*Tellus* (1979), *31*, 295–307

# Chemical composition of the ambient aerosol in the Sudan Gezira

By S. A. PENKETT and D. H. F. ATKINS, *Environmental and Medical Sciences Division, A.E.R.E., Harwell, Oxfordshire OX11 0RA, England*

and M. H. UNSWORTH, *University of Nottingham, School of Agriculture, Sutton Bonington, Loughborough LE12 5RD, England*

(Manuscript received November 24, 1978; in final form February 1, 1979)

ABSTRACT

Measurements of the composition of aerosol in the Sudan Gezira were made in southerly and northerly airstreams during September and October 1973. By using iron as a normalizing element and calculating enrichment factors it is shown that natural dust is the source of most elements. Exceptions are chlorine, bromine, sulphur and nitrogen which appear to have gaseous sources. Substantial concentrations of oxidized nitrogen and sulphur compounds were measured and are probably produced photochemically. Concentrations of sulphur and nitrogen compounds were lower than in Europe but suggest that anthropogenic sources are having equal impact on their respective natural cycles. Finally, comparisons of aerosol in the Sudan and at Harwell show that the natural Sudanese aerosol is potentially basic whereas anthropogenic European aerosol is acid.

## 1. Introduction

The Gezira region in the Sudan, between the Blue and White Niles is part of a much larger area of North and Central Africa which is known to have large concentrations of dust in the atmosphere (Joseph et al., 1973). In September or October each year there is a distinctive shift in the direction of prevailing winds in the Gezira as the intertropical convergence zone (ITCZ) retreats southward, replacing humid southerly with dry north to north-easterly trade winds (Lebon, 1965). This transition gives opportunities to study aerosols in two very different air masses, since the northerly trajectory passes over the deserts of Asia Minor and the Sahara, whereas the southerly air mass flows from sources in the South Atlantic over predominantly grass land and forests. The air masses which arrive over the Sudan are thus probably typical of those present over large sections of the African continent.

In September and October 1973 we operated aerosol sampling apparatus in the Gezira. This paper discusses results from the samplers in the two air masses and compares the elemental distributions of the aerosols with those of aerosols in regions where air pollution is a significant source. The data, particularly for sulphur, nitrogen and chlorine are discussed with reference to a number of current problems in air chemistry.

## 2. Sampling and site

Two types of sampler were used in the exercise, Research Appliance Company samplers (AISI Model F1) and a high volume sampler constructed to Harwell specification by Rotheroe and Mitchell (Eggleton and Atkins, 1972). Both samplers were able to operate without attention for periods of one month. The Research Appliance Co. sampler (RAC) operated at a flow rate of 10 l $min^{-1}$ on a 4-hour sampling cycle, air being drawn through a 2.5 cm diameter area of Whatman No. 1 filter paper. The Rotheroe and Mitchell sampler (RM) used flow rates of 300 l $min^{-1}$ and hourly sampling periods with collection of the aerosol on Whatman 41 filter paper of diameter 6.2 cm.



0040-2826/79/040295-13$02.50/0 

Preliminary measurements with both types of samplers were made at Khartoum. The main sampling site was about 15 km west of Wad Medani, a small town on the Blue Nile about 150 km southwest of Khartoum. At this remote site there was insufficient power to operate the RM sampler reliably and so all results presented here were obtained with two RAC samplers operating in parallel. A comparison of the RM sampler with Whatman 41 paper of proven high efficiency (Lindeken et al., 1962) with the RAC samplers using Whatman No. 1 paper showed that the latter paper gave a consistently poorer collection efficiency for some ions. Further tests at A.E.R.E. confirmed the same pattern and results have been corrected for the lower collection efficiency of the RAC instrument.

Local wind direction data and also the position of the ITCZ in relation to the sampling site were kindly provided by staff of the Sudanese Meteorological Service at Wad Medani. Samples chosen for analysis by wind direction were selected when the position of the ITCZ was clearly well removed either north or south of the sampling site.

## 3. Analysis

The soluble ions $NH_4^+$, $SO_4^=$ and $NO_3^-$ were determined colorimetrically in aqueous extracts prepared from the samples. Ammonium ion was determined as indophenol blue, $SO_4^=$ with thoronol and $NO_3^-$ by a modification of the Saltzmann method (Eggleton and Atkins, 1972). All analyses were carried out on a Technicon Autoanalyser and the analytical methods were modified for use with the instrument (Eggleton and Atkins, 1972).

Species other than the soluble ions mentioned above were measured by neutron activation analysis (Atkins et al., 1972a). For the determination of elements giving rise to induced activities of short half-life (Al, V, Cl, Mn, Na, Cu, Ca, I and Br) the samples as collected on filter paper were irradiated together with filter paper blanks and a flux monitor ($Na_2CO_3$) in fluxes of $10^{14}$ neutrons $cm^{-2}$ $s^{-1}$ for periods of up to 20 s. For elements yielding induced activities of longer half-life (In, Cd, Au, As, La, W, Ce, Th, Hg, Cr, Sb, Sc and Fe) samples were sealed into silica ampoules together with blanks and flux monitor (Fe) and irradiated for between one and seven days. Computer resolution using at least squares technique was used in the examination of the complex $\gamma$ spectra emitted by the irradiated samples.

## 4. Results and interpretation

### 4.1. *Distribution of elements found in the Sudan aerosol*

The majority of elements were determined by the activation procedure and as this is rather lengthy, the number of filters that could be analysed was limited to six when the wind direction was northerly and six when the wind direction was southerly. To further reduce the effort the filters were analysed in pairs with consecutive numbers being subjected to the same irradiation. Filter numbers 34–35, 36–37 and 38–39 were taken on October 12, 1973, when the wind was northerly; filter numbers 47–48 (October 14) and filter numbers 58–59 and 60–61 (October 15) were taken when the wind was southerly. The results of the activation analyses are shown in Table 1 for 29 different elements. In eleven cases "less than" data are given but levels are quoted for 18 elements in the north wind aerosol and 17 elements in the south wind aerosol by this method of analysis. The table also contains values of the ions $NH_4^+$, $NO_3^-$ and $SO_4^=$ which were obtained from the same filters by the colorimetric procedure.

The three concentrations for each element are remarkably consistent for both the north and south winds and this suggests that the distributions shown are typical of the aerosol material being carried by the two wind systems. The elemental concentrations are larger in the north wind than the south and this reflects the well known dustiness of winds from the Sahara. A comparison of the concentrations of iron measured in aerosols in different locations round the world is shown in Table 2 and it can be seen that the level recorded in the north wind aerosol in the Sudan is as high as iron levels recorded in urban centres in the USA and Europe. Both Sudan values are considerably higher than values observed in more remote parts of Europe.

The source of elements such as iron in the aerosol observed in the Sudan is almost certainly wind raised soil and this becomes more apparent when enrichment factors rather than concentrations are considered. The enrichment factor

Table 1. *Elemental concentrations of aerosols collected in the Sudan (ng $m^{-3}$)*

| | North wind | | | South wind | | |
|---|---|---|---|---|---|---|
| | Filter reference number | | | | | |
| Element | 34–35 | 36–37 | 38–39 | 47–48 | 58–59 | 60–61 |
| Al | 2970 | 3130 | 3000 | 300 | 210 | 370 |
| V | 7.5 | 9.7 | 12.4 | 2.9 | 1.7 | 3.1 |
| Cl | 1120 | 900 | 890 | 280 | 260 | 240 |
| Mn | 34.8 | 33 | 38 | 2.6 | 2.3 | 6.0 |
| Na | 520 | 430 | 490 | 250 | 160 | 180 |
| Cu | 45 | 94 | <9 | <8 | <8 | <9 |
| Ca | <1000 | <1000 | <1000 | <1000 | <1000 | <1000 |
| I | <8 | <8 | <8 | <8 | <8 | <9 |
| In | <0.01 | <0.01 | <0.01 | 0.4 | 0.8 | 1.0 |
| Cd | <40 | <40 | <40 | <40 | <40 | <40 |
| Au | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| Br | 12.2 | 17.1 | 14.5 | 9.6 | 5.2 | 8.6 |
| As | <1 | <1 | <1 | <1 | <1 | <1 |
| La | 2.6 | 2.6 | 1.5 | <1 | <1 | <1 |
| W | <1 | <1 | <1 | <1 | <1 | <1 |
| Se | <0.3 | <0.3 | <0.3 | <0.3 | <0.3 | <0.3 |
| Ce | 2.5 | 2.5 | 2.7 | 0.85 | 0.79 | 1.38 |
| Th | 0.43 | 0.33 | 0.35 | 0.17 | 0.096 | 0.17 |
| Hg | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 | 0.59 |
| Cr | 4.4 | 5.3 | 6.8 | 6.1 | 3.2 | 6.22 |
| Sb | 0.52 | 0.48 | 0.68 | 0.21 | 0.33 | 0.16 |
| Sc | 0.65 | 0.60 | 0.62 | 0.18 | 0.14 | 0.21 |
| Fe | 3090 | 2890 | 3010 | 800 | 770 | 1250 |
| Zn | 45 | 18 | 30 | 22 | 17 | 5.8 |
| Co | 1.1 | 0.88 | 1.2 | 0.26 | 0.22 | 0.22 |
| Cs | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| Rb | <5 | <5 | <5 | <5 | <5 | <5 |
| Ag | 1.2 | 0.93 | 1.1 | 1.1 | 0.52 | 0.24 |
| Eu | 0.090 | 0.074 | 0.031 | 0.031 | 0.025 | 0.036 |
| $NH_4^+$ | 455 | 670 | 720 | 270 | 315 | 605 |
| $NO_3^-$ | 1885 | 2495 | 3035 | ? | 2745 | 2495 |
| $SO_4^=$ | 1575 | 2660 | 2725 | 2380 | 3690 | 3400 |

$E_{Fe}$ is defined by

$$F_{Fe} = \frac{\left\{\begin{array}{r}\text{elemental concentration in aerosol/}\\ \text{elemental concentration in soil}\end{array}\right\}}{\left\{\begin{array}{r}\text{iron concentration in aerosol/}\\ \text{iron concentration in soil}\end{array}\right\}}$$

Iron was chosen as the reference element although scandium is almost equally good (Peirson et al., 1974). An aerosol that has a larger number of $E_{Fe}$ values close to unity will almost certainly be derived from soil and Table 3 shows that this is very much the case for the two Sudan aerosols (N and S wind). For the north wind aerosol the elements, Al, V, Mn, Na, Cu, La, Ce, Th, Cr, Sb, Zn, Co, Ag and Eu all give values of $E_{Fe}$ between 0.5 and 2.0 with many very close to unity. The south wind aerosol is not quite as uniform but most elements are still obviously soil derived. For comparison some enrichment factors are shown for elements at sites, such as urban areas, where soil is not the source (Table 4) and it can be seen that elements such as Sb, Se and Zn show very large enrichments in Liége and Chicago. To make the comparisons in Table 4 we have used Mason's estimates (1952) of the average crustal element distribution, and

Table 2. *Comparison of iron concentrations in aerosols collected at various locations*

| Site | Location | Fe mass ng/m³ | Reference |
|---|---|---|---|
| Harwell | Central England | 310 | Peirson et al., 1974 |
| Lerwick | Shetland Isles | 67 | Peirson et al., 1974 |
| Jungfrau | European Alps | 77.5 | Rahn, 1976 |
| N. Norway | N. Norway | 51.0 | Rahn, 1976 |
| Liége | Belgium | 2670 | Rahn, 1976 |
| Chicago | Central, U.S.A. | 2427 | Brar et al., 1975 |
| Osaka | Japan | 7710 | Mamuro et al., 1975 |
| Urban, U.S.A. | Urban, U.S.A. | 1580 | US Dept. of Health, Education and Welfare, 1966 |
| Columbia Mo. | Central U.S.A. | 1100 | Gray et al., |
| S. Pole | S. Pole | 0.84 | Zoller et al., 1974 |
| Twin Gorges | Northern Canada | 71 | Rahn, 1976 |
| Sudan (N wind) | Central Africa | 2996 | This work |
| Sudan (S wind) | Central Africa | 940 | This work |

Table 3. *Enrichment factors, $E_{Fe}$, for the Sudan aerosols, based on a comparison with the average analysis of six local soils*

| | Average concentrations | | | Enrichment factors | |
|---|---|---|---|---|---|
| Element | North wind ng/m³ | South wind ng/m³ | Average soil analysis p.p.m. | North wind $E_{Fe}$ | South wind $E_{Fe}$ |
| Al | 3033 | 293 | 74,500 | 0.88 | 0.28 |
| V | 9.087 | 2.57 | 232 | 0.95 | 0.79 |
| Cl | 970 | 260 | <600 | >36 | >31 |
| Mn | 35.3 | 3.7 | 915 | 0.86 | 0.28 |
| Na | 480 | 197 | 6605 | 1.6 | 2.1 |
| Cu | 49 | <9 | 1724 | 0.61 | <0.37 |
| Ca | <1000 | <1000 | <20,000 | | |
| Br | 13.6 | 7.8 | <2 | >150 | >277 |
| As | <1 | <1 | 5.6 | <4 | <10 |
| La | 2.23 | <1 | 42.8 | 1.16 | <1.6 |
| Se | <0.3 | <0.3 | <8 | | |
| Ce | 2.6 | 1 | 56.4 | 1.04 | 1.26 |
| Th | 0.37 | 0.14 | 8.9 | 0.95 | 1.2 |
| Hg | <0.2 | <0.2 | <11 | | |
| Cr | 5.5 | 5.17 | 85.3 | 1.5 | 4.3 |
| Sb | 0.56 | 0.23 | <7 | >1.9 | >2.4 |
| Sc | 0.63 | 0.18 | 16.6 | 0.85 | 0.77 |
| Fe | 2996 | 940 | 66,820 | 1 | 1 |
| Zn | 31 | 14.9 | 557 | 1.25 | 1.9 |
| Co | 1.06 | 0.24 | 26 | 0.91 | 0.65 |
| Cs | <0.05 | <0.05 | <4 | | |
| Rb | <5 | <5 | <30 | | |
| Ag | 1.07 | 0.62 | 22.6 | 1.05 | 1.9 |
| Eu | 0.087 | 0.031 | 2.6 | 0.75 | 0.85 |
| S | 767 | 1052 | 59.2 | 289 | 1263 |
| $N(NO_3)$ | 557 | 572 | 79.2 | 157 | 531 |

Table 4. *Enrichment factor comparisons based on Mason's average crustal composition*

| Element | Sudan (N. wind) | Sudan (S. wind) | Harwell | Liége | Chicago |
|---|---|---|---|---|---|
| Br | 91 | 166 | 2572 | 793 | 104 |
| Cl | 123 | 106 | 2567 | 283 | 329 |
| Co | 0.71 | 0.5 | 2.2 | 2.0 | 1.7 |
| Cr | 0.92 | 2.7 | 7.1 | 5.2 | 3.5 |
| Mn | 0.62 | 0.21 | 3.2 | 1.7 | 9.0 |
| Na | 0.28 | 0.37 | 4.3 | 0.44 | 0.23 |
| Sb | 12.5 | 16.4 | 459 | 229 | 343 |
| Se | <19 | <59 | 343 | 279 | 587 |
| V | 1.2 | 1.0 | 17.0 | 3.0 | 3.4 |
| Zn | 7.9 | 12 | 379 | 784 | 182 |

consequently although values of $E_{Fe}$ for the Sudan aerosols are much lower than for urban aerosols they are not unity. Interestingly this table shows that the enrichment factors observed at Harwell are much closer to urban values than to the Sudan values and this is a point which will be taken up later when the elemental distribution at these two sites is compared.

### 4.2. *Elements with high enrichment factors in the Sudan aerosols*

A small number of the elements shown in Table 3 show large enrichments which cannot be ascribed to experimental uncertainty. These are sulphur, nitrogen, chlorine and bromine, all of which are non-metallic elements with a substantial number of known gaseous compounds. In view of this it is important to find the chemical form and the source of these elements at a site such as the Sudan Gezira where the anthropogenic influence is minimal.

4.2.1. *Chlorine and bromine.* The enrichment factor for chlorine in both aerosols is greater than 30 (Table 3) and that for bromine is greater than 150 or 277 depending on whether the wind is northerly or southerly. Using the converse of the argument to determine the source of the bulk of the elements shown in Table 3, it appears that these two elements are not soil derived. It is possible that they could be picked up as salts either from salt flats or possibly in an area where surface evaporation of rainwater has left a salt rich layer, but there are other reasons to account for the data that seem to us more plausible. It can be said with some certainty that the chlorine is not present as sodium chloride from the sea, since this would show up as a large enrichment factor for sodium, whereas the sodium is present only in slightly enriched quantities above that which is normally expected to be present in the soil found locally. Junge (1963) also suspected that most of the sodium found in rain over the continental U.S.A. was of continental rather than maritime origin. The explanation of the high enrichment factors for both chlorine and bromine is more likely to be collection of gaseous halogen compounds by the air filter material.

There is substantial evidence for the presence of gaseous halogen compounds in the atmosphere, for instance Duce et al. (1973) found a level of gaseous bromine between 7 and 8 ng/m$^3$ in Antarctica and 6 ng/m$^3$ in Hawaii. Duce also detected about 2 ng/m$^3$ of a gaseous iodine compound in Antarctica using the same technique of absorption on activated charcoal, and one of us (D.H.F.A.) has detected concentrations of about 1000 ng/m$^3$ of a gaseous chlorine compound at Harwell using base-impregnated filter papers. Rahn et al. (1976) collected air samples at a number of remote sites on the north American continent using a combination of impregnated filter papers and charcoal filters and in this way separated what they believed to be inorganic and organic constituents. The concentrations were similar to those quoted above and the organic species predominated; approximately 85% of the chlorine and bromine was organic as was 70% of the iodine. These compounds will undoubtedly be halocarbons such as Freons, carbon tetrachloride, methyl chloride, methyl bromide and methyl iodide, all of which have been detected in the atmosphere by specific gas chromatographic techniques (Lovelock, 1973, 1975; Grimsrud and Rasmussen, 1975). The nature of the "inorganic" species, which is collected by the impregnated filter, is in more doubt, but the most likely possi-

bilities are halogen hydrides which would react readily with the filter and thus be retained, or possibly halogen compounds which are absorbed on the surface of the rest of the aerosol. It is known from infra-red analyses that hydrogen chloride is present in the stratosphere and the troposphere (Farmer et al., 1976) where it can be formed by reaction of hydroxyl radicals with methyl chloride (Cox et al., 1976a), or possibly by acidic displacement reactions such as reaction of sulphuric and nitric acids with sea salt (Erikson, 1959). Alternatively absorption of organic halogen compounds onto the surface of the bulk of the aerosol has been suggested by Lovelock (pers. comm.) as a possible removal mechanism for halocarbons. This would be a very important process if it occurred since it represents a tropospheric sink which takes halocarbons out of the atmosphere before they can enter the stratosphere and take part in ozone removal. The data which we have cannot, of course, give an unequivocal answer as to the nature of the halogens observed on the filters but it is not inconsistent when considered in terms of Lovelock's hypothesis. In particular the chlorine, and to a lesser extent, the bromine concentrations shown in Table 1 are proportional to the iron concentrations and hence to the total mass of aerosol collected on the filters. Further work would be needed, however, to show that this phenomenon is more widespread before any firm conclusions can be drawn.

4.2.2. *Sulphur and nitrogen.* The enrichment factors for sulphur and nitrogen in Table 3 are the largest values obtained. This makes us suspect "a priori" that the elements are not simply wind derived. Further analysis of the aerosol samples for these two elements allowed a more thorough investigation of their source.

The analytical procedures measured sulphur as sulphate and nitrogen as nitrate and ammonium ions, so it is assumed that the elements were present in these chemical forms in the atmosphere, i.e. these are present as aerosols when collected. Figs. 1, 2 and 3 show the frequency distributions of air concentrations of the ammonium, sulphate and nitrate ions respectively for the 4 h filter samples over the period 6th to 21st October 1973. For ammonium ion the concentration varies from 0.1 to 2.5 $\mu g/m^3$, for sulphate from 0.6 to 8.7 $\mu g/m^3$ and for nitrate from 0.1 up to 4.8 $\mu g/m^3$. From considerations of background levels of these ions on the filter paper used in sampling and the precision and limit of detection of the analytical methods, we know that the ammonium concentrations are the most precisely determined and the nitrate the least.

The frequency distributions which result may be log-normal, but there are insufficient data to plot a probability diagram. The mean concentrations are respectively 0.67 $\mu g/m^3$ for $NH_4^+$, 3.06 $\mu g/m^3$ for $SO_4^=$ and 1.81 $\mu g/m^3$ for $NO_3^-$ and if the data is

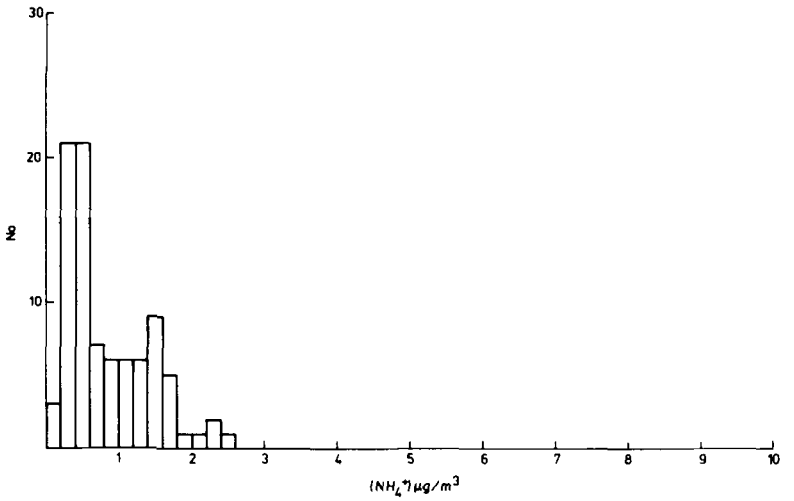


*Fig. 1.* Distribution of ammonium ion concentrations observed at Wad Medani over the period 6th to 21st October 1973.

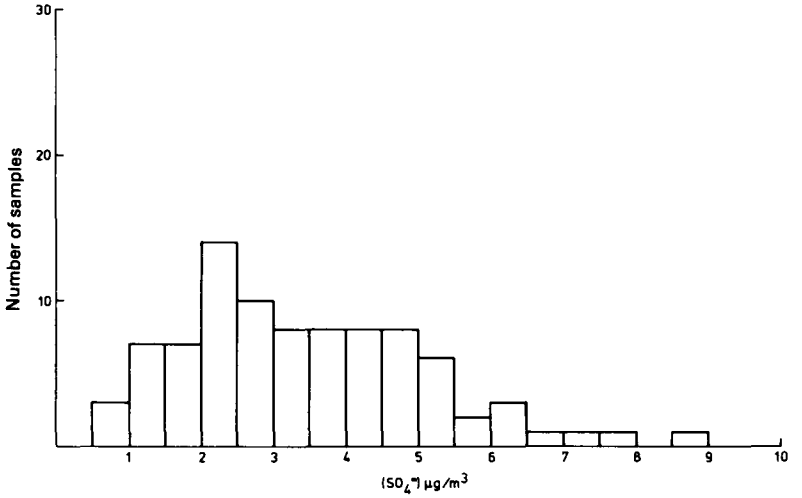


*Fig. 2.* Distribution of sulphate ion concentrations observed at Wad Medani over the period 6th to 21st October 1973.

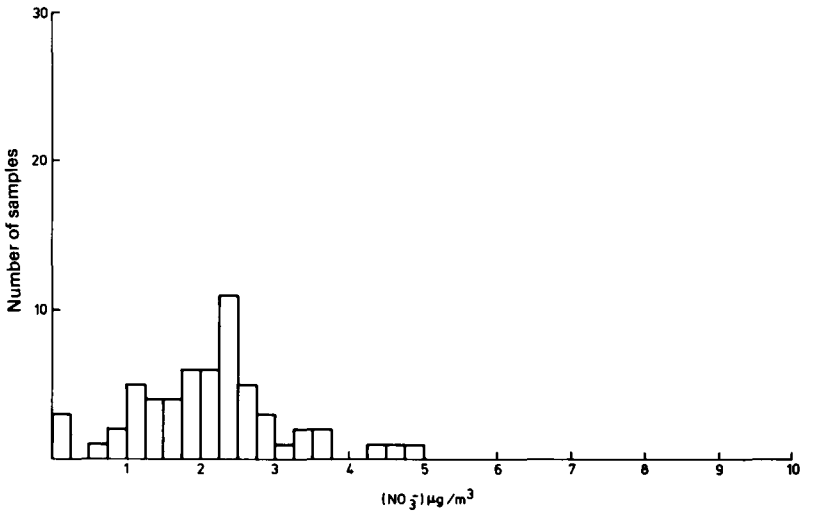


*Fig. 3.* Distribution of nitrate ion concentrations observed at Wad Medani over the period 6th to 21st October 1973.

expressed in terms of equivalents this leads to an anion excess of $NO_3^-$ and $SO_4^=$ over $NH_4^+$ of 0.056 micro-equivalent/$m^3$. The balancing cation may be one of those shown in Table 1 or it may be protons.

When the sulphate data are plotted out by wind direction throughout the sampling period it appears that the southerly wind shows a single distribution; the northerly wind may have more than one component (Fig. 4) but there is insufficient data for the phenomenon to be established by proper statical methods. The wide spread of concentrations in the north wind may indicate that there is more than one source of the sulphate carried by the north wind. Fig. 4 demonstrates that for much of the time equal amounts of sulphate are carried by both wind systems, and the sulphate observed at the site is not solely a feature of the dustier north wind.

Some of the features noted above are shown in more detail by considering the sequential variation of concentration of the individual ions with time. Fig. 5 shows how the concentrations varied with

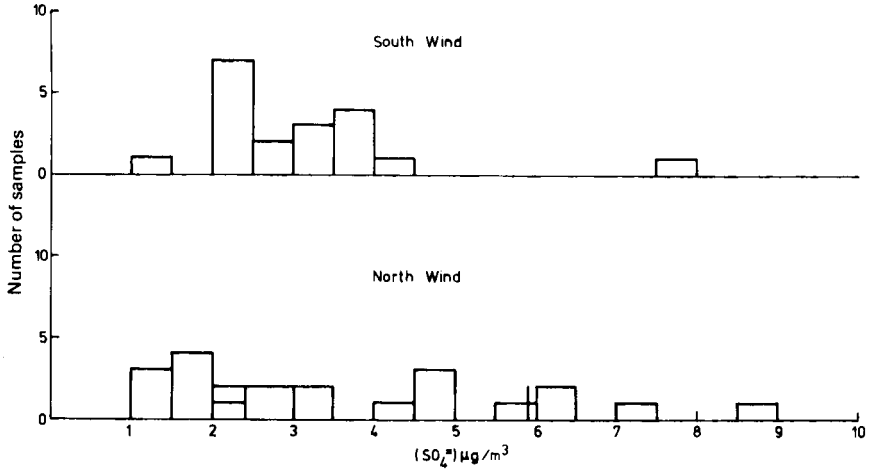


*Fig. 4.* Distribution of sulphate ion concentration produced from a separation by wind direction over the period 6th to 21st October 1973.

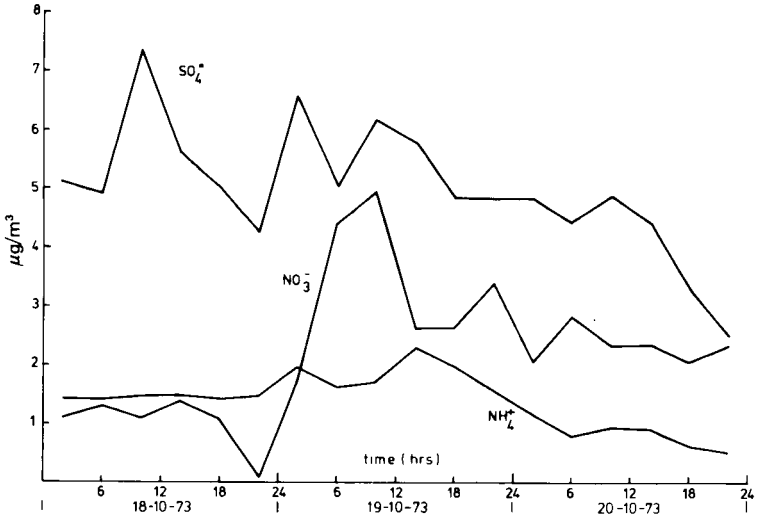


*Fig. 5.* Sequential variation of ammonium, sulphate and nitrate ion concentrations over a 3-day period.

time over a 3-day period. At the beginning of the period the sulphate ion shows a maximum which is not matched either by the nitrate or the ammonium ions. This occurred when the wind suddenly moved round from a southerly to a northerly direction. This sulphate excursion was superimposed on top of periods when the ammonium and sulphate ions followed similar trends. The correlation coefficient obtained from a linear regression analysis of $NH_4^+$ and $SO_4^=$ is 0.83 for the period 20.00 hours on the 18 October to 20.00 hours on the 20 October. The corresponding coefficient for $NH_4^+$ and $NO_3^-$ is only 0.17 indicating that the ammonium ion is largely present as ammonium sulphate rather than ammonium nitrate. The average ratio of ammonium ion to sulphate ion in Fig. 5 is 0.28 which is only slightly smaller than the ratio in ammonium sulphate (0.375).

There are several possible origins for the sulphur and nitrogen compounds found in the Sudan aerosol. The ammonium and sulphate when collected were probably particulate, the nitrate may have been nitric acid vapour (see later). It is possible, therefore, that $NH_4^+$ and $SO_4^=$ may be picked up by

the wind in a similar manner to the rest of the elements such as iron, etc. It is also possible, and in our opinion more likely, that these compounds are initially emitted in gaseous form and are then converted by chemical processes occurring in the atmosphere into particulates. This commonly occurs in polluted atmospheres where sulphur dioxide is oxidized to sulphuric acid which is then neutralized by ammonia gas (Cox and Penkett, 1970, 1971; Atkins et al., 1972b). The evidence which we have is not in favour of a particulate source since the nitrogen and sulphur levels in both the north and south wind aerosols are much enriched over those expected from soil. It also appears that the most likely form of the sulphate is ammonium sulphate. In order to account for these two observations the particles would have to be collected by the wind in an area where the surface was greatly enriched by ammonium sulphate, and whereas sodium sulphate has been observed on the land surface of Patagonia (Darwin, 1897) there are no reports of similar phenomena with ammonium sulphate. Any such surface deposits would need to be very widespread to account for the approximately equal concentrations observed in both N and S wind aerosols.

If the sulphate aerosol had been analysed by particle size it would have been possible to ascribe the source with some certainty since large particles would indicate a particulate source and small particles would indicate a gaseous source. Unfortunately we do not have such data but Winkler (1975) recently published some observations of the particle size of sulphate ions associated with aerosols collected over the Atlantic ocean. He found that most of the sulphate was associated with Aitken nuclei (i.e. very small particles) and that the sulphate concentrations were largest in winds which had originated over the Sahara. The average concentration of 11 samples of sulphate in these Saharan aerosols was 1.4 $\mu g/m^3$, which is of similar order of magnitude to the average sulphate concentration observed in the Sudan (3.06 $\mu g/m^3$). This is good evidence in favour of a gaseous source for the sulphate observed in the Sudanese aerosols. The source of sulphur could either be anthropogenic pollution or natural emissions and with the Sudanese aerosols the latter source provides the better explanation of the data.

If the sulphur had a gaseous source then the method of formation of sulphate is almost certainly photochemical oxidation to form sulphuric acid which is then neutralized by gaseous ammonia. If we exclude sulphur dioxide then the most probable form of precursor compounds are hydrogen sulphide ($H_2S$) and dimethyl sulphide (DMS), both of which have been proposed as source compounds for most of the sulphate observed in the natural sulphur cycle (Conway, 1942; Lovelock et al., 1972). The oxidizing agent is probably the hydroxyl radical which is produced in the natural atmosphere by photochemical processes (Levy, 1973). This will react with $H_2S$ to produce sulphur dioxide which can then be further oxidized to produce a sulphuric acid aerosol. DMS reacts with hydroxyl radicals to produce an aerosol which can either be sulphuric acid or an organic sulphate. Both $H_2S$ and DMS are oxidized rapidly and the atmospheric lifetimes have been calculated to be 2.3 days and 0.8 days respectively (Cox, 1975). The estimated lifetime of $SO_2$ by reaction with hydroxyl radicals is 8 days (Cox, 1975) so that other conversion mechanisms for $SO_2$ to sulphate may also play some part. In particular, oxidation of $SO_2$ in droplets by ozone has been shown to be very rapid (Penkett, 1972) and this can also produce substantial amounts of sulphate if the meteorological conditions are favourable for cloud formation. It does not appear very likely that the sulphate observed in the Sudan is transported from areas of high pollution such as Western Europe. Sulphate of this type would also be present in small particles and therefore probably indistinguishable from naturally formed sulphate. However, the sulphate levels in the south wind are very similar to those in the north wind and there are no sources of pollution to the south of the sampling site. Also the track of the northerly winds is such that they would not cross Western Europe.

Nitrate formation will also occur in the atmosphere by a number of mechanisms. It has been shown for instance that nitrogen dioxide ($NO_2$) will react with ozone in the presence of a hygroscopic aerosol, such as ammonium sulphate, to produce nitrate (Cox, 1974); this mechanism will be intensified greatly in a cloud system where the water droplets have a much larger surface area and this will lead to nitric acid production on cloud droplets. Another mechanism which will lead to nitric acid production directly in the gas phase is the reaction of hydroxyl radicals with $NO_2$. This reaction has been proposed to account for nitric

acid production in the stratosphere (Crutzen, 1970) and the rate constant has been measured by Anastasi and Smith (1976) as $9.6 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 23 °C. If it is assumed that the hydroxyl radical concentration is approximately $3 \times 10^6$ molecule/cc (Levy, 1973; Ehhalt, pers. comm.) then the lifetime of $NO_2$ due to this reaction is only 9 h, so this is a very effective way of making nitric acid.

It is of great interest in this context that our observations of nitrate in the Sudan suggest that it is present in the form of nitric acid vapour. This is because there were at least four occasions during squalls, one of which is shown in Fig. 5, when the nitrate level was reduced to zero whilst the other two ions remained relatively constant and there were four other occasions, again during squalls, when the nitrate level was substantially lower than the levels recorded immediately preceding the squall. The efficient removal by the presence of large amounts of suspended liquid water droplets during the squall is almost certainly associated with the high solubility of nitric acid. The point is emphasized in a recent publication dealing with the efficiency of rainwater as a sink for various atmospheric gases (Stedman et al., 1975).

### 4.3. *Comparisons of the concentrations of aerosol constituents measured in the Sudan Gezira and at Harwell, England*

The data collected in the Sudan Gezira represent the atmospheric concentrations of a large range of substances which are most probably produced by non-anthropogenic processes. It is of some interest, therefore, to compare these with the levels of the same substances measured at Harwell where there is much evidence to suggest that the aerosol substance is almost all produced by air pollution. This can be illustrated by the enrichment factors in Table 4 which show that the elements concerned have very similar values of $E_{Fe}$ to those observed in cities. Also the levels of sulphur dioxide and nitrogen dioxide at Harwell are such as to suggest that the sulphate and nitrate observed will originate from pollution sources (Cox et al., 1976b). Table 5 presents a comparison of the major aerosol components which are present in the Sudan and at Harwell. The main omissions are silicon and oxygen but these are of little consequence to the argument. The concentrations of calcium, potassium and magnesium are estimates based upon the measured level of iron and the distribution of elements in the earth's crust published by Mason (1952). The table shows that the concentrations of elements such as iron, and by inference, calcium, potassium and magnesium, are much higher in the Sudan than at Harwell. This is almost certainly a universal phenomenon associated with mid-continental sites in temperate and subtropical latitudes where the wind is capable of raising large quantities of dust from the dry surface of the earth (see Table 2). The sodium level is similar at both locations but the source is different. In the Sudan it is derived from soil whereas at Harwell it almost certainly comes from sea salt. (We have adjusted the magnesium level expected at Harwell in Table 5 to take account of this.) The concentration of the ammonium ion observed at Harwell is much larger than in the Sudan, which suggests it is present at Harwell as a pollutant, although its source is presently unknown (pollutant is used in this context in its widest sense to mean produced as a result of anthropogenic activity).

Among the anions shown in Table 5, the chloride observed at Harwell is only slightly larger than that shown in the Sudan N wind aerosol. Some of the chloride observed at Harwell will undoubtedly be associated with sea salt and there is almost certainly a contribution from gaseous HCl. For the Sudan some of the chlorine may be present as HCl but we have suggested that some of the chlorine observed comes from halocarbons absorbed on the surface of the large amounts of aerosol observed there. The ratio of nitrate in the Sudan to nitrate at Harwell is close to 0.6 and the same ratio for sulphate is 0.4. This almost certainly means that anthropogenic emissions of nitrogen oxides are having as much impact on the nitrogen oxide side of the nitrogen cycle as anthropogenic emissions of sulphur are having on the total sulphur cycle. The impact on the total nitrogen cycle will be less marked, however, since large amounts of molecular nitrogen pass through it. Also $N_2O$ is possibly a major nitrogen carrier. Increasing the levels of highly oxidized nitrogen and sulphur compounds will undoubtedly lead to greater acidity in the aerosol, however, and this point is clearly demonstrated in Table 5, where the total level of acid anions at Harwell is over twice the level found in the Sudan.

The total acid or basic potential of the material making up an aerosol is an important quantity

Table 5. *Comparison of major aerosol components in the Sudan* and at Harwell†*

Numbers in brackets are estimates based upon the iron concentration in the aerosol and Mason's estimate of average composition of crustal rock.

| | | Sudan concentration | | | | Harwell concentration | |
|---|---|---|---|---|---|---|---|
| | | N. wind | | S. wind | | | |
| Component | Category | $\mu g/m^3$ | $\mu equiv/m^3$ | $\mu g/m^3$ | $\mu equiv/m^3$ | $\mu g/m^3$ | $\mu equiv/m^3$ |
| Iron | | 2.99 | — | 0.94 | — | 0.31 | — |
| Sodium | base | 0.48 | 0.02 | 0.17 | 0.01 | 0.71 | 0.03 |
| Calcium | base | (2.15) | (0.11) | (0.08) | (0.03) | (0.22) | (0.02) |
| Potassium | base | (1.50) | (0.04) | (0.49) | (0.01) | (0.16) | (0.01) |
| Magnesium | base | (1.20) | (0.10) | (0.39) | (0.03) | (0.16) | (0.02) |
| Ammonium | base | 0.51 | 0.03 | 0.51 | 0.03 | 3.29 | 0.18 |
| | TOTAL | | (0.30) | | (0.11) | | (0.26) |
| Chloride | acid | 0.97 | 0.03 | 0.26 | 0.01 | 1.49 | 0.04 |
| Nitrate | acid | 2.47 | 0.04 | 2.62 | 0.04 | 4.28 | 0.07 |
| Sulphate | acid | 2.32 | 0.05 | 3.16 | 0.06 | 7.49 | 0.16 |
| | TOTAL | | 0.12 | | 0.11 | | 0.27 |

* From present data (Table 1).
† Yearly average for 1973.

since deposition of the aerosol can either lead to a deterioration or an improvement of the soil that it lands on. Most acid soils are infertile and have lost much of their nutrient ionic material, such as calcium and potassium, by leaching of soluble salts. Most basic soils are fertile and some of the most fertile soils in the world have been produced by wind deposition (e.g. loess). It is of interest, therefore, to compare the acid-base potential of the two aerosols observed at Harwell and in the Sudan. Table 5 shows that the base potential of the Sudan aerosol in the form of calcium, sodium, potassium and magnesium, is far larger than the base potential of the same components of the Harwell aerosol.

The total acids and bases in the Harwell aerosol are in balance but only because of the presence of a substantial amount of ammonia which accounts for about 80% of the bases $Ca^{++}$, $Na^{+}$, $K^{+}$, $Mg^{++}$ and $NH_4^{+}$. Deposition of this aerosol will undoubtedly give rise to an acid regime since it has been shown that ammonium ions are oxidized to nitric acid by the soil (Alexander, 1961). On the other hand, in the south wind Sudan aerosol the acid and basic substances are in balance, with ammonium only accounting for 27% of the bases, and in the N wind aerosol there is a considerable excess of basic substances. The deposition of this aerosol should, therefore, give rise to a relatively fertile soil. This is consistent with the well-known alkaline soils of the Gezira (Lebon, 1965). Another illustration of the difference in acid–base potential of aerosols is found in the acidity of rainwater. European rain is almost always acid (Granat, 1972) but rain collected in arid continental sites in the U.S.A. is either neutral or slightly basic because of the large dust components of the aerosols in that region (Gorham, 1976). We have no data on the pH of rain in the Sudan but some data collected in Kampala, Uganda shows the average rain pH to be 7.9 (Visser, 1961). It is not unreasonable to expect similar rain pH's in the Sudan during south wind situations since the air mass will have a similar origin.

## 5. Acknowledgement

This study was part of a project sponsored by the Department of the Environment. We thank Ciba Geigy for their hospitality and assistance to one of us (MHU) in the Sudan.

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## ХИМИЧЕСКИЙ СОСТАВ ФОНОВОГО АЭРОЗОЛЯ В СУДАНСКОИ ДЖЕЗИРЕ

В течение сентября и октября 1973 г. в Суданской Джезире производились измерения состава аэрозоля южнее и севернее воздушных течений. При использовании железа в качестве нормализующего элемента и вычислении факторов обогащения показано, что пыль естественного происхождения является источником большинства элементов. Исключение составляют хлор, бром, сера и азот, которые представляются имеющими газовые источники. Были измерены значительные концентрации окисленных азотных и серных компонент и которые, вероятно, имеют фотохимическую природу. Концентрации серных и азотных компонент были ниже, чем в Европе, но они дают основание полагать, что антропогенные источники имеют одинаковое влияние на их соответствующие природные циклы. Наконец, сравнение аэрозоля в Судане и в Харуэлле показывает, что естественный суданский аэрозоль является потенциально основным, в то время как антропогенный европейский аэрозоль – кислый.