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The occurrence of sulfate-rich rains in the Negev desert, Israel

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ABSTRACT

Rain water was sampled in the Negev Desert, Israel for the past six years. Events with relatively high amounts of sulfate were detected and studied for their chemical, isotopic and synoptic features. It was found that sulfate-rich rain events were usually enriched with respect to the median isotopic value for the area $\delta\,^{18}O$ (‰) (relative to SMOW) and were associated with dust storms and a continental direction of surface winds prior to the rain event.

1. Introduction

The Negev desert comprises the southern arid half of Israel (Fig. 1), and is part of the desert belt extending from the Sahara through Egypt and Sinai to the Arabian desert. The average annual precipitation over most of the Negev is about 100 mm yr^{-1} (I.M.S. 1977). Owing to its proximity to the southeastern Mediterranean coast, it is affected from time to time by the winter cyclones of the Mediterranean sea (Evenari et al., 1971).

Rain water has been sampled for chemical and isotopic analyses since 1978 by the Institute for Desert Research, located at Sede Boqer in the central Negev desert plateau. The mean concentration of various ions and the mean values of environmental isotopes, based on 5 years of sampling, is given in Table 1. The usual prevailing ions in the Negev rain water are Ca^{+2} and HCO_3^- which is sometimes exchanged for Cl^- (Nativ et al., 1983). This composition was also found to be typical for the northern humid part of Israel, which is characterized by 400–800 mm of rainfall per year (Yaalon and Katz, 1962; Rosenthal, 1980). This chemical distribution of ions is to be expected in the light of the large portion of limestone, dolstone and chalk (Cenomanian to Eocene age) exposed in the Israeli land surface. However, few rain events during each winter were characterized by sulfate as the dominant anion.

The purpose of this preliminary analysis is to find a connection between the chemical and isotopic character of the sulfate-rich rain storms in the Negev and the general wind flow pattern in the region prior to and during the storm. At this point, no attempt has been made to distinguish between nearby or remote sources of sulfates, or to build a specific model for the mechanism of sulfate-rich rain formation. What has been done is to identify typical large-scale flow patterns that lead to these rain storms. The fact that such an analysis gave meaningful results is encouraging.

2. Methods of research

The sampling of rain water was facilitated through the development of sequential self-sealing special samplers (Adar et al., 1980). The rain sampler included a collecting funnel whose diameter was calculated to give a 0.5 l sample from 2 mm of rain. After the containers were sequentially filled with rain water, measuring at the same time the amount of rain, they were automatically sealed off by a magnetic catch, preventing evaporation and consequent concentration of the salts during the time between the storm and the collection of samples (Nativ et al., 1983).

To overcome this problem of dust collection in the funnel, the water in the first two containers including most of the accumulated dust, was not

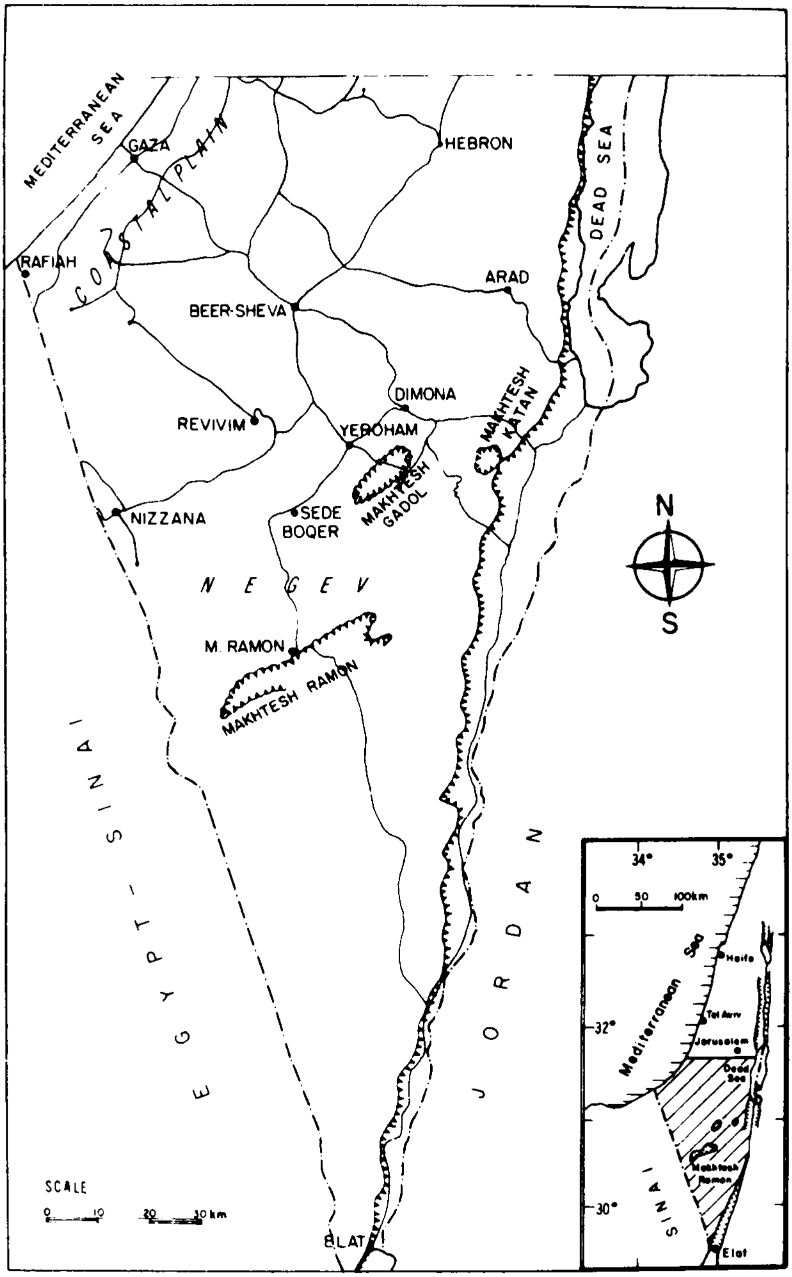

Fig. 1. Location map.

analyzed during the years 1978/79–1980/81. Later on when the sampling network became smaller (1981/82–1982/83), it was possible to flush the funnel of each sampling device with distilled water just before the storm, thus removing the dust to enable a full analysis of the rain event.

The location of the rain samplers is shown in Fig. 1. As can be seen, the most northern station (Revivim) lies about 25 km to the south of the nearest urban center of Beer Sheva; thus no local sources of sulfur or sulfate, as a result of siting in an urban area, should be expected.

Table 1. *Mean values for anion concentration* (mg l^{-1}), for ionic ratios (meq l^{-1}) and for environmental isotopes† (‰) in Sede Boqer rains*

Sampling‡ period	Cl^-	SO_4^{2-}	HCO_3^-	HCO_3^-/SO_4^{2-}	Cl^-/SO_4^{2-}	O^{18}	D
1978/79 1980/81	72	67	24.5	2.883	1.457	−5.09	−27.07
1981/82	17.08	20.47	31.81	1.225	1.318		

* Based on Nativ et al. (1983) and on published measurements of 1981–1983.
† From Leguy et al. (1983).
‡ The values of 1978/79–1980/81 refer only to the samples representing the 2 mm and above.
Values of 1981/82–1982/83 represent rain fall samples from the beginning of the rain to its end.

The rain samples were analyzed for their main constituents, cations and anions: Na^+ and K^+ were measured with a flame photometer, and (Ca^{2+} Mg^{2+}), (HCO_3^- CO_3^{2-}), Cl^- and SO_4^{2-} were titrated against EDTA, HCL, $AgNO_3$, and Ba-Acetate, respectively. Reaction errors are given in Table 2.

During the 5 years of this study, 60 rain events were sampled and analyzed for their chemical composition. A sulfate-rich rain event was defined when sulfate proved to have the highest concentration in meq l^{-1} amongst the anions. The isotopic composition analysis of the water samples (^{18}O D) was performed at the Isotope Laboratory of the Weizmann Institute of Science. Oxygen-18 and deuterium were reported in δ (‰) relative to SMOW, in the accepted manner. The average reproducibility of the stable isotopes measurement was ±0.15‰ for $\delta\,^{18}O$ and ±1.5‰ for δ D.

As regards the synoptic analysis, the fundamental hypothesis is that the flow pattern near the surface is mainly responsible for the presence or lack of sulfates in precipitation. The general trajectory of the surface flow in the 48 h preceding the rain event was determined by inspection of the surface charts. No quantitative trajectory calculations were undertaken at this stage.

3. Results

3.1. *Chemical and isotopic composition*

The sulfate-rich rain occurrences are listed in Table 2 with their chemical, isotopic and synoptic description. The data reveals that sulfate-rich events are characterized by an unusual concentration of sulfate, not only relative to other anions, but also as compared to its mean concentration (Table 2). Out of 21 events, 7 had a sulfate concentration which was even higher than one standard deviation above the mean values. During these events, chloride and bicarbonates showed an inconsistent behavior. Bicarbonate concentration was lower than its mean value in 11 out of 21 cases, and the same was true for chloride in 12 out of 24 cases. During the remaining events, the concentration of bicarbonate and chloride increased, as did the sulfate's values, but they still were not high enough for HCO_3 and chloride to be the dominant anions. As a result, the mean equivalent ratios of Cl/SO_4 (1.318) and HCO_3/SO_4 (1.225) are reduced to extremely low values, such as 0.28 and 0.14, respectively (lowest measured value).

Out of 20 cases of sulfate-rich rain events, only 11 contributed more than one sample (i.e., more than the first 2 mm of rain fall) for sulfate analysis. It was found that sulfate-rich water is usually encountered at the beginning of a rain event (Fig. 2). Only 45% of the rain events included sulfate water in the second 2 mm (Fig. 3b). The rest were changed eventually to the more common type of $Ca(HCO_3)$ or $Ca(Cl)_2$ water (Fig. 2a,c,d).

The oxygen-18 values were rather enriched relative to regular values during the sulfate-rich rain events. Values ranged from −5.77 up to +2.29 (‰) as compared to the regular values of −5.45 to −4.72, usually encountered in the Negev rains (Leguy et al., 1983). In a few cases where D values were available, they showed the same pattern: values ranged from −21.4 up to +27.4 (‰) as compared to the more frequent, but depleted,

Table 2. *Rain events and their characterization*

Date	mm of rainfall represented by the sample	Total rainfall in the event (mm)	Sampling* station	SO_4	HCO_3	Cl	HCO_3/SO_4	Cl/SO_4	O^{18}	D	Dust storm preceding the rain event	Air mass direction	Reaction error (%)
				concentration (meq. l^{-1});			on equivalent basis;		values in ‰				
4 May 1979	2–3		REV	0.874	0.736	0.46	0.84	0.52	+2.29	+27.4	—	Cont. N	7.0
11 Dec. 1980	0–1	47	SB	5.224	0.960	3.684	0.184	0.705	—	—	Yes	Cont. W	12.8
11 Dec. 1980	1–2		SB	1.171	0.417	0.66	0.355	0.564	—	—			3.7
27 Jan. 1981	0–2	19	SB	1.614	1.320	1.461	0.818	0.905	—	—	No	Cont. WSW	7.0
12–13 Nov. 1981	0–2	3.2	SB	2.190	0.872	0.620	0.399	0.283	—	—	Yes	Cont. WSW	—
12–13 Nov. 1981	2–4	7.1	SB	0.72	0.590	0.479	0.82	0.67	—	—	Yes		—
6 Jan. 1982	0–2	2.6	SB	0.655	0.74	0.583	1.129	0.891	−1.67	—		East	4.0
22–23 Feb. 1982	0–2	7.1	SB	0.778	0.595	0.431	0.764	0.56	−4.82	—	Yes	Cont. SW	4.3
22–23 Feb. 1982	2–4		SB	0.184	0.357	0.148	1.940	0.804	−6.62	—			3.8
22–23 Feb. 1982	4–6		SB	0.281	0.473	0.192	1.683	0.683	−5.12	—			0.2
28 Feb. 1982	0–2	1.6	SB	0.788	0.497	0.375	0.631	0.477	−3.12	—	Yes	Cont. SW	1.3
8 May 1982	0–2	4.3	SB	3.026	0.418	1.286	0.138	0.423	−1.72	—	Yes	Cont. E	−0.6
8 May 1982	2–4		SB	1.206	0.317	0.541	0.263	0.448	−1.59	—			3.9
13 May 1982	0–4	3.4	RAM	1.019	0.836	0.677	0.824	0.651	−0.24	—	Yes	Cont. E	−2.9
28 Sept. 1982	0–1	1.7	SB	1.075	0.359	0.321	0.333	0.298	+1.53	—	—	Cont. N	−2.9
23 Oct. 1982	0–2	7.2	SB	0.961	0.535	0.857	0.555	0.891	−5.77	—	—	Cont. NE	6.6
23 Oct. 1982	2–4		SB	0.207	0.214	0.312	1.034	1.507	−7.51				−0.3
23 Nov. 1982	0–4	5.6	RAM	0.449	0.42	0.44	0.935	0.98	−3.83	—	Yes		−1.9
5 Dec. 1982	0–2	8.45	SB	0.459	0.403	0.457	0.878	0.996	−4.46	—	Yes	Cont. SW	4.2
5 Dec. 1982	2–4		SB	0.170	0.223	0.152	1.312	0.894	−5.75				−3.2
14 Dec. 1982	0–2	3.2	SB	0.589	0.469	0.431	0.798	0.735	−1.75	—	Yes	Mar	2.2
14 Dec. 1982	2–4		SB	ND	0.238	0.22	ND	ND	−2.92	—			ND
21 Dec. 1982	0–2	1.4	SB	0.688	0.503	0.389	0.733	0.564	−2.8	—	Yes	Cont. SW	4.4
9 Jan. 1983	0–2	1.8	SB	0.686	0.356	0.384	0.518	0.559	−5.66	—	No	Cont. S	3.4
14 Jan. 1983	0–2	2.4	SB	0.649	0.541	0.313	0.836	0.481	—	−21.4	No	Cont. SW	4.8
14 Jan. 1983	2–4		SB	ND	0.334	ND	ND	ND	−4.64	—			ND
23 Jan. 1983	0–2	12.5	SB	0.842	0.686	0.744	0.815	0.885	−5.48	−6.9	Yes	Cont. WSW	−0.6
23 Jan. 1983	2–4		SB	ND	1.048	ND	ND	ND	−7.35	—			ND
23 Jan. 1983	4–6		SB	0.29	0.492	0.457	1.697	1.576	−6.04	—			10.2
24 Jan. 1983	0–4	1.1	RAM	0.580	0.594	0.527	1.022	0.910	−4.06	—			−5.8
2 Feb. 1983	0–2	3.3	SB	0.709	0.628	0.541	0.886	0.764	−0.06	—	Yes	Cont. WSW	5.1
4 Mar. 1983	8–10	10.7	SB	0.2	0.192	0.127	0.96	0.643	−5.28	—	Yes	Cont. W	3.5
21 Mar. 1983	0–2	7.0	SB	0.526	0.384	0.446	0.729	0.842	—	—	Yes	Cont. SW	6.5

* Station: SB is Sede Boqer, REV is Revivim and RAM is Machtesh Ramon (Fig. 1).
Cont.: Continental. ND: not determined.

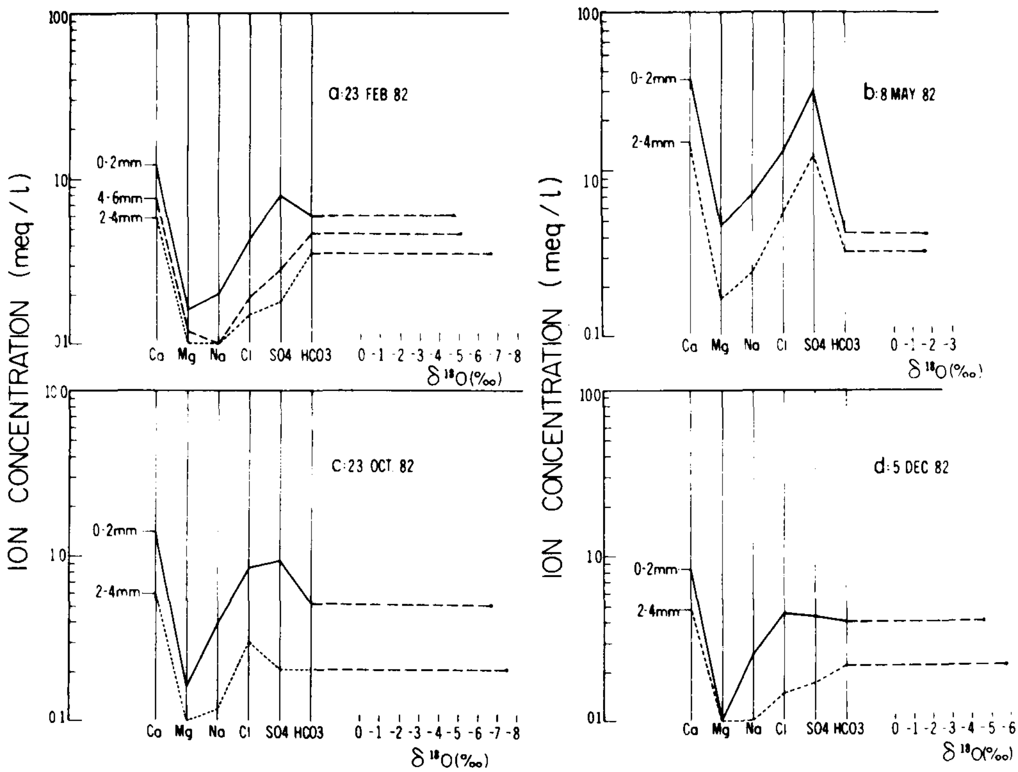

Fig. 2. Chemical composition of different fractions of rain water.

values of −39.7 to −20.3. Just as the chemical evolution of the rain water along the storm changed, the enriched values of O^{18} that were encountered at the beginning of the storm became gradually changed into depleted values (see Table 2). During some rain storms, a slight enrichment is observed in the later stage of the storms. This may be due again to evaporation due to the fading out of the humidity saturated environment characterizing the center of the storm. However, more data is needed in order to suggest a more conclusive mechanism.

3.2. Synoptic analysis

If the surface flow pattern prior to and during the rain storm is from a continental direction (in Sede Boqer, a continental direction is from an azimuth of about 030° to about 280°), we should expect more sulfates in the rain water. If the flow pattern at the surface is from a maritime direction (for example, 280° to 030°), the chance for sulfate-rich rain is smaller.

There appears to be at least two different flow patterns associated with sulfate-rich precipitation. We were also able to associate these patterns with distinct seasons, namely fall and spring, on the one hand, and winter on the other. For our purposes, the months of September and October were defined as fall, and the months of April and May were defined as spring.

3.2.1. First type: fall and spring. Only four storms were determined to be sulfate-rich events in the above two seasons and they showed similar characteristics. At the surface, a general easterly to northeasterly flow prevailed several days prior to the sulfate-rich storm; then an upper trough moved in from the west. The effect of this trough was to bring in cool air aloft, thus increasing the gravitational instability of the air mass and also inducing some low-level convergence and high level divergence of air that could generate local showers.

It is interesting to note that very little coupling existed between the upper air and surface flow patterns. The latter showed very little change

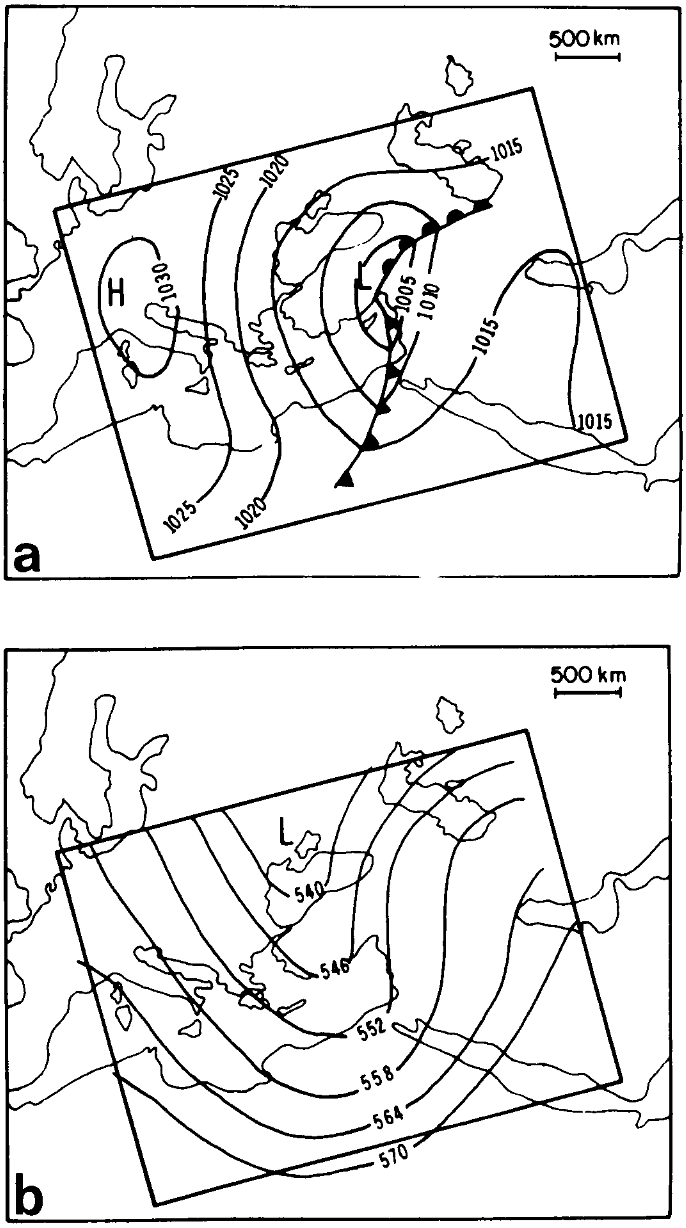

Fig. 3. Typical synoptic situation for a sulfate-rich rainstorm 00 GMT 4 March 1983; (a) surface chart (numbers denote surface pressure (mb); (b) 500 mb chart (numbers denote height of the 500 mb surface (dm)).

before and throughout the rain event. This behavior of the atmosphere is typical of the transition seasons (and the summer).

In these cases, the whole eastern Mediterranean was covered by continental dry air (in two of the cases, the air spent a short time over the north-eastern Mediterranean before entering the Negev). The upper trough induced convergence of low-level air from large areas and caused the sulfate-rich rainfall.

3.2.2. Second type: winter. In mid-winter, the atmosphere is much more baroclinic and as a result there is strong coupling between all the layers of the troposphere. The rainfall in the southeastern Mediterranean is generally associated with migrating cyclonic storms which appear as deep troughs in the 500 mb synoptic charts and as low-level depressions. Most major rain events in the Negev occur after the center of the surface depression has already moved to eastern Turkey or northern Syria and the surface flow over the Negev has shifted to the northwest.

On several occasions rain starts before the shift of the surface wind. In the majority of the cases of sulfate-rich rain, the surface flow before the rain was easterly to southerly. During the rain event, the wind began to blow from a southwest to westerly direction. On a few occasions, the rain was accompanied by a flow from an easterly to a southerly direction. This observation is based on careful inspection of surface maps, and not from surface wind measurements. (The reason for not using surface wind measurements is that the wind is affected, to a large extent, by the local topography.) On those occasions, the rain falls before or during the passage of the cold front associated with the surface depression, and *before* the passage of the upper trough (Fig. 3).

It is also worth mentioning that on most occasions, the rain followed a dust storm or heavy haze (Table 2). At this point, however, one cannot determine whether the source of the sulfate is in the local dust or in dust brought from further away.

Finally, out of 17 storms studied, only three had a general northwesterly flow pattern. The most prevailing flow was from the southwest to westerly direction.

4. Summary and discussion

According to the data presented above, a typical sulfate-rich rain occurrence in mid-winter, can be characterized as a surface low centered over the eastern Mediterranean, accompanied by an upper trough whose axis extends from north to south or from northwest to southeast. The trough axis is located to the west of the Levant coast. The surface winds blow prior to the event, from the easterly to the southerly quadrant and during the event, from a southwesterly to westerly direction. In both cases, the associated rain is usually small in quantity and therefore, through the process of scavenging the suspended particles from the atmosphere, the rain becomes more concentrated (as reflected by its dissolved anions).

The source of the sulfates carried by the wind blowing from the east and southwest directions could be either the large sabkhas (Desert saline marshes) along the Sinai shores in the west, where gypsum is currently precipitating, or similar sabkhas along the Persian Gulf in the east. The giant refineries in Kuwait and Saudi Arabia also produce large amounts of SO_2 that oxidizes into SO_4. It is hoped that in the future, the sulfur isotope (^{34}S) content of the sulfate in the rain water will enable a better distinction to be made regarding the sulfate's origin. Such research is now under way.

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