



THE INFLUENCE OF BROWN COAL EXPLOITATION IN POLAND ON THE GROUNDWATER POLLUTION AS DETERMINED BY ISOTOPIC ANALYSES OF SULPHATE

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Abstract - *This research deals with pollution impact on natural water resources in the industrial area of Bełchatów, central Poland, where a large brown coal deposit is exploited and the coal is burned in an electric power plant. To trace the sources of groundwater pollutants the stable isotope analysis of oxygen and sulphur in sulphates was applied. The mass-spectrometric analysis was performed on SO_4^{2-} samples from numerous wells and piezometres in the excavation area. By repetitive sampling performed in November 1994, May 1995 and December 1996 significant changes of SO_4^{2-} concentration and sulphur and oxygen isotopic ratios in several sites were recorded. The interpretation of isotope ratios allowed us to recognize three groups of sulphates: (1) from the leaching of Permian salt dome, (2) produced by the leaching of soluble sulphates from an ash pool and (3) produced by oxidation of natural sulphides in water-bearing rocks.*

1. INTRODUCTION

Sulphates belong to common pollutants in groundwaters. By means of a standard chemical method one can only indicate the presence of sulphates and study the variations of their content. Chemical methods say little about the origin of sulphates. The sources of sulphates can be elucidated by means of $\delta^{34}S$ and $\delta^{18}O$ measurements. The isotopic compositions, combined with SO_4^{2-} concentration can indicate sources and processes in groundwater systems.

Sulphates of different origin in waters comprise: (1) *Dissolved evaporites*. They are easy to identify because of their $\delta^{34}S$ values $>10\text{‰}$ and $\delta^{18}O$ values $>12\text{‰}$ [1]. The waters that dissolve the sulphates are characterized by considerable sulphate concentrations, usually about a few hundred mg/L up to 2 g/L. (2) *Sulphates formed by sulphide oxidation* have similar sulphur isotope composition with respect to oxidized sulphides [2], [3], [4]. Usually $\delta^{34}S$ values of those sulphates are negative. Also $\delta^{18}O$ values are negative, because most of their oxygen is derived from water oxygen [5], [6], [7], [8]. The concentration of those sulphates in water does not need to be high. (3) *Atmospheric sulphates* are mainly formed during the combustion of fuels. Usually their $\delta^{34}S$ values range from 2‰ to 8‰ , while $\delta^{18}O$ values $>12\text{‰}$, which results from oxidation in air [9], [10], [11], [12], [13]. Atmospheric sulphates may also be derived from sea water sulphates in coastal areas [14]. The concentration of these sulphates is rather low, typically between 1 and 30mg/L. (4) *The sulphates from oxidized organic matters* have a similar $\delta^{34}S$ values to that of sulphur in plants [15], [11], [4]. These values are often similar to atmospheric sulphates while $\delta^{18}O$ values $<10\text{‰}$ makes them distinct from atmospheric sulphates [13]. Their concentration varies seasonally from several tens to several mg/L. (5) *The sulphates which come from the leaching*

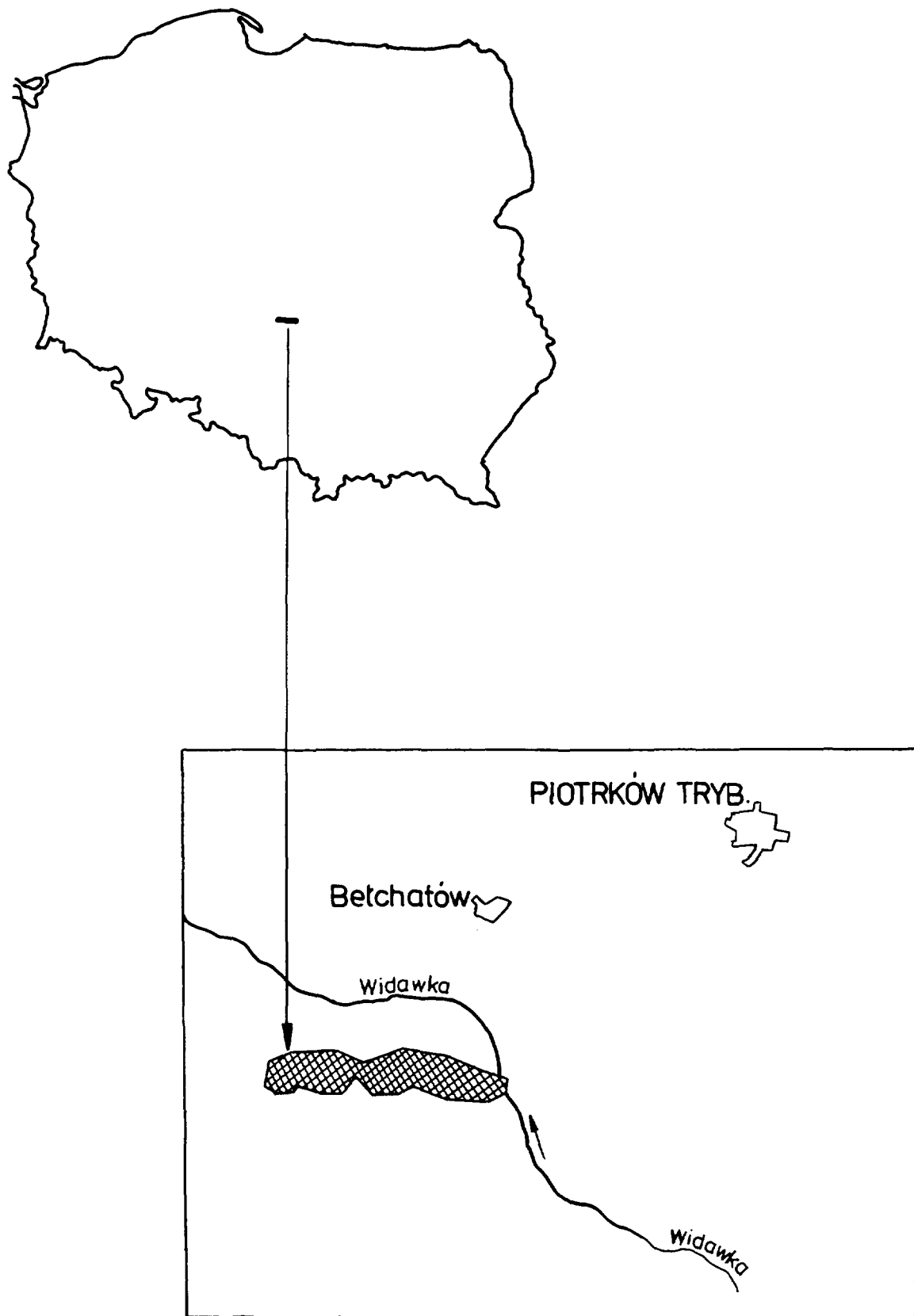


FIG.1. The location of the study area.

of artificial fertilizers may occur locally. Their $\delta^{34}\text{S}$ values usually exceed 10‰ and $\delta^{18}\text{O}$ values >16‰, as a consequence of their production procedures.

The original isotopic compositions of sulphates can be altered by some processes, such as bacterial reduction of sulphates. This process diminishes the sulphate concentration and significantly enriches the remaining sulphate in heavy isotopes. The isotope enrichment can be enormous for sulphur and somewhat smaller for oxygen. Inasmuch as both elements are enriched in heavy isotopes simultaneously their isotopic compositions are correlated [16]. During the formation of sulphates by oxidation of reduced forms of sulphur (S^0 , S^{2-}) oxygen is mainly incorporated from water [5], [6], [2], [4], [17], [7], [8] and enriches the formed sulphates in the lighter isotope of oxygen. The isotopic composition of sulphur changes little during the oxidation and thus sulphates formed possess sulphur whose isotopic composition is similar to the primary components [15], [11], [4]. The dissolution of sulphates does not change their isotopic compositions. When different sulphates are mixed, the final isotopic composition of the mixture becomes the weighted mean.

Ashes produced by power stations are the curse of our times. They contain a lot of harmful ingredients which seep into groundwaters and contaminate them. The ashes contain sulphur compounds from combusted coal, which are oxidized to sulphates and get into waters. Sulphates do not belong to the most dangerous compounds, however they may be easily monitored and their presence enables us to observe the infiltration of polluting substances into waters. The $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ measurements have been used for studying the infiltration of ash-borne pollutants into groundwaters in the Czech Republic [18], [19].

In central Poland, near the Bełchatów town there is a big brown coal mine and an electric power station (see Fig. 1 for location of this area). The industrial region of Bełchatów provides a good opportunity for testing stable isotope techniques in tracing sources of pollution. The research was initiated in 1983, only for a narrow practical aspect - a warning against the infiltration of the brines into outpumped water. The first results were published [20]. This more extensive work presents the patterns of sulphates from groundwaters in Bełchatów area, whose origin was identified using the isotopic compositions.

2. DESCRIPTION OF THE STUDY AREA

The large resources of brown coal lie in a tectonic trough 40 km long and from 1.5 km to 2 km wide (see Fig. 2). The deposit lies under a 140 m thick cap-rock (Quaternary and Tertiary). The cap-rocks consist of sands and clays. The average thickness of the coal deposit is about 55 m. The coal deposits are underlain by Jurassic and Cretaceous rocks [21], [22].

Weakly mineralized groundwaters occur to a depth of 700 m. Their chemical composition is variable. Shallow groundwaters appear at depth of ca. 10 m under the surface in the Quaternary sands and clays. These waters are more variable in their chemical composition than deeper waters. Their mineralization varies from 120 mg/L to 3,000 mg/L, predominantly about 500 mg/L. Deeper waters with mineralization about 300 mg/L are characterized by smaller chemical variability. All of the water horizons have good hydraulic contact and they are practically connected. The filtration factors are different, from 2 m/d in the Tertiary rocks to 20 m/d in the Quaternary. Impermeable layers are present too [22].

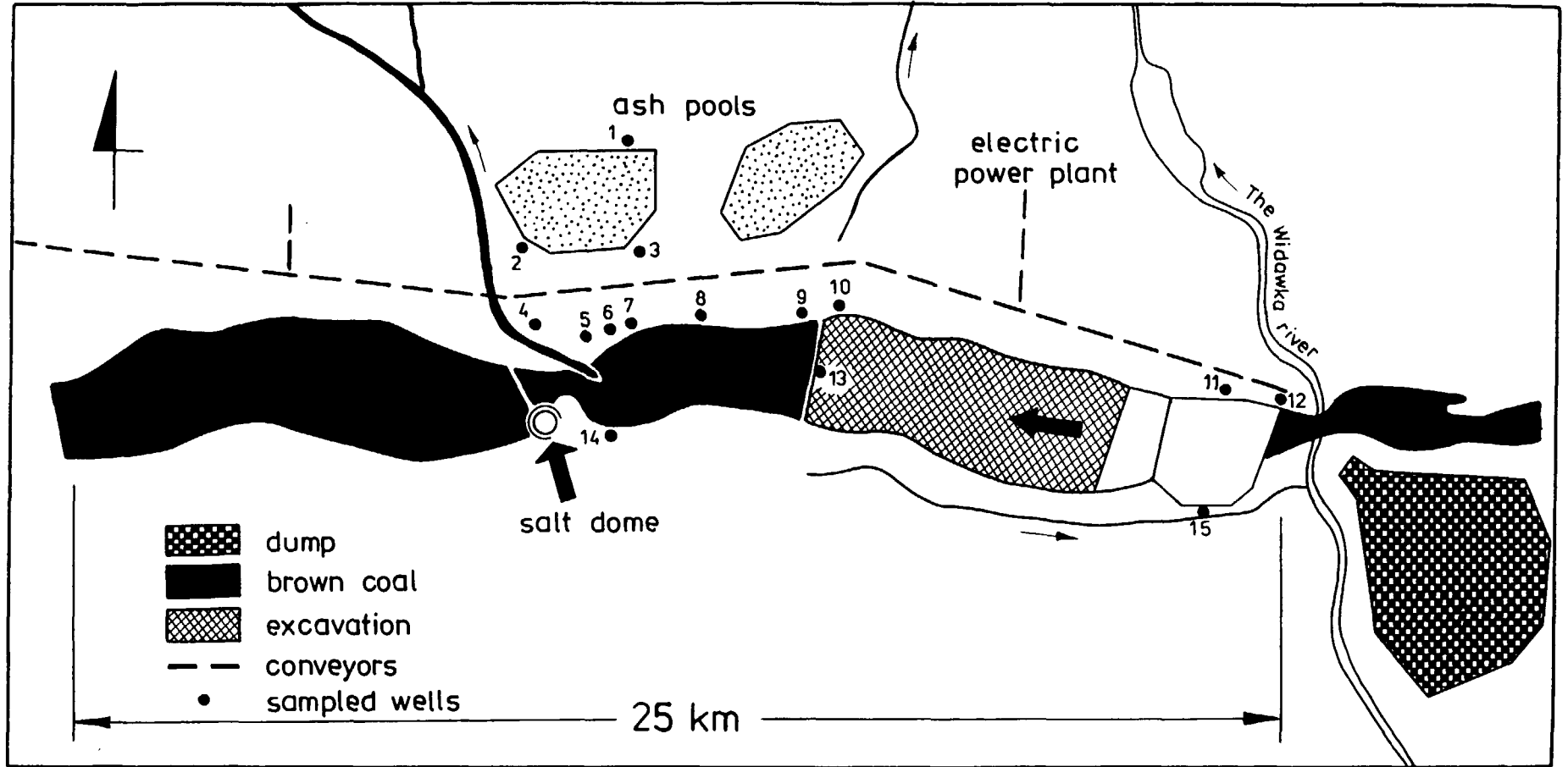


FIG.2. The study area. The numbers of the wells are: **No. 1** is P-4, **No. 2** is P-35, **No. 3** is 66/30, **No. 4** is 139 N, **No. 5** is 136 N, **No. 6** is 125 N, **No. 7** is 131 N, **No. 8** is 115 N, **No. 9** is 109 N, **No. 10** is 106 N, **No. 11** is 27 N-2, **No. 12** is 5 N bis, **No. 13** is 108H, **No. 14** is 101S, **No. 15** is 18 S bis.

The drainage system of the wells around the Belchatów mine forms a parallel barrier which protects the excavation against flooding. Some of these wells are 200 m deep or even deeper, up to 400 m. The total rate of water pumping exceeds 500 m³/min. The depression radius is estimated to be 20 km and the depression area is about 1,600 km².

The exploitation of brown coal resources causes major disturbances in the natural environment. Intense dewatering of the exposure area causes extended depression and disappearance of surface waters. The circulation of groundwaters becomes disturbed. Waters do not flow down a natural slope, but from the surrounding to the depression centre (i.e. to the excavation). The changes of the waterflow cause further complications. Many chemical species can now appear in the water, their concentration has increased over the period of exploitation.

The changes in the groundwater system have been detected by means of 200 piezometres and 2,000 wells in the depression area. The reduction of the water table exceeds 10 m. The groundwaters are intensively mixed while pumped up to the depth of 350 m. Deeper groundwaters which lie under this depth are not disturbed, so the admixture of deeper, more mineralized groundwater may be excluded. The lateral infiltration does not introduce water of different chemical composition. The outpumped water is weakly mineralized and is utilized to supply the tap-water pipe system.

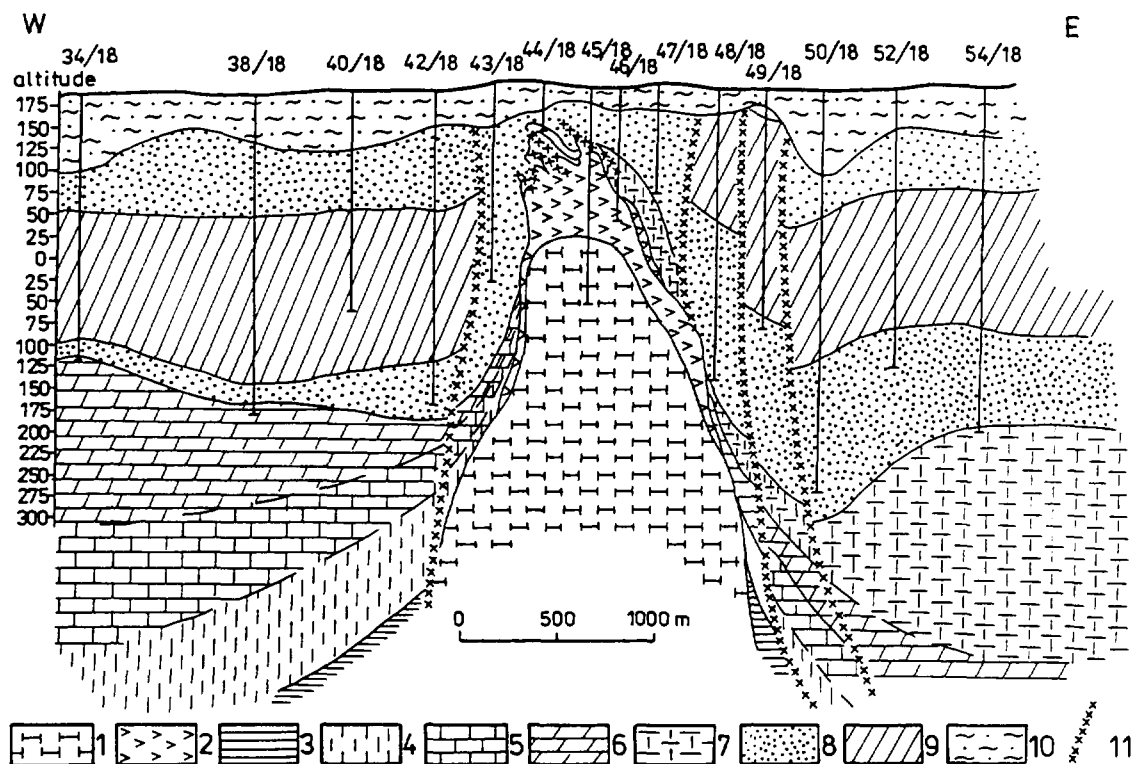


FIG.3. Geological section through the Dębina salt dome (after Baraniecka, 1980).
 1-Permian salt, 2-dome cap rock, 3-Lower Jurassic, 4-Middle Jurassic; Upper Jurassic: 5-Oxfordian, 6-Kimmeridgian; Upper Cretaceous: 7-Maestrichtian; Tertiary: 8-sub- and supra coal series of sands and silts, 9-coal series; 10-Quaternary, 11-fault lines.

The presence of a salt dome in the middle part of the deposit (Fig. 3) causes another disturbance. The lowering of the water table near the salt dome may cause the infiltration of the brine into the outpumped water, which can destroy the pumps and strongly increase the mineralization of the water. Therefore, careful monitoring of the water is necessary in the wells in the vicinity of the salt dome.

The combustion of coal in the electric power station pollutes the environment with gases, dusts and ashes. The ashes are washed out from the site of the conflagration and conveyed by water by means of the pipeline system into the sedimentation pools. The ash has been stored there since 1983. The excess of water seeps down and the pollutant infiltrates into groundwaters. Thus, the chemical composition of the groundwater and of the pumped water is changed and monitoring is necessary. At present, the wet ashes are transported by the conveyor without water and stored in the excavation. This method was applied to reduce the groundwater pollution.

Since 1983 the groundwaters have been studied by both chemical and isotope methods for early warning against increase of salinity. If the sulphate concentration increases, it will be necessary to know the origin of sulphates and to determine whether they come from the ashpool or from the salt dome. The latter would be a warning signal. We applied $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ analyses of dissolved sulphates in order to identify their origin. It was necessary to monitor the groundwater and also measure $\delta^{34}\text{S}$ values to detect the presence of the dissolved sulphate of the Permian gypsum which covers the salt dome. The isotopic composition of the Permian evaporites is well known [1]. $\delta^{34}\text{S} = 11\text{‰}$ and $\delta^{18}\text{O} = 11\text{‰}$. The presence of SO_4^{2-} ion with such an isotope composition would be the result of the leaching of the salt dome cover. Hence, it would be an early signal that brines may be infiltrating into groundwaters. The determination of the rate of sulphate penetration into groundwaters, especially from the ashpools, is another application of the $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ analyses of sulphates.

3. ANALYTICAL PROCEDURES

The samples of water were poured into very clean plastic vessels of about 3 L volume. The samples were collected from the studied area and transported to the laboratory by car. Then the water samples were filtered and the sulphate ion was precipitated as BaSO_4 by BaCl_2 solution acidified with HCl. In this way an influence of any microbiological activity in the collected sulphate samples was excluded. Then the pure BaSO_4 was weighed, so that the SO_4^{2-} concentration could be found, and subsequently prepared in separate vacuum lines to CO_2 or SO_2 . For $\delta^{18}\text{O}$ analysis the BaSO_4 was reduced with graphite at 1,000 °C by the Rafter-Mizutani method to CO which subsequently was converted to CO_2 in a glow discharge [23]. For $\delta^{34}\text{S}$ analyses the BaSO_4 was decomposed to SO_2 , with NaPO_3 at 850°C, by the Hałas and Wołacewicz method [24].

The measurements of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values were performed with the dual inlet system and the triple collector mass spectrometer [25], [26]. The isotope data of $\delta^{18}\text{O}$ are expressed versus VSMOW standard while $\delta^{34}\text{S}$ is expressed versus CDT (see [27]). Every sample had been prepared twice and also measured at least twice, in order to obtain better precision of the average delta values than 0.08 ‰ (in terms of standard deviation of the average delta), from both $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ measurements.

4. RESULTS AND DISCUSSION

We have studied the sulphates coming from waters sampled in the following areas: (i) the salt dome area, (ii) the wells surrounding the ash-pool and (iii) the wells near the dry ash storage. The samples were collected three times: in November 1994, in May 1995 and in December 1996. In May 1995 we collected only 16 samples of groundwaters. Most of them came from the same groundwaters which were sampled in November. In December 1996 samples of groundwaters were taken only from the wells lying on the edge of the excavation. Table 1 presents the results of measurements for groundwaters dewatering the salt dome area. Samples Nos. 1 - 11 are the sulphates from the wells, while Nos. 12 - 20 are from piezometers.

Table 2 presents the results for other groundwaters: samples Nos. 21 - 28 represent the sulphates from the wells surrounding the ashpool, Nos. 29 - 43 the sulphates from the wells dewatering the storage of dry ashes in the excavation from the South and the North, Nos. 44 - 54 the sulphates from the wells lying between the ashpool and the excavation. The difference

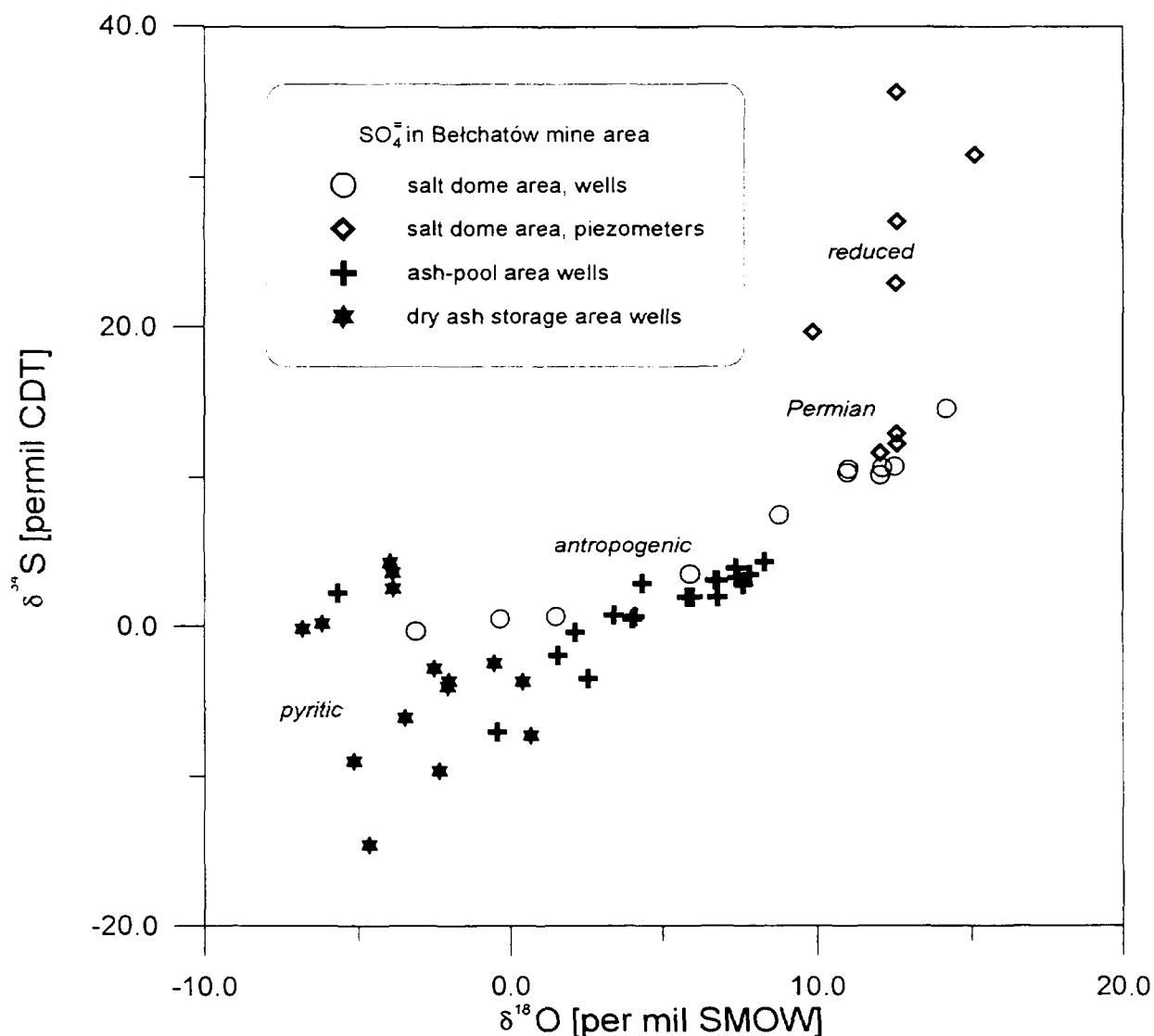


FIG.4. $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of sulphates from different groundwaters of the Bełchatów mine.

Table 1. The isotopic and chemical data of selected groundwaters from the Bełchatów brown coal mine in the salt dome area.

sample No.	well No.	depth [m]	SO ₄ ²⁻ [mg/L]	δ ³⁴ S _{CDT} [‰]	δ ¹⁸ O _{VSMOW} [‰]
wells					
1	5 SD	242.0	42.3	+0.46	-0.35
2	6 SD	241.0	73.6	-0.38	-3.13
3	11 SD	191.0	283.2	+10.71	+12.48
4	12 SD	200.0	214.2	+10.61	+12.08
5	22 SD	240.3	20.1	+0.65	+1.52
6	27 SD	178.7	3.3	+7.48	+8.77
7	30 SD	239.8	199.3	+10.13	+12.01
8	24 SD ^b	242.6	18.0	+3.47	+5.86
9	26 SD ^b	262.5	9.0	+14.55	+14.16
10	30 SD ^b	239.8	240.0	+10.55	+11.00
11	10 SD ^b	156.9	65.8	+10.30	+10.97
piezometers					
12	PD-8	287	4.3	+35.58	+12.54
13	PD-5C	255	2.5	+27.00	+12.59
14	PD-6C	252	1.1	n.a.	
15	19 SDp	272	91.2	+22.90	+12.52
16	PD-7	175	3.8	+19.60	+9.85
17	PD-27	208	1011.4	+11.59	+12.01
18	PD-9 B	60	1001.3	+12.87	+12.55
19	PD-39	141	1471.1	+12.20	+12.57
20	PD-41	182	9.5	+31.44	+15.08

^bsampled in May 1995

in their isotopic composition is significant, which helps to identify their origin. These results are plotted in Fig. 4, where the distinction is made according to the location of the wells. It is seen, however, that points in Fig. 4 are also grouped according to the origin of the sulphates (see comments below).

The salt dome area. A higher concentration of sulphate, more than 200 mg/L, may be observed in the groundwaters in some of the wells (samples Nos. 3, 4, 7, 10 and 11 in Tab. 1). These sulphates have δ³⁴S values ≈ 10‰ and δ¹⁸O values ≈ 12‰, typical values for the Permian evaporate [1]. Sample No. 10 (taken in May) comes from the same well as sample No. 7 (sampled in November). The well represented by sample No. 11 sampled in May is located between wells Nos. 3 and 4 measured in November.

Sample No. 9 has sulphur and oxygen enriched in heavy isotopes, and this may be caused by reducing bacteria because the concentration of the sulphate is low (9 mg/L). However, this sulphate may be of different origin.

Table 2. The isotopic and chemical data of selected groundwaters from the Bełchatów brown coal mine in locations specified.

sample No.	well No.	depth [m]	SO ₄ ²⁻ [mg/L]	δ ³⁴ S _{CDT} [‰]	δ ¹⁸ O _{VSM} OW [‰]
the ashpool					
21	from the ashpool	surface	183.4	+1.94	+5.93
22	P-4	15	125.0	+3.21	+7.39
23	P-35	32	195.8	+1.95	+6.74
24	66/30	24	89.3	+3.86	+7.33
25	from the ^b ashpool	surface	190.0	+0.65	+4.10
26	P-4 ^b	15	150.0	+4.28	+8.28
27	P-35 ^b	32	108.0	+2.76	+7.56
28	66/30 ^b	24	258.0	+0.46	+4.02
the wells lying on the edge of the excavation					
29	41 N ^c	176.0	52.0	-2.44	-0.54
30	33 N ^c	175.0	145.0	-7.22	+0.68
31	29 N-1 ^c	179.0	147.0	-2.80	-2.53
32	27 N-2	179.0	161.9	-6.11	-3.47
33	5 N-bis	311.0	60.8	-9.03	-5.15
34	1 A-1 ^c	330.0	7	-3.65	+0.40
35	2 E-2 ^c	307.0	54.0	-4.02	-2.08
36	14 E-bis ^b	209.7	109.0	-14.62	-4.64
37	14 S-1 ^c	242.0	552.0	+3.56	-3.88
38	18 S-bis	244.0	309.6	-0.18	-6.80
39	18 S-bis ^b	244.0	258.0	+0.17	-6.16
40	18 S-bis ^c	244.0	462.0	+2.50	-3.86
41	22 S-bis ^c	238.0	113.0	+4.24	-3.96
42	89 N ^c	230.0	61.0	-9.66	-2.37
43	93 N ^c	225.7	47.0	-3.65	-2.05
the wells lying on the edge of the ashpool					
44	106 N ^b	167.0	110.0	-1.92	+1.58
45	109 N ^b	243.0	92.0	+2.82	+4.34
46	115 N	240.0	31.3	-0.39	+2.16
47	125 N	244.5	67.8	+3.04	+6.73
48	63 A-1 ^b	202.0	70.0	+3.08	+6.67
49	131 N	230.0	15.5	+0.74	+3.42
50	81 A ^b	233.0	4.0	+3.42	+7.78
51	136 N	243.0	3.2	+1.92	+5.78
52	139 N ^b	244.0	8.0	-3.46	+2.58
53	108 H ^b	120.5	600.0	+2.16	-5.69
54	101 S	246.0	9.6	-7.04	-0.45

^bsampled in May 1995

^csampled in December 1996

In other wells the sulphates have nothing in common with gypsum (samples Nos. 1, 2, 5. These sulphates may come from oxidized pyrites or from soil. Sample 6 may be a mixture of sulphates of evaporitic and other origin. This well is located between the wells which are represented by samples 5 and 7. The investigation of the isotopic composition of sulphates in the wells of this area is very useful. Also sample No. 8 has nothing in common with gypsum, as well as samples No. 1 or No. 5.

The piezometers turned out to be worse indicators for isotope analyses than the wells. The values $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of sulphates Nos. 17, 18 and 19 suggest evaporitic origin (the $\delta^{34}\text{S}$ about 12‰ and $\delta^{18}\text{O} \approx 12‰$), but other results of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ are typical for the reducing process which enriches sulphates in heavy isotopes (sulphur is usually more enriched than oxygen) and decreases the concentration of sulphates. It is hard to say what the primary isotopic composition of these sulphates was, hence their origin remains unknown. During the reduction, the concentration of the sulphate decreases and the δ values increase. Such high values $\delta^{34}\text{S}$ up to 35‰ and $\delta^{18}\text{O}$ up to 15‰ were observed together with a very low concentration of the sulphate, from 9 to 1 mg/L (see sample No. 20). Probably these groundwaters do not flow fast enough and the stagnancy of the water permits the bacterial reduction of sulphates. Only in the waters in which the concentration of sulphates is high, the values of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ may be unchanged. So, the values of samples Nos. 17, 18, 19 which represent the waters with a high concentration of sulphates (more than 1 g/L) are similar to the evaporitic sulphate. These waters come from the piezometers situated under the top of the salt dome.

Wells surrounding the ashpool. The brown coal used in the power station contains about 0.5% sulphate and 0.78% sulphide, which are oxidized during combustion [28]. The concentration of sulphates has increased since the beginning of the storage (since 1983) in the wells surrounding the ashpool. These wells are represented by samples Nos. 21 - 28 in Table 2. The sulphate ion concentration in these waters is high, about 100 - 250 mg/L. Samples No. 21 and 25 come directly from the pool. Samples Nos. 22, 26, 23, 27, and 24, 28, which come from the wells surrounding the ashpool, have similar isotopic composition. The $\delta^{34}\text{S}$ values range from 0 to 4‰ and $\delta^{18}\text{O}$ values from 4 to 8‰, respectively and they are similar in November and in May. These patterns are typical for anthropogenic sulphates and the isotopic composition of these sulphates confirms their origin; there is no doubt that these sulphates come from the ashes.

Samples Nos. 45, 47, 48, 49, 50, 51, which come from the wells located between the ashpool and the excavation, have similar isotopic composition. Also these sulphates come from the ash.

Sample No. 54 comes from the well which is bored on the other side of the excavation and has nothing in common with the ashpool. Indeed, $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ are typical for oxidized sulphides. Also, sulphate of sample No 46 comes from the well which is not influenced by the ashpool (see Fig. 2).

The isotopic composition of samples Nos. 44 and 52 is rather typical for oxidized sulphides, like in sample No. 54 or No. 46. Water in these wells is not influenced by the ashpool.

Wells near the dry ash storage. Presently, ashes are conveyed without water and stored in the excavation. An increase of the sulphate concentration in the groundwaters which are outpumped from this region has been noticed by Sołtyk [29]. These groundwaters are represented by samples Nos. 29 - 43. Their sulphates have the most negative values of $\delta^{34}\text{S}$ up to -14.6 and $\delta^{18}\text{O}$ -6.8‰, which excludes the possibility that these sulphates might be coming from the ash. The δ values are typical for the sulphide oxidation processes. The negative values of $\delta^{18}\text{O}$ suggest that more than 70% of the oxygen [7], [8] comes from the water with $\delta^{18}\text{O} = -10.5\text{‰}$, typical value for shallow groundwater in Poland [13]. The oxidized material may come from sulphides in coal or from the Cretaceous rocks.

Sample No. 53 from the centre of the excavation is very interesting. This groundwater has a very high concentration of sulphate (600 mg/L) but $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ value suggests that this sulphate is formed by sulphide oxidation rather in water than during combustion in air, so it probably has nothing in common with ashes.

5. CONCLUSION

The use of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ allows us to distinguish between sulphates coming from the leaching of a Permian salt-dome, those coming from oxidized sulphides in the groundwater and those of anthropogenic origin (leached from the ashes). It is clear from the data obtained so far that the oxygen and sulphur isotope ratios of the dissolved sulphates are informative of their origin.

The samples of groundwaters from the wells are more representative for the investigation of the isotopic compositions of sulphates than from the piezometers.

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