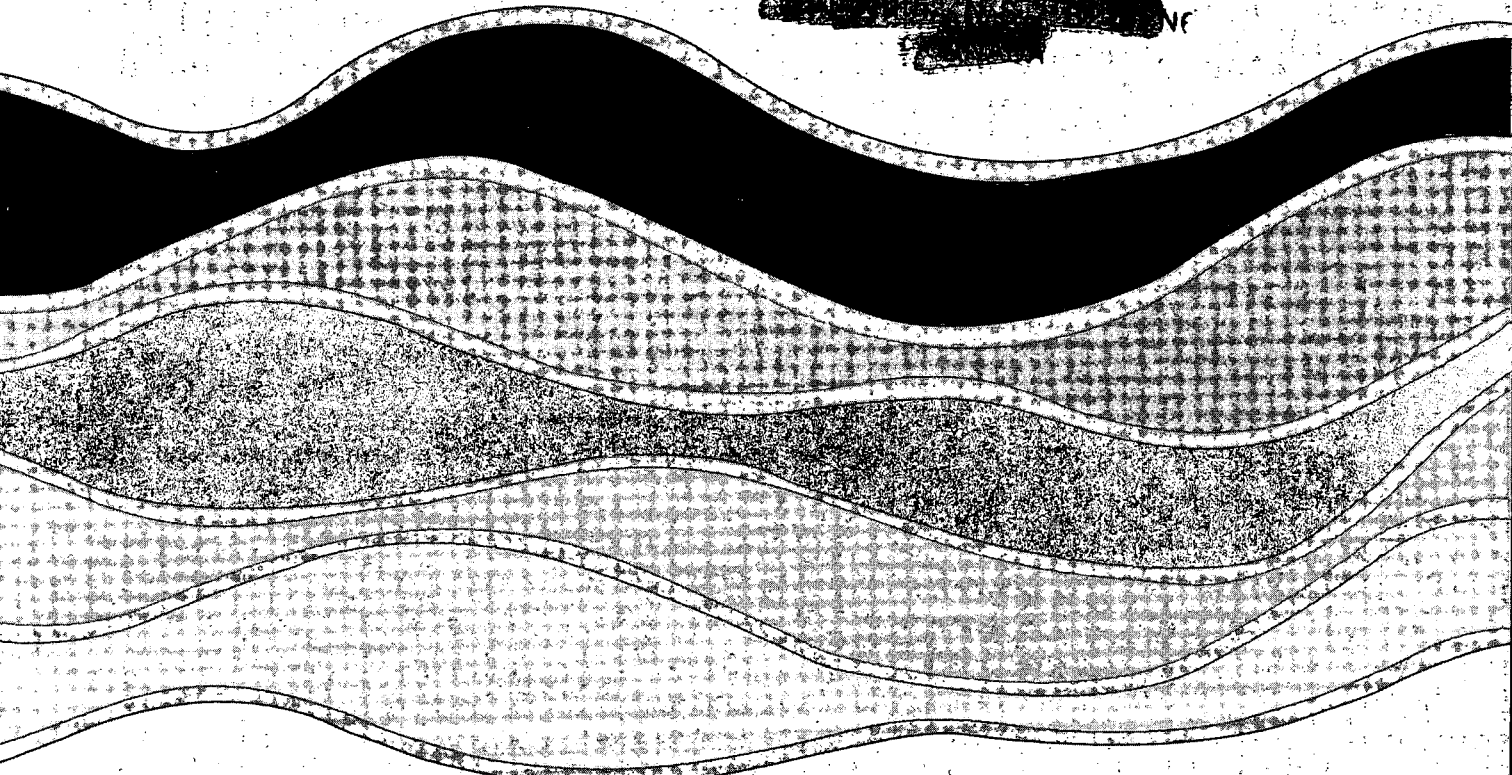
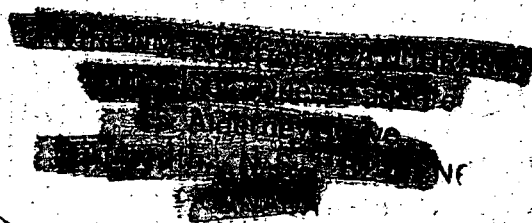
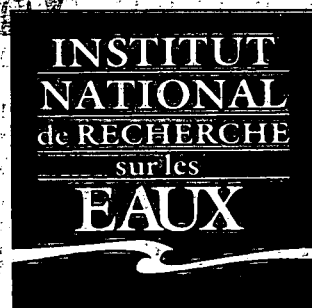
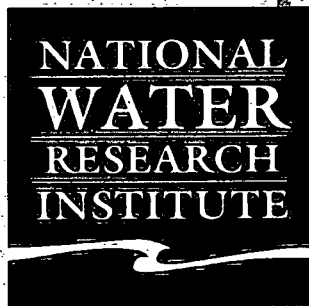


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**ORIGIN OF SULFUR IN  
CANADIAN ARCTIC HAZE FROM  
ISOTOPIC MEASUREMENTS**

J.O. Nriagu, R.D. Coker and L.A. Barrie

NWRI Contribution No. 90-49

Canada - Environnement Canada

Sulfur in Canadian Arctic haze from  
measurements

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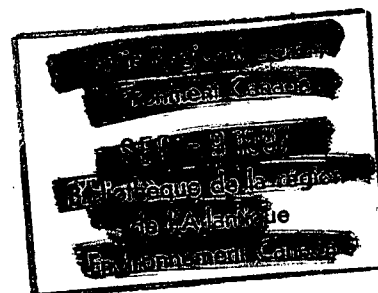
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**ORIGIN OF SULFUR IN  
CANADIAN ARCTIC HAZE FROM  
ISOTOPIC MEASUREMENTS**

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NWRI Contribution No. 90-49

## **MANAGEMENT PERSPECTIVE**

Since the mid 1950's, there has been a marked increase in the air pollution levels in the Arctic region. Today, this phenomenon is manifested by a pervasive haze which covers about 9% of the earth's surface and can be detected in large parts of the northern hemisphere peaking during the winter months of January to April. Such a haze is characterized by a reduction in visibility and a dominance of organic and inorganic compounds of the type found in polluted areas and at concentrations far greater than one would expect in a pristine environment. Sulfur is the principal constituent of this polluted air mass. Although elemental ratio techniques and trajectory analyses have been used in the study of the origin of the Arctic haze, they tell us little about the sources of the sulfur compounds or their hemispheric movement.

Sulfur emitted from any given natural or anthropogenic source carries an isotopic signature which can be used to fingerprint its origin and trace its flow through the environment. This unique and direct method has been used in this study to confirm that most of the sulfur in the Arctic haze comes from Europe. More importantly, this study documents the pervasive and global nature of the air pollution problem.

## **PERSPECTIVES DE LA DIRECTION**

Depuis le milieu des années 1950, le taux de pollution atmosphérique dans la région de l'Arctique a augmenté de façon marquée. Aujourd'hui, ce phénomène se manifeste par une brume sèche envahissante qui couvre environ 9 % de la surface terrestre et qui peut être décelée dans de vastes secteurs de l'hémisphère nord et dont les valeurs maximales sont enregistrées entre les mois de janvier et avril. Cette brume sèche est caractérisée par une réduction de la visibilité et une dominance de composés organiques et inorganiques du même genre que ceux qui sont présents dans les zones polluées, et à des concentrations beaucoup plus élevées que celles prévues dans un environnement intact. Le soufre est le principal élément de cette masse d'air polluée. Même si on a eu recours à des techniques d'établissement de rapport entre les éléments et d'analyses de trajectoires, ces méthodes nous renseignent peu sur les sources des composés sulfurés ou sur leur déplacement hémisphérique.

Le soufre émis par toute source naturelle ou anthropogénique a une signature isotopique qui peut être utilisée pour déterminer son origine et suivre son déplacement dans le milieu. Cette méthode exceptionnelle et directe a été utilisée dans la présente étude pour confirmer le fait que la plus grande partie du soufre contenu dans la brume sèche de l'Arctique provient d'Europe. Fait encore plus important, la présente étude étaye la nature envahissante et globale du problème de la pollution atmosphérique.

## RÉSUMÉ

Depuis le milieu des années 1950, le taux de pollution atmosphérique dans la région de l'Arctique a augmenté de façon marquée (1-3). Aujourd'hui, ce phénomène se manifeste par une brume sèche envahissante qui couvre environ 9 % de la surface terrestre et qui peut être décelée dans de vastes secteurs de l'hémisphère nord (3-6). Cette brume atteint une valeur maximale pendant les mois d'hiver, soit de janvier à avril, et elle est caractérisée par une réduction de la visibilité et une dominance de composés organiques et inorganiques du même genre que ceux qui sont présents dans les zones polluées, et à des concentrations beaucoup plus élevées que celles prévues dans un environnement intact (3, 6-7). La majeure partie de nos connaissances sur l'origine des constituant chimiques de la brume sèche proviennent de techniques d'établissement de rapport entre les éléments et d'analyses de trajectoires (2,4,6-7). Le soufre émis par toute source naturelle ou anthropogénique porte une signature isotopique qui peut être utilisée pour déterminer son origine et suivre son déplacement dans le milieu. Cette méthode exceptionnelle et directe a été utilisée dans la présente étude pour confirmer le fait que la plus grande partie du soufre présent dans la brume sèche de l'Arctique provient d'Europe, et documenter la nature envahissante et globale de la pollution atmosphérique actuelle.

## ORIGIN OF SULFUR IN CANADIAN ARCTIC HAZE FROM ISOTOPIC MEASUREMENTS

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### ABSTRACT.

Since the mid 1950's, there has been a marked increase in the air pollution levels in the Arctic region (1-3). Today, this phenomenon is manifested by a pervasive haze which can cover about 9% of the earth's surface and has been detected in large parts of the northern hemisphere (3-6). Such a haze peaks during the winter months of January to April and is characterized by a reduction in visibility and a dominance of organic and inorganic compounds of the type found in polluted areas and at concentrations far greater than one would expect in a pristine environment (3, 6-7). Most of what is known about the origin of the chemical constituents of the haze comes from elemental ratio techniques and trajectory analyses (2, 4, 6-7). Sulfur emitted from any given natural or anthropogenic source carries an isotopic signature which can be used to fingerprint its origin and trace its flow through the environment. This unique and direct method has been used in this study to show that most of the sulfur in the haze comes from Europe, and hence to document the pervasive and global nature of current air pollution.

The samples used in the study were obtained from the archived aerosol collection at the Atmospheric Environment Service, Downsview, Ontario. Alert (82.5°N, 62.3°W), in the Ellesmere Island, and Mould Bay (76.2°N, 119.3°W), on Prince Patrick Island, are among the stations in the Canadian Arctic Aerosol Sampling Network. Weekly aerosol samples were collected from each station by drawing approximately 16000 m<sup>3</sup> of air through 25x20 cm Whatman 41 filters. Field blank filters were collected every 4-weeks. These field blanks were subsequently analyzed with the exposed filters. To exclude the influence of local sources, the sampler at Mould Bay was located about 1.5 km upwind of the camp site while at Alert, it was placed on a 200 m plateau about 6 km from the camp. Detailed descriptions of the sampling stations and the air sampling strategy are given in Refs. 8-9

A section of each filter paper was cut out, leached with distilled water and the sulfate concentration in the leachate measured by means of an ion chromatograph. The reproducibility in the determination of the sulfate aerosol concentration in the air is believed to be  $\pm 13\%$  of the reported value (9). Another section of the filter paper was extracted ultrasonically in distilled water. The sulfate in the extract recovered as BaSO<sub>4</sub> and then converted to SO<sub>2</sub> by direct thermal decomposition (10-11). Because of the low ambient SO<sub>4</sub> concentrations in summer months, samples collected during several weeks were combined to obtain enough sulfur for the isotopic measurement. The isotopic ratio of the SO<sub>2</sub> was measured on a VG Micromass 602C mass spectrometer. The results are expressed in the usual  $\delta^{34}\text{S}$  notation:

$$\delta^{34}\text{S} (\text{permil}) = 1000 \times (R_{\text{sample}}/R_{\text{std}} - 1)$$

where  $R_{\text{sample}}$  and  $R_{\text{std}}$  are the  $^{34}\text{S}/^{32}\text{S}$  ratios of the sample and the standard Canyon Diablo troilite respectively. The reproducibility of the  $\delta^{34}\text{S}$  data is  $\pm 0.3$  permil based on replicate analyses of the filter papers.

The ground level concentrations of sulfate at Alert are highest in winter and lowest in summer, the difference between the winter and summer concentrations being over 10-fold (Figure 1). Similar seasonal variations have also been reported in many other regions of the Arctic with the winter concentrations sometimes approaching the levels found in rural and urban areas (6, 12-13). There are significant differences in the amplitude of the peaks which have been attributed to peculiar weather conditions during

each winter (3). Detailed discussions of the spatial and temporal variations in the chemical composition of Arctic aerosols can be found in a number of published reports which also show that sulfate is a major component (representing up to 30%) of the aerosols (Refs. 2-9).

The  $\delta^{34}\text{S}$  data for the weekly aerosol samples at Alert also show a pronounced seasonality with the sulfur being heavier in summer compared to winter (Figure 2). On the average,  $\delta^{34}\text{S}$  for the haze is remarkably constant from year to year, the values [with the standard errors and the number of samples, n] being  $+5.7 \pm 0.67$  (n=20) during the winter of 1983/84,  $+5.6 \pm 0.62$  (n=20) for 1984/85 and  $+5.9 \pm 0.54$  (n=19) during 1985/86. The isotopic composition of sulfur aerosols at Mould Bay also shows a very similar seasonal behavior (Figure 2) and the average  $\delta^{34}\text{S}$  at this station during the winter of 1983/84 is  $+5.9 \pm 0.45$  (n=9), which is almost identical to that at Alert. The uniformity in chemical characteristics of the haze throughout the Arctic region is already well documented (2, 14-16). The small inter-winter differences in the weekly pattern of the  $\delta^{34}\text{S}$  values (Figure 2) can be attributed to vagaries in the weather conditions and meridional transport processes during each year (17).

The key features of the isotopic composition of Arctic sulfur are quite different from those of airborne sulfur in the southern part of Canada. For example,  $\delta^{34}\text{S}$  values for the haze are higher than those of the atmospheric sulfur in urban and rural areas of eastern and central North America which generally fall between 0 and +5 permil (10, 18-21). More importantly, the nature of the seasonal variations is very different. In rural and remote areas of southern Canada, the  $\delta^{34}\text{S}$  values of atmospheric samples peak in winter and are lowest during the warm summer months (10, 18). By contrast, the heaviest sulfur is observed in the Arctic during the summer months (Figure 2). The differences in the key features of the isotopic signature suggest that the atmospheric sulfur in the Arctic has a different origin from that in the southern parts of Canada.

In southern Canada, most of the airborne sulfur during the winter period is derived from space heating and industrial sources and the  $\delta^{34}\text{S}$  generally reflects the regional source pattern. In summer, the large emission of lighter biogenic sulfur from soils, vegetation, marshes and wetlands results in the lowering of the  $\delta^{34}\text{S}$  values of the airborne sulfur (10, 18, 21-22). This is so because the  $\delta^{34}\text{S}$  of terrestrial ecosystems in southern Canada typically is less than +5 permil and the biogenic sulfur is depleted in  $^{32}\text{S}$  relative to the parent material (18). Apparently these dominant natural and



anthropogenic sources in southern Canada make only a minor contribution to the Arctic sulfur pool in view of the difference in the isotopic signature. Indeed, meteorological and tracer studies as well as transport models using emissions inventories suggest that only a small fraction (less than 10%) of the sulfur flux to the Arctic comes from North America (23-25).

The isotopic data can be related to differences in the sources of sulfur in the Arctic during the winter and summer months. Sulfur in Arctic air can be derived from anthropogenic sources, seasalt aerosols, the oxidation of biogenic sulfur compounds and, to a lesser extent, with entrained dust particles (26-29). Measurements of air pollutants as well as chemical/transport models generally suggest that up to 80% of the sulfur in the Arctic haze is derived from anthropogenic sources in Europe (3, 7, 26). Published data on the isotopic composition of the atmospheric sulfur from sources in the Soviet Union and Eastern Europe are extremely sparse and range from +1.0 to >21 permil (30); the available information does not include anything on the  $\delta^{34}\text{S}$  of the Arctic sulfur pool, however. It may be noted that the mean  $\delta^{34}\text{S}$  for rainfall sulfate in the Soviet Union of +5.9 permil (n=49, see Ref. 31) falls within the range of the isotopic composition of the haze.

In an effort to verify the European origin of the sulfur in the Canadian Arctic, we have determined the  $\delta^{34}\text{S}$  of aerosols collected at Ny Alesund (Norway) throughout the month of January, 1988. The average  $\delta^{34}\text{S}$  value of  $+6.4 \pm 0.82$  (n=13) permil for the Norwegian samples (see Table 1) is comparable to the data for Alert and Mould Bay and points to a common origin. These results are very similar to those obtained from stable lead isotope measurements made by Sturges and Barrie (Ref. 16) using aliquots of the same samples collected between November 1983 and May 1984. They found that the mean  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios of  $1.160 \pm 0.010$  at Alert and  $1.161 \pm 0.006$  at Mould Bay were very close to that of aerosol samples at Spitsbergen (Norwegian Arctic) during air flow from the USSR and also to the mean isotope ratio of  $1.158 \pm 0.014$  for Soviet non-ferrous ore deposits (16). We have also analyzed some of the daily aerosol samples collected during the spring of 1988 at Aspverten, located about 100 km south of Stockholm, Sweden. The samples were selected according to origin using air parcel back trajectory. The  $\delta^{34}\text{S}$  values for the sulfur from Western European, USSR and Eastern European sectors are fairly similar (Table 1). The  $\delta^{34}\text{S}$  values fall within the range observed in the Canadian Arctic although the average value for the Swedish samples of  $+5.0 \pm 1.0$  permil is slightly lower than those of the haze (Figure 2). The disparity may be attributed to the

additional inputs of heavier sulfur from marine sources (see below) to the polluted air masses as they travel to North America (27-29).

In contrast to the winter time when industrial emissions account for most of the airborne sulfur, the contributions from seasalt sprays and biogenic sources assume paramount importance during the summer months (6, 16-17, 27-29). Seasalt aerosols typically account for 10-30% of the atmospheric sulfur burden during the summer (Figure 1). The  $\delta^{34}\text{S}$  value for seasalt aerosols can be assumed to be identical to that of seawater, or about +20 permil (31). The average flux of dimethyl sulfide (DMS) from the oceans above the 60°N in summer ( $280 \text{ ug m}^{-2}\text{yr}^{-1}$ ) is about 10-fold higher than in winter ( $31 \text{ ug m}^{-2}\text{yr}^{-1}$ ) months (32). Measurements of methanesulfonic acid (MSA) in the Arctic air and a principal component analysis of the aerosol data suggest that a large fraction (> 50%) of the non-seasalt sulfur may be produced from the oxidation of the DMS derived biogenically from the Arctic Ocean, marine sources in the lower latitudes and possibly from terrestrial ecosystems near the Arctic circle (7; 29). The isotopic composition of marine DMS is unknown but is believed to be <10 permil lighter than the seawater sulfur (21). If seasalt spray and marine biogenic sources were responsible for all of the airborne sulfur during the Arctic summer, the expected  $\delta^{34}\text{S}$  value would fall in the range of +10 to +20 permil; rainfalls in the open ocean generally fall in this range as well (31). Our data in Figure 2 however show summer time  $\delta^{34}\text{S}$  values of +7 to +10 permil, implying additional inputs of lighter sulfur believed to be of anthropogenic origin. Local soils represent a very minor source of aerosols at the sampling stations (3, 8).

The isotopic data are thus consistent with previous studies which show that the sulfur in Arctic haze comes primarily from anthropogenic sources in Eurasia. In summer, however, a large fraction of the atmospheric sulfur burden can be derived as seasalt sprays and from oxidation of DMS released from marine and continental ecosystems. Quantification of the relative contributions of sulfur from the various sources however is impossible on the basis of the current isotopic measurements.

#### *Acknowledgements.*

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Table 1: Isotopic composition of sulfur aerosols at Ny Ålesund (Norway) and Aspverten (about 100 km south of Stockholm, Sweden)

Sampling date (1988) -----	Air source* -----	$\delta^{34}\text{S}$ ----
Ny Alesund, Norway		
Jan. 1-4	Unknown	+6.9
Jan. 4-6	"	+7.4
Jan. 6-8	"	+6.6
Jan. 8-11	"	+5.1
Jan. 11-13	"	+5.5
Jan. 13-15	"	+6.4
Jan. 15-18	"	+6.6
Jan. 18-21	"	+7.7
Jan. 21-22	"	+7.1
Jan. 22-25	"	+6.5
Jan. 25-27	"	+6.4
Jan. 27-29	"	+5.4
Jan. 29-Feb. 1	"	+5.4
Aspverten, Sweden		
Feb. 10	W. Europe	+7.6
Feb. 11	W. Europe	+6.3
Feb. 14	W. Europe	+5.4
May 3	W. Europe	+4.6
May 4	W. Europe	+4.4
Feb. 23	USSR	+5.0
Feb. 24	USSR	+4.2
Feb. 25	USSR	+4.4
Feb. 26	USSR	+4.7
Mar. 22	USSR	+3.8
March 23	USSR	+4.4
Feb. 15	E. Europe	+4.4
Feb. 16	E. Europe	+6.1
April 16	E. Europe	+5.1
May 2	E. Europe	+4.4

\* -----  
Determined using air parcel trajectories

## FIGURE CAPTIONS.

Figure 1. Average weekly, ground level concentrations of  $\text{SO}_4$  at Alert (upper figure). The percentage of seasalt sulfate (lower figure) in the aerosol was calculated using 0.25 as the  $\text{SO}_4\text{:Na}$  ratio in seawater.

Figure 2. Isotopic composition of sulfur in aerosols at Alert (circles) and Mould Bay (squares). The monthly average  $\text{S}^{34}\text{S}$ , with ranges, are shown as an insert

# ALERT GROUND LEVEL OBSERVATIONS

## WEEKLY AEROSOL SULPHATE CONCENTRATIONS

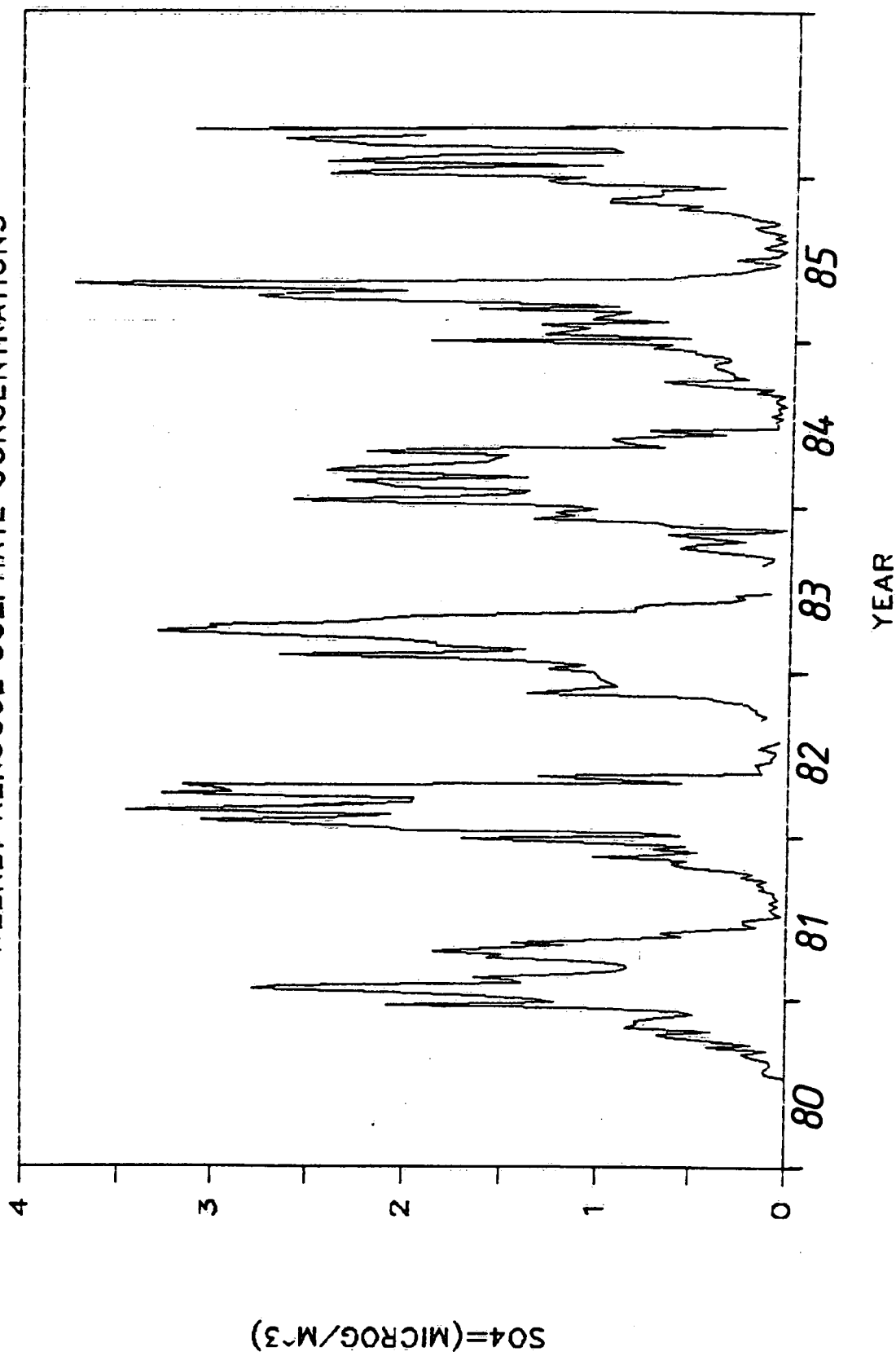


FIGURE 1 a



# ALERT GROUND LEVEL OBSERVATIONS

## FRACTION SEA SALT SULPHATE

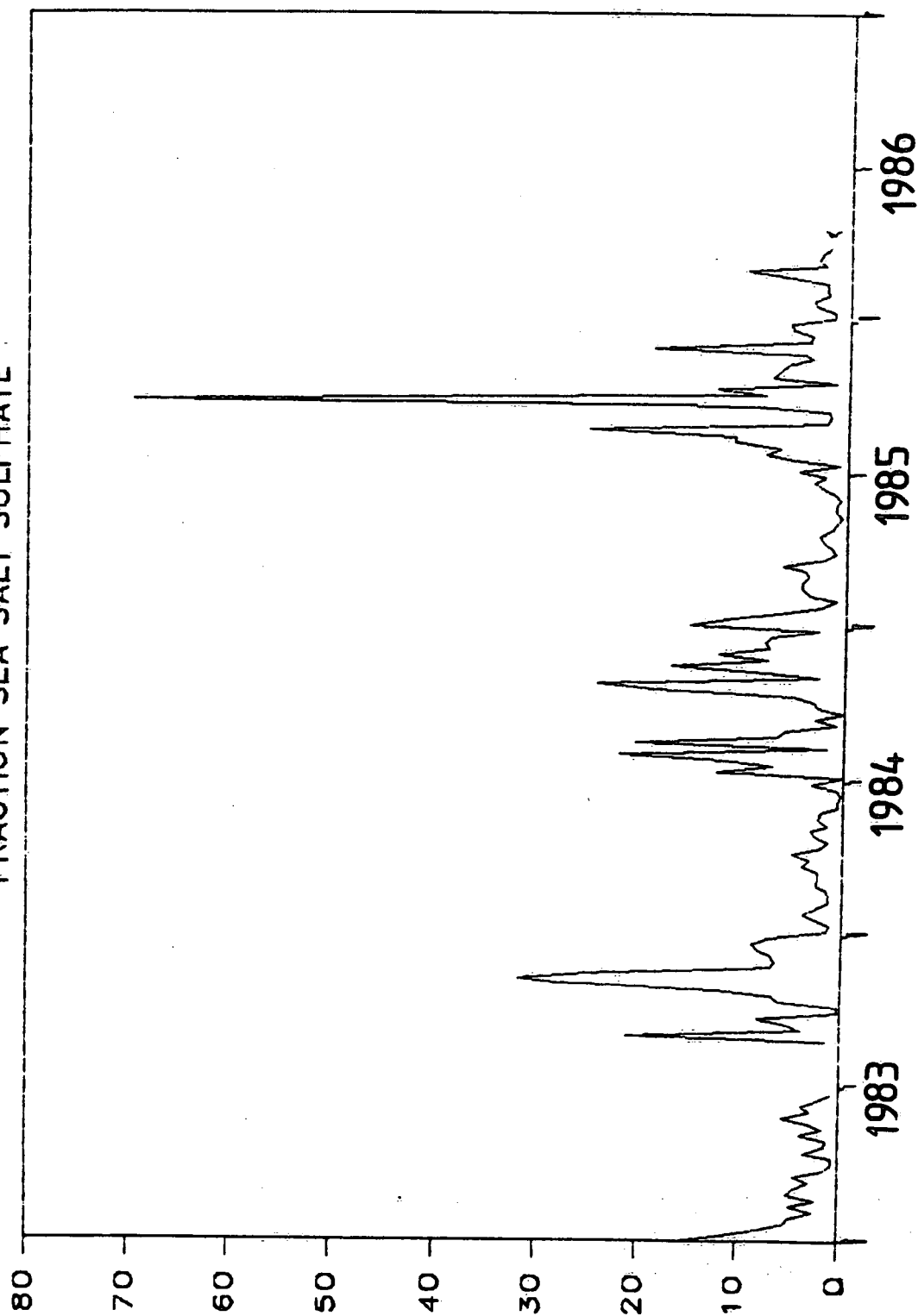


FIGURE 1b

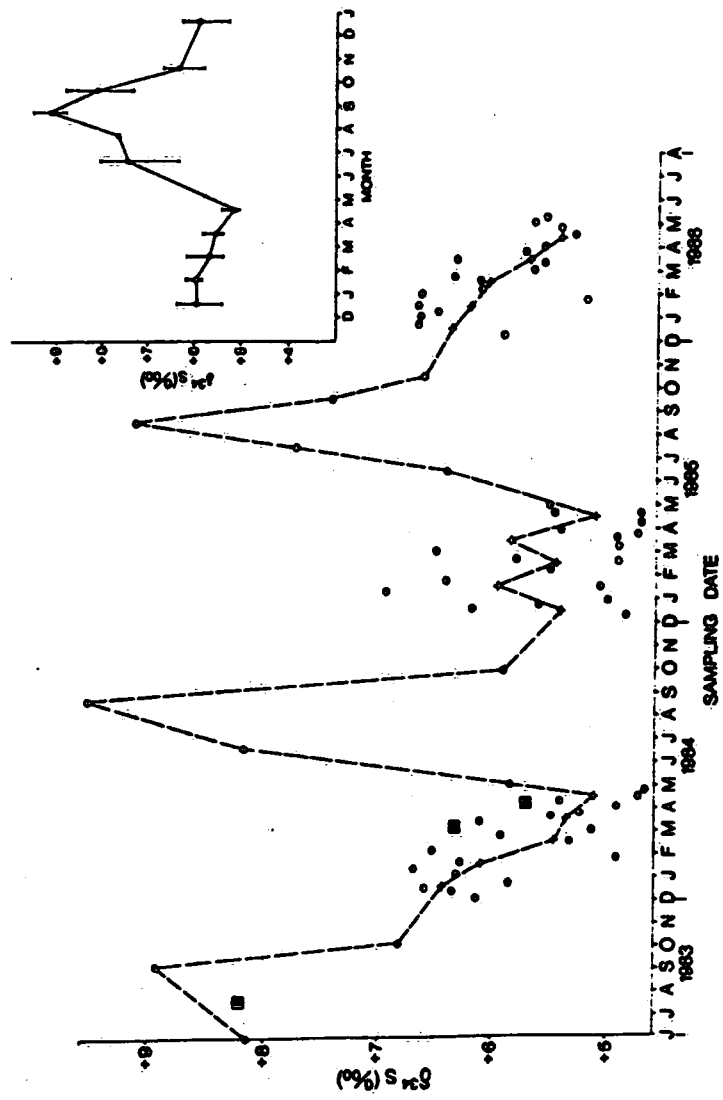


FIGURE 2

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A large decorative graphic consisting of several horizontal, wavy bands. The top band is solid black. Below it are several bands with a stippled or textured pattern, separated by thin white lines.

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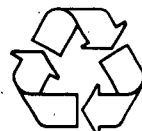


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