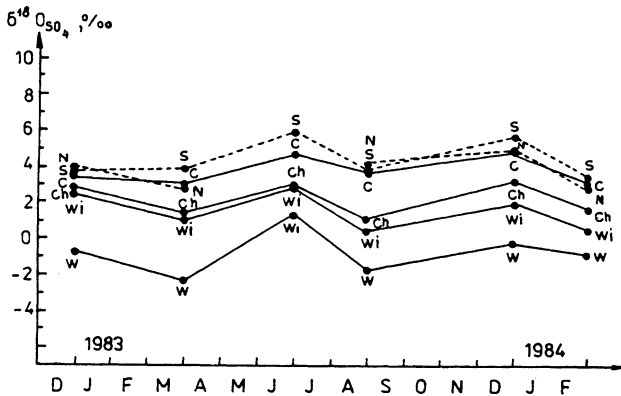
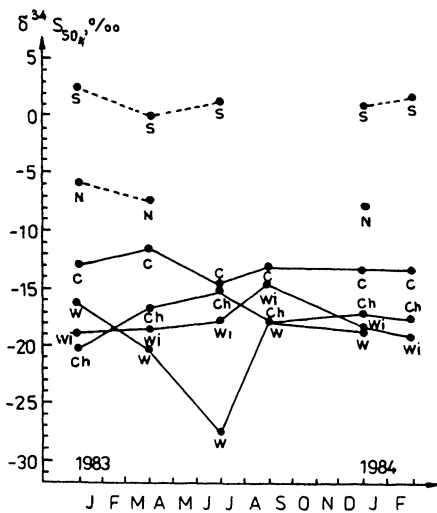


Fig. 4. The variations of $\delta^{18}\text{O}$ values of sulphate ion of six springs in the Bystra river valley.



The Cretaceous (deeper) groundwaters are marked by symbols W, Wi, Ch and C, after the names of villages given in Tables 2-4, shallower groundwaters are drafted by dotted line.

Fig. 5. The variations of $\delta^{34}\text{S}$ values of sulphate ion of six springs in the Bystra river valley.

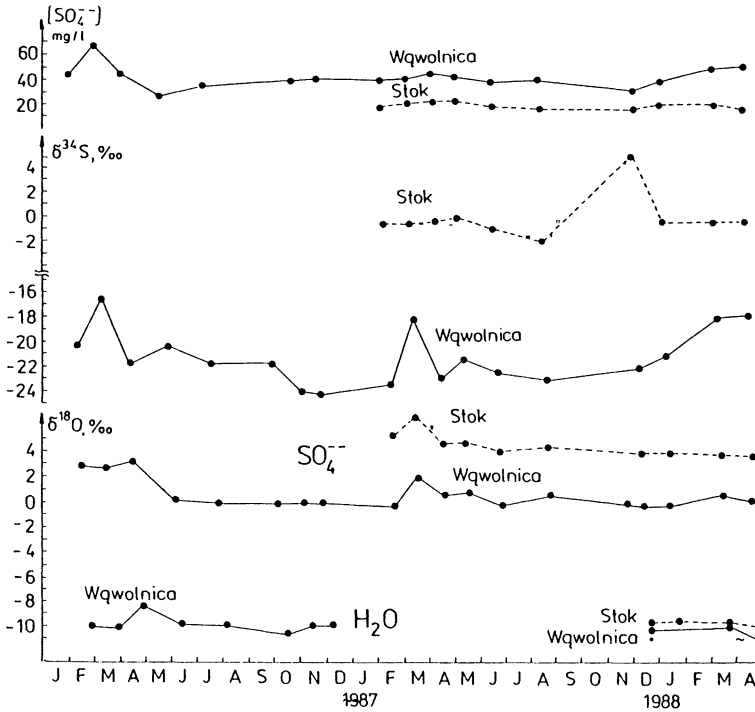


Fig. 6. The results of precise long-term observations of $\delta^{18}\text{O}$, $\delta^{34}\text{S}$, and concentration of sulphates of shallower (Stok) and Cretaceous (Wąwolnica) groundwaters.

It may be noticed that: i) concentration of sulphate ion varies in the shallow groundwaters (see Fig. 3), whereas the sulphate ion concentration of Cretaceous groundwaters shows considerable stability. ii) The $\delta^{18}\text{O}$ value varies regularly and simultaneously in all groundwaters (see Fig. 4). iii) The $\delta^{34}\text{S}$ changes were more intricate than $\delta^{18}\text{O}$ and not correlated (see Figs. 4 and 5). Further study of one of the shallow groundwaters (spring in the Stok village) and one of the Cretaceous groundwaters (spring in Wąwolnica) was carried monthly from January 1986 to May 1988. These results are presented in Table 5 and Fig. 6. The $\delta^{18}\text{O}$, $\delta^{34}\text{S}$ values and concentration of sulphate ion varied intricately, but some regularity of these changes may be observed. The largest variations occur in the spring period, whereas in the summer – autumn they diminish. It may be observed, that these changes are mutually correlated.

Atmospheric Precipitations

Atmospheric sulphur and oxygen isotopic composition was studied in Lublin through 1979. About 70 % of the atmospheric precipitations have been sampled for $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ determination. Table 6 and Fig. 7 present the results of these

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Table 6 - Sulphur and Oxygen isotopic composition of atmospheric sulphates.

date & kind of precipitation	$\delta^{34}\text{S}_{\text{CDT}} \%$	$\delta^{18}\text{O}_{\text{SMOW}} \%$	$\delta^{18}\text{O}_{\text{SMOW}} \%$	[SO ₄ ⁻] mg/l	[Cl ⁻] mg/l
	sulphate ion		water		
1-5 J snow	+4.65	+13.44	-	5.0	-
14-15 J snow	+5.04	+10.23	-18.92	2.0	2.5-3.0
24 J snow	+5.03	+ 8.18	-18.20	8.9	2.5-4.0
30 J snow	+2.36	+ 9.98	-19.00	5.9	≤ 2.5
8 Fb snow	+2.59	+10.82	-15.74	7.5	2.5-5.0
8 F snow	+2.84	+ 8.96	-16.34	7.7	2.5-5.0
12 F snow	+2.49	+10.89	-14.77	3.9	≤ 2.5
10 M snow	+3.54	+ 9.85	-14.96	2.6	≤ 2.5
24 M rain	+1.04	+10.24	-11.05	9.2	3 = 5
7 A rain	-	+12.60	-13.37	1.0	3
19 A snow	+2.36	+14.34	-14.44	8.4	≤ 2.5
29 A rain	+3.29	+14.18	-11.71	4.1	-
3 M rain	-	+15.20	-	13.8	-
14 J rain	+3.89	+19.40	- 5.28	5.0	-
18 J rain	+4.14	+17.23	- 5.04	3.8	≤ 2.5
6 J rain	+1.82	+17.21	- 8.28	4.2	-
holydays break					
4 S rain	-	+13.54	- 6.31	8.7	-
24 S rain	+1.97	+14.70	- 4.21	19.3	-
17 O rain	+6.43	+11.99	-11.03	9.3	≤ 2.5
19 O rain	-	+11.97	- 8.27	7.2	-
8 N rain					
and snow	+2.01	+ 9.19	- 9.72	16.3	5 = 7.5
9 N rain	-	+11.85	- 6.48	13.7	3 = 5
10-11 N rain	+4.08	+ 7.75	-15.99	7.3	2.5- 5
11-12 N rain	+4.25	+ 9.34	-14.28	2.1	≤ 2.5
12 N rain					
and snow	-	-	-11.77	5.1	-
17 N rain	+2.83	+ 9.10	- 7.61	17.6	2.5- 3.5
27 N rain	-	+10.08	- 8.44	18.7	2.5- 5
30 N rain	-	+14.50	- 4.86	12.7	2.5- 5
1 D rain	-	-	- 8.67	-	2.5- 3
4 D rain	-	-	-10.22	-	≤ 2.5
7-8 D rain	-	+12.74	- 8.42	4.8	2.5- 5
8-9 D rain	-	+ 9.97	-11.20	3.6	2.5- 3
10 D rain	-	+ 8.09	-15.77	3.9	≤ 2.5
11 D rain	-	+10.13	-11.01	3.7	≤ 2.5
12 D snow	-	+ 8.57	-18.31	4.9	2.5- 4
15 D snow	-	+ 5.49	-18.30	3.8	3 = 5
17-18 D rain	-	-	-10.01	-	≤ 2.5
21 D snow	-	-	-	2.3	-
29-30 D snow	-	+11.69	-22.82	3.6	≤ 2.5
Atlantic Ocean (standard)	+20.06	+ 9.88	0.0		
redistilled water (for [Cl ⁻] testing)					≤ 2.5

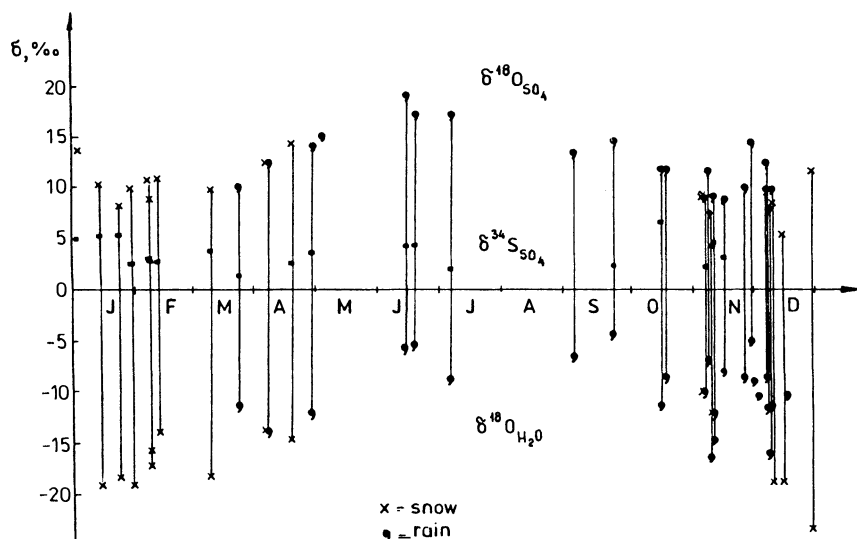


Fig. 7. Seasonal variations of oxygen and sulphur isotopic compositions of atmospheric precipitation in Lublin through 1979. Upper points present $\delta^{18}\text{O}$ of atmospheric sulphates, lower points - $\delta^{18}\text{O}$ of rain (or snow) water, squares - $\delta^{34}\text{S}$ of sulphates.

observations. It has been noticed that: a) No correlation occurs between sulphur and oxygen isotopic compositions in the atmospheric sulphates. b) $\delta^{34}\text{S}$ varies in limited scale. The same values of $\delta^{34}\text{S}$ have been observed for a few days (see Table 6) being: +4.9‰, +1.8‰, +2.8‰, +4.1‰, +1.1‰, and +6.4‰. It suggests several different sources of SO_2 emitted into the atmosphere. The average value of $\delta^{34}\text{S}$ was about +3.3‰. It must be mentioned that very low concentration of Cl^- confirm non-marine origin of sulphates. The results of these observations are very similar to those obtained by Cortecchi and Longinelli in Pisa (1970) and may be recognized as typical atmospheric sulphate samples (Cortecchi and Longinelli 1970, Fuller *at al.* 1986, Grinienko and Grinienko 1974, Krouse 1980, Nielsen 1974), and may be assumed as representative for the studied area. c) A distinct correlation between water and sulphates oxygen isotopic composition in precipitations has been observed together with seasonal variations, see Fig. 7 and Fig. 8. It was a result of oxidation SO_2 to sulphate in atmosphere by water oxygen and probably $\text{SO}_2 - \text{H}_2\text{O}$ isotopic exchange (Mizutani and Rafter 1969, Cortecchi and Longinelli 1970). The maximum values of $\delta^{18}\text{O}$ of atmospheric sulphates were about +10‰ in winter, and about +14‰ in the warm season, and even up to about +18‰ in summer. The range of $\delta^{18}\text{O}$ variations has been from +5.5‰ to +19.4‰. The average value for the whole year observation was +11.6‰. It must be noticed, that atmospheric sulphates have always much heavier oxygen than sulphates in the groundwaters if the groundwaters do not dissolve any evaporatic sulphates.

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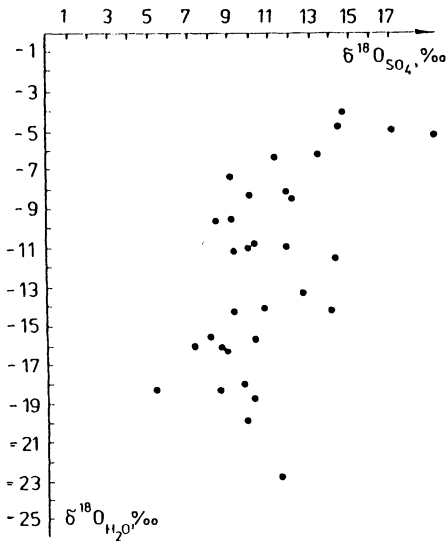


Fig. 8.
The correlation of $\delta^{18}\text{O}$ of sulphates and $\delta^{18}\text{O}$ of water of atmospheric precipitation.

Comparison of Sulphates in Groundwaters and Atmosphere

Comparison of the isotopic composition of sulphur and oxygen of groundwater and that of atmospheric sulphates of studied area is shown in Fig. 9. The sulphur isotopic composition of atmospheric sulphates is like the one which may be observed for a part of groundwaters sulphates, while the atmospheric sulphates oxygen is always heavier isotopically. Comparison of sulphate concentrations in the groundwaters and in atmospheric precipitation suggests that about 30% or even more of groundwater sulphates may be of atmospheric origin. Other sources of the sulphates in the groundwaters are the oxidation of sulphur compounds, processes which occur in the soil or in the aquifer. Thus these sulphates may have $\delta^{34}\text{S}$ values characteristic for sulphur of the organic origin or similar to $\delta^{34}\text{S}$ of sulphides, if any

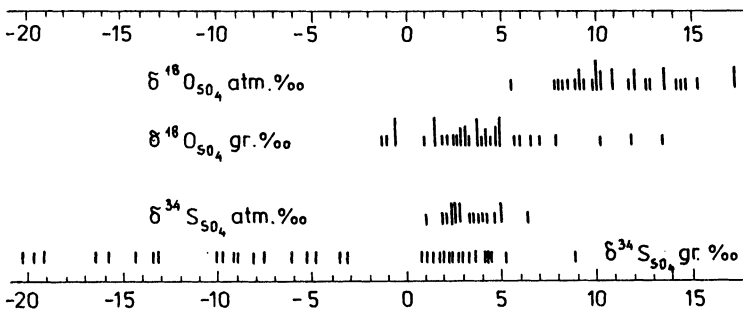


Fig. 9. The comparison of sulphur and oxygen isotopic composition of sulphates of studied groundwater (gr) and atmospheric precipitation water (atm).

sulphides are oxidized (Krouse 1980, Krouse and Tabatabai 1986, Mizutani and Rafter 1973, Nakai and Jensen 1964). It should be mentioned, that the $\delta^{18}\text{O}$ values of these sulphates must be equal and dependent only on the $\delta^{18}\text{O}$ of water in which the oxidation occurs (Lloyd 1968). Thus we may observe the sulphates which have different $\delta^{34}\text{S}$ values while their $\delta^{18}\text{O}$ values are the same. The Lloyd's formula gives $\delta^{18}\text{O}$ of sulphate in terms of $\delta^{18}\text{O}$ of water

$$\delta^{18}\text{O}_{\text{sulphate}} = 0.68 \delta^{18}\text{O}_{\text{water}} + 4.7\% \quad (1)$$

Assuming -10.5% as representative value for $\delta^{18}\text{O}$ of the groundwater accumulated in the aquifer in Lublin Upland, (Trembaczowski *at al.* 1981) we receive from Lloyd's formula -2.4% for $\delta^{18}\text{O}$ of sulphates produced during oxidation processes. These values would be more negative if water taking part in oxidation of sulphur compounds was much more depleted in heavy isotope of oxygen.

All of the observed groundwaters have $\delta^{18}\text{O}$ values of sulphates higher than -2.4% (see Table 1 and Fig. 2). Lloyd (1968) shows experimentally, that reduction processes may change $\delta^{18}\text{O}$ values of sulphates by about 4.6% towards higher values. It is not well known how dissimilatory reducing processes change $\delta^{18}\text{O}$ of sulphates in nature, probably this shifting may be such as presented by Lloyd's model or a little more. If we assume that this model is true, we shall observe the $\delta^{18}\text{O}$ of sulphates which are close to -2.4% , if the oxidation is the main controlling process, or close to values $+2.2\%$, or higher, when the reduction of sulphate occurs.

It is not easy to define the $\delta^{34}\text{S}$ values of sulphates produced by the oxidation processes. The experiments by Nakai and Jensen (1964) and Mizutani and Rafter (1973) show that $\delta^{34}\text{S}$ values are changed insignificantly during oxidation. Therefore the sulphate produced should have $\delta^{34}\text{S}$ values similar to that of primary material. If these materials are sulphides, which may exist in rocks, then more negative values of $\delta^{34}\text{S}$ of sulphates would be expected (Krouse 1980), while the $\delta^{34}\text{S}$ of sulphates of organic origin which exist in the soil may be more differentiated, as it was described by Krouse (1980, 1986). Probably this difference is not so great when only one region is considered. No ion exchange between sulphate and surroundings may occur in usual conditions (low temperature).

Atmospheric-Biogenic Sulphate Mixing Model

Certainly a large part of the soil sulphur has an atmospheric origin. It has been absorbed by plants directly as atmospheric SO_2 or as the atmospheric precipitation sulphate assimilated in the organic compounds of the sulphur by plants (Krouse 1980, Krouse and Tabatabai 1986). Probably, as Krouse showed, their $\delta^{34}\text{S}$ values did not change significantly in these processes (Fuller, *at al.* 1986, Krouse 1980, Krouse and Tabatabai 1986). When the plants die and decay these sulphur com-

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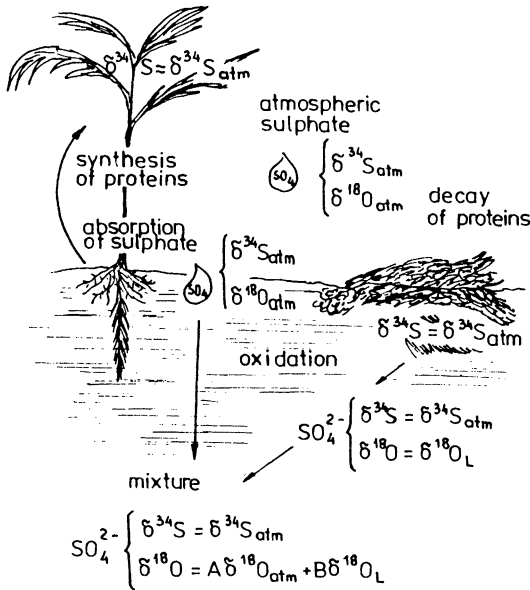


Fig. 10. The atmospheric – biogenic sulphate mixing model.

pounds penetrate into the soil and are transformed to sulphates by oxidation microbiological processes (Krouse and Tabatabai 1986). In this way sulphates are produced in the soil and their $\delta^{34}\text{S}$ values are therefore similar to those of atmospheric SO_2 . The $\delta^{18}\text{O}$ values are characteristic of the oxidation process which is described by Lloyd's formula. Subsequently these sulphates meet the sulphates of atmospheric origin, the $\delta^{34}\text{S}$ values of which are similar, but the $\delta^{18}\text{O}$ values are different (depending on the season, $\delta^{18}\text{O}$ values being about +10‰ to +18‰) and are mixed together (see Fig. 10).

The proportion of the mixing may be different, surely in the period from November to March the fraction of the atmospheric sulphate in the shallow groundwater will be the greatest. In the warm months part of the rain water flows down rapidly and does not get into groundwater. Most of the rain water comes back to the atmosphere through plants transpiration process. Plants catch their sulphates, utilize them as a source of sulphur and turn to aminoacides. Thus part of atmospheric sulphate in the groundwater is smaller in warm months, than in the cold period.

We may try to consider the groundwater sulphate as mixture of sulphates, mainly of atmospheric and biogenic origin, where biogenic sulphates are created by bacterial oxidation processes. Sulphur of biogenic sulphates comes from organic compounds (remains of plants), it is atmospheric sulphur, which plants have introduced into biochemical cycle and it has $\delta^{34}\text{S}$ like atmospheric sulphates, as it was considered above. Oxygen of biogenic sulphates partly comes from the water and its $\delta^{18}\text{O}$ value may be estimated by Lloyd's model. Oxidation of other sulphur com-

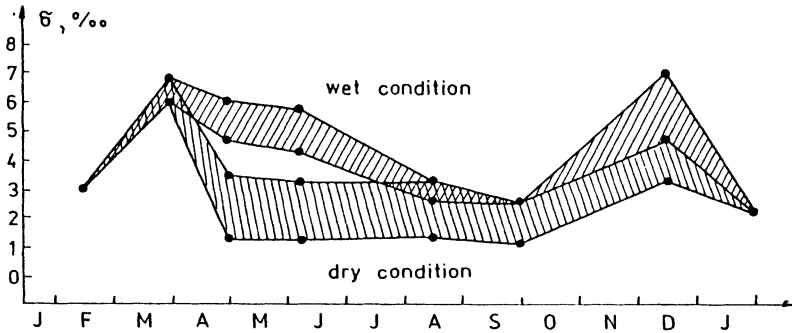


Fig. 11. $\delta^{18}\text{O}$ -foreseen seasonal variations according to the model presented, upper line = for wet, lower for dry conditions.

pounds gives the same $\delta^{18}\text{O}$ value of created sulphates. So, we may try to describe changes of $\delta^{18}\text{S}$ of sulphate-mixture with the following formula

$$\delta^{18}\text{O} = A \delta^{18}\text{O}_{\text{atm}} + B \delta^{18}\text{O}_L \quad (2)$$

where A and $B = 1-A$ mean fractions of the sulphates of atmospheric A and biogenic B origin respectively, $\delta^{18}\text{O}_{\text{atm}}$ of atmospheric sulphates depends upon the season and may be from $+10\%$ in winter to $+18\%$ in summer months. Biogenic sulphates have $\delta^{18}\text{O}_L$ values, which may be calculated with Lloyd's model. The calculations must be different, referring to different conditions. In further consideration $\delta^{18}\text{O}_L$ values from $+2.2\%$ for the reducing conditions, to -2.4% , for oxidizing conditions, have been accepted. Table 7 presents these calculation, values A , B , $\delta^{18}\text{O}_L$ and $\delta^{18}\text{O}_{\text{atm}}$ have been guessed. Most probable data are underlined. Fig. 11 refers to these calculations and presents foreseen seasonal variations of $\delta^{18}\text{O}$ of sulphate-mixture.

It should be noticed, that in all the possibilities considered above, the $\delta^{34}\text{S}$ of the sulphates mixture will be similar to the $\delta^{34}\text{S}$ of the atmospheric SO_2 .

All of the described cases present the model behaviour of the sulphate ions $\delta^{18}\text{O}$ values which may be possible in the shallow groundwater reservoirs, for which infiltration from precipitation is significant. For groundwaters whose water level lies much deeper, as in the case of samples as Nos. 7-11 and 17-31, (see Table 1), the rain sulphate cannot mix directly. The main sulphate-ions purveyor is the sulphides oxidation process. The sulphides which exist in the Cretaceous rocks in dispersion are exposed during the decay of the carbonate rock by the water containing dissolved CO_2 . These sulphides are oxidized to sulphates and their $\delta^{34}\text{S}$ values probably do not change considerably, thus their $\delta^{34}\text{S}$ are negative (see the samples Nos. 7-11 and No. 17-31 in Table 1). The $\delta^{18}\text{O}$ values of these sulphates should be characteristic of the oxidation process described by Lloyd's formula, yielding -2.4% , or more positive as $+2.2\%$, if the sulphates are reduced later on.

Certainly some of the upper groundwaters penetrate into deeper Cretaceous

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Table 7 – Calculated seasonal variations of $\delta^{18}\text{O}$ of sulphate-mixture.

WINTER, $\delta^{18}\text{O}_{\text{atm}} = +10\%$					
<i>reducing conditions are predominant</i>			$\delta^{18}\text{O} = 0\%$	$\delta^{18}\text{O} = +2.2\%$	
A	B				
0.1	0.9	<i>frozen soil</i>	+1.0	+2.98	
0.2	0.8		+2.0	+3.76	
0.3	0.7		+3.0	+4.54	
0.4	0.6		+4.0	+5.32	
0.5	0.5		+5.0	+6.10	
0.6	0.4	<i>thaw</i>	+6.0	+6.88	
0.7	0.3		+7.0	+7.66	
0.8	0.2		+8.0	+8.44	

EARLY RAINY SPRING, EARLY DRY SPRING and LATE RAINY, COLD AUTUMN					
$\delta^{18}\text{O}_{\text{atm}} = +11.6\%$					
			$\delta^{18}\text{O}_{\text{L}} = -2.4\%$	$\delta^{18}\text{O}_{\text{L}} = 0\%$	$\delta^{18}\text{O}_{\text{L}} = +2.2\%$
A	B	<i>reducing conditions are more probable</i>			
0.1	0.9	-1.0	+1.16	+3.14	
0.2	0.8	+0.4	+2.32	+4.08	
0.3	0.7	+1.8	+3.48	+5.02	
0.4	0.6	+3.2	+4.64	+5.96	
0.5	0.5	+4.6	+5.80	+6.90	
0.6	0.4	+6.0	+6.96	+7.84	

LATE RAINY SPRING, $\delta^{18}\text{O}_{\text{atm}} = +14\%$					
			$\delta^{18}\text{O}_{\text{L}} = -2.4\%$	$\delta^{18}\text{O}_{\text{L}} = 0\%$	$\delta^{18}\text{O}_{\text{L}} = +2.2\%$
A	B	<i>various conditions</i>			
0.2	0.8	+0.88	+2.8	+4.56	
0.3	0.7	+2.52	+4.2	+5.74	
0.4	0.6	+4.16	+5.6	+6.92	
0.5	0.5	+5.80	+7.0	+8.10	

LATE DRY SPRING, RAINY SUMMER, HOT SUMMER and EARLY DRY AUTUMN					
<i>oxidizing conditions are predominant</i>					
$\delta^{18}\text{O}_{\text{L}} = -2.4\%$					
			$\delta^{18}\text{O}_{\text{atm}} = +14\%$	$\delta^{18}\text{O}_{\text{atm}} = +16\%$	$\delta^{18}\text{O}_{\text{atm}} = +18\%$
A	B	<i>small concentration of atmospheric sulphates</i>			
0.1	0.9	-0.76	-0.56	-0.36	
0.2	0.8	+0.88	+1.28	+1.68	
0.3	0.7	+2.52	+3.12	+3.72	
0.4	0.6	+4.16	+4.96	+5.76	

aquifers and their sulphate-ions are mixed. Thus with the infiltration process the atmospheric sulphates get into the deep groundwaters, and so they may change the isotopic composition of the deep groundwater sulphates too. We may assume that the infiltrating water sulphates have $\delta^{34}\text{S}$ values close to +3.3‰, as a medium value of atmospheric sulphates and the $\delta^{18}\text{O}$ close to +3.8‰ as average values of the studied groundwater samples (Nos. 2-10, 13-22 and 29-38 in Table 1). Likewise

Table 8 = Calculation $\delta^{18}\text{O}$ of sulphates of Cretaceous groundwaters.

parts of mixture		$\delta^{18}\text{O}_x=+3\%$			$\delta^{18}\text{O}_x=+3.7\%$			$\delta^{18}\text{O}_x=+4.5\%$	
		$\delta_L -2.4$	$\delta_L 0$	$\delta_L +2.2$	$\delta_L -2.4$	$\delta_L 0$	$\delta_L +2.2$	$\delta_L -2.4$	$\delta_L +2.2$
0.9	0.1	+2.46	+2.7	+4.68	+3.09	+3.33	+3.55	+3.8	+4.3
0.8	0.2	+1.92	+2.4	+4.16	+2.48	+2.96	+3.40	+3.1	+4.0
0.7	0.3	+1.38	+2.1	+3.64	+1.87	+2.59	+3.25	+2.4	+3.8
0.6	0.4	+0.84	+1.8	+3.12	+1.26	+2.22	+3.10	+1.7	+3.6
0.5	0.5	+0.30	+1.5	+2.60	+0.65	+1.85	+2.95	+1.0	+3.4
0.4	0.6	-0.24	+1.2	+2.08	-0.04	+1.48	+2.80	+0.4	+3.1
0.3	0.7	-0.78	+0.9	+1.56	-0.57	+1.11	+2.65	-0.3	+2.8
0.2	0.8	-1.32	+0.6	+1.04	-1.18	+0.74	+2.50	-1.0	+2.7
0.1	0.9	-1.86	+0.3	+0.52	-1.79	+0.37	+2.35	-1.7	+2.4

X is fraction of admixture sulphate, $\delta^{18}\text{O}_x$ its guessed $\delta^{18}\text{O}$ value, $\delta^{18}\text{O}_L$ is value of $\delta^{18}\text{O}$ of sulphates formed by oxidizing processes, calculated by Lloyd's formula.

the most probable mean value from $\delta^{18}\text{O}$ calculation is close 4‰ (see Table 7), as it was considered previously. We may try to describe the variations of $\delta^{18}\text{O}$ of the deeper groundwater sulphates caused by the infiltration with the following formula

$$\delta^{18}\text{O}_{\text{sulphate mixture}} = (1-X) \delta^{18}\text{O}_L + X \delta^{18}\text{O}_x \quad (3)$$

where X is the fraction of admixture sulphate and $\delta^{18}\text{O}_x$ means its $\delta^{18}\text{O}$ value, from +3‰ to +4‰. The $\delta^{18}\text{O}_L$ means characteristic values for the oxidation process and may be equal to -2.4‰ or +2.2‰ as it was considered above. Table 8 presents model values $\delta^{18}\text{O}$ of sulphate mixture calculated for manifold proportion of mixing, different $\delta^{18}\text{O}_L$ according to environmental condition, and $\delta^{18}\text{O}_x$ accepted equal: +3‰, +3.7‰ and 4.5‰.

If we accept for example the values of $\delta^{18}\text{O}_x = +3.7\%$ and $\delta^{18}\text{O}_L = -2.4\%$, we may obtain the $\delta^{18}\text{O}$ value of the groundwater sulphate mixture to be equal to -1.79‰, when we accept the fraction X of the admixture sulphate as 0.1, or equal to +0.65‰ for the $X = 0.5$. If the most negative $\delta^{18}\text{O}$ values of sulphates are observed (see Table 1 and Table 3), which correspond to $X = 0.1$, it suggests that in these groundwaters oxidizing conditions are predominant. Oxidation of sulphides is the main process, and admixture of soil sulphates is insignificant in these cases.

The $\delta^{34}\text{S}$ of the admixture sulphates will have values between those characteristic for the sulphides and of the atmospheric sulphates (see Figs. 2 and 9).

Conclusion

The SO₂ emitted into the atmosphere during the combustion of fuels (the main supply SO₂ process) is the precursor of atmospheric sulphate which enters the groundwater system with precipitation. The atmospheric admixture changes the groundwater sulphate $\delta^{34}\text{S}$ towards the value +3.3‰ and $\delta^{18}\text{O}$ towards +11.6‰. We may compare these effects in Fig. 2 as the dots which are on the right hand side of the line characteristic of the reduced sulphates (Mizutani and Rafer 1973, Krouse 1987). Part of the atmospheric sulphates is absorbed by plants and it gets into the groundwater system after the biochemical transformation

sulphate → organic sulphur compounds → sulphate

However, their $\delta^{34}\text{S}$ values are probably unchanged in these processes and are close to that of atmospheric SO₂, while their $\delta^{18}\text{O}$ values are characteristic of the sulphates produced by the oxidation processes. The admixture of such sulphate into the deeper groundwater during the infiltration will move $\delta^{34}\text{S}$ of groundwater sulphates only, towards +3.3‰, while their $\delta^{18}\text{O}$ values will remain unchanged. The dots representing $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ in Fig. 1 will be distributed parallel to the $\delta^{34}\text{S}$ axis. The microbiological reduction of sulphates causes simultaneous shift of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of the sulphates towards the heavier values, and if the sulphates are strongly reduced, their $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values will move along the line of slope 3 (Krouse 1987). Probably reduction of sulphates has changed δ -values later on.

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