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BACKGROUND AEROSOL COMPOSITION IN THE NAMIB DESERT, SOUTH WEST AFRICA (NAMIBIA)

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Abstract—A remote site in the Namib Desert was selected for sampling background aerosols in southern Africa, as one of a wide network of stations spanning the Southern Hemisphere in a programme designed to measure the background concentrations of trace elements in the atmosphere. A series of samples was collected over a 6-month period using a single-orifice cascade impactor, which fractionated the particles into six size groups. Analysis was performed using particle-induced X-ray emission (PIXE), yielding results for S, Cl, K, Ca, Ti, Mn, Fe, Br and Sr, and occasionally also for V, Cr, Ni, Cu, Zn and Pb. No direct correlations with wind direction were observed excluding strong local or regional sources of particles. K, Ca, Ti, Mn and Fe can be identified with a dust dispersion source. Cl, large particle S and Br, and part of the K and Sr are derived from sea spray. Relative to the soil components small particle K is not enriched as it normally is in regions with less scarce vegetation. Cr, V, Ni, Cu, Zn and Pb concentrations and enrichments in the aerosol are lower than practically all values measured at any other location hitherto. The concentration of the small particle sulphur, 200 ng m^{-3}, is believed to be related to anaerobic conditions and plankton blooms in the ocean upwelling zones off Namibia.

Index keywords: aerosols, remote, desert air, trace analysis, PIXE, size distributions and sulphur.

1. INTRODUCTION

Concern about long-range transport of atmospheric pollutants has recently led to a quest to determine background levels of sulphur and trace metals in atmospheric particulates. Truly remote areas of the Southern Hemisphere are appropriate in this context since the time of mixing with the more polluted Northern Hemisphere is in excess of typical atmospheric residence times of aerosols. Several stations for background aerosol measurement have been operated in the Southern Hemisphere. However, no data are available for desert environments, where terrestrial organic processes cannot add significantly to local aerosol concentrations. Therefore, a sampling project was instituted at the Namib Research Institute at Gobabeb, Namibia, to characterise the composition, size distributions and interelement relationships in the aerosols of the unique environment of the Namib Desert.

2. EXPERIMENTAL

2.1. *Sampling station*

The Namib Research Institute at Gobabeb is situated at 23°45′ S and 15°03′ E. This site is 100 km distant from the nearest town, Walvis Bay (population 25,000). The only other sizeable city in this region is Windhoek, which is 250 km to the northeast. The isolation of Gobabeb from major roads is shown in Fig. 1. Vehicle movements in the direct vicinity of the sampling station, which is 200 m southeast of the central building of the Institute, are limited to 2–4 day^{-1}. Geographical features of Gobabeb are its position on the ephemeral Kuiseb river, on the northern limit of the Namib dune desert and the southern edge of an extensive sparsely vegetated gravel plain. At its nearest point, the Atlantic Ocean is at 60 km. The location of Gobabeb, its climate and soils have been fully described by Schulze (1969), Goudie (1972), Scholz (1972) and Tyson and Seely (1980).

2.2. *Sampling methods*

Samples were collected with a five-stage 1.2 ℓ min^{-1} single-orifice Battelle-type cascade impactor (Mitchell and Pilcher, 1959) with after-filter. The 50% cut-points of the impactor operated at 1 ℓ min^{-1} are 4, 2, 1, 0.5 and 0.25 μm aerodynamic diameter. The impaction surfaces were 4-μm Mylar film, supported by metal slides and made sticky by coating with a thin layer of paraffin. A 0.4-μm pore diameter Nuclepore filter served as a back-up filter.

Sampling began on 1 November 1976 and continued until 25 April 1977. Each sample was collected over a period of 126 h extending over 7 days. Since the diesel-powered electricity generator was switched off during the night from 0130 to 0730 h, these periods were not included in the sampling. Samples 12 and 17 were collected over an extended period of 2 weeks, while 3, 14, 15 and 19 were invalidated due to loss of target material during sample preparation or insects blocking the impactor orifices.

As part of the routine meteorological observations carried out at Gobabeb, continuous recordings are taken of wind speed and direction, air temperature and relative humidity. These data were available for the interpretation of the aerosol data. Precipitating fog occurred on an average of three nights per month at Gobabeb during the sampling period. However, the onset of the fog is usually in the early hours of the morning and it is usually completely dispersed by 1000 h. As this time span was mostly excluded from the sampling period due to the electricity supply hours, the fog is not an important factor

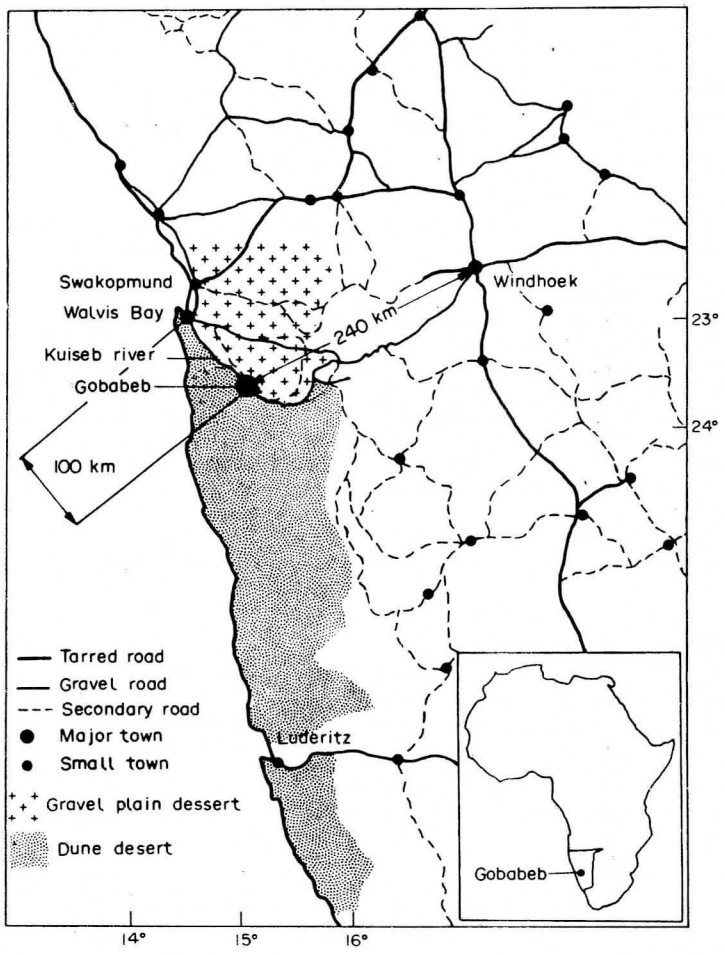


Fig. 1. Sketch map of Namibia showing the relative isolation of the sampling site at Gobabeb from large towns and major roads.

in the overall results. The collected aerosol can therefore be regarded as originating from desiccated air with a humidity of less than 50 %.

2.3. *Analytical methods*

The analyses were based on particle-induced X-ray emission (PIXE) using the Super FN Tandem Van de Graaff accelerator of Florida State University. The experimental set-up, the characteristics of PIXE analysis, and its geographical applicability for aerosol size distribution measurements using cascade impactors have been discussed elsewhere (Johansson *et al.*, 1975; Johansson and Johansson, 1976; Van Grieken *et al.*, 1976). All individual aerosol size fractions, deposited on a Mylar impaction foil, were irradiated with 5 MeV protons during 3–5 min, and the resulting X-ray spectra were evaluated by the computer programme REX (Kaufmann *et al.*, 1977). Details about the procedure have been given elsewhere, together with preliminary results and interpretations of the first part of the samples (Annegarn *et al.*, 1978).

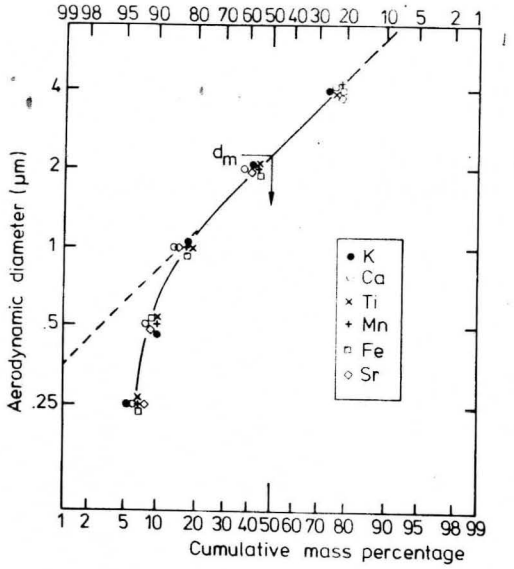
The precision of the sampling and analytical procedure has been tested thoroughly in a previous study (Van Grieken *et al.*, 1976). A 10 % error arising from the sampling step, mainly the volume measurement, should be added quadratically to an analytical uncertainty of 4–30 %, depending on the element concentration level. The accuracy of the analytical method has been demonstrated to be in the 10 % range (Johansson *et al.*, 1975).

The six stages of sample 11 were also examined by scanning electron microscope (SEM) and qualitative energy dispersive X-ray analysis (EDAX). The samples were mounted on Al stubs and coated with C and then Au–Pd alloy.

3. RESULTS AND DISCUSSION

3.1. *Size distributions*

The measured size distributions for K, Ca, Ti, Mn, Fe and Sr, and of S, Cl and Br averaged over all 19 analysed impactor sets are presented as cumulative mass distributions in Figs 2(a) and 2(b). Table 1 lists the corresponding geometric means and the standard deviations. Variations in concentrations over the whole sampling period are shown in Fig. 3. It is clear that K, Ca, Ti, Mn, Fe and Sr all show remarkable similarity in size distribution and time dependence. This points obviously to a common predominant source, namely soil dust. Even at first sight, it appears



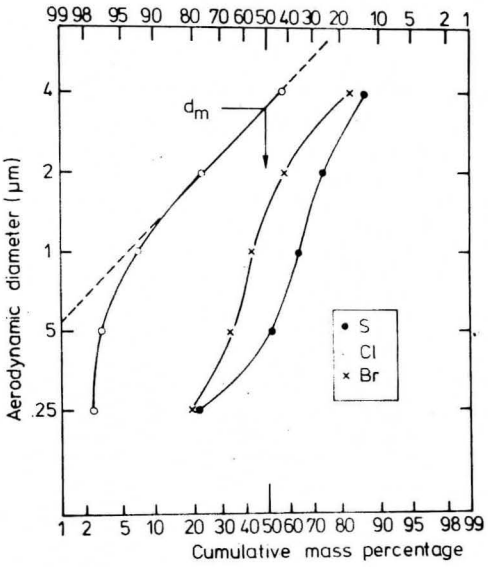


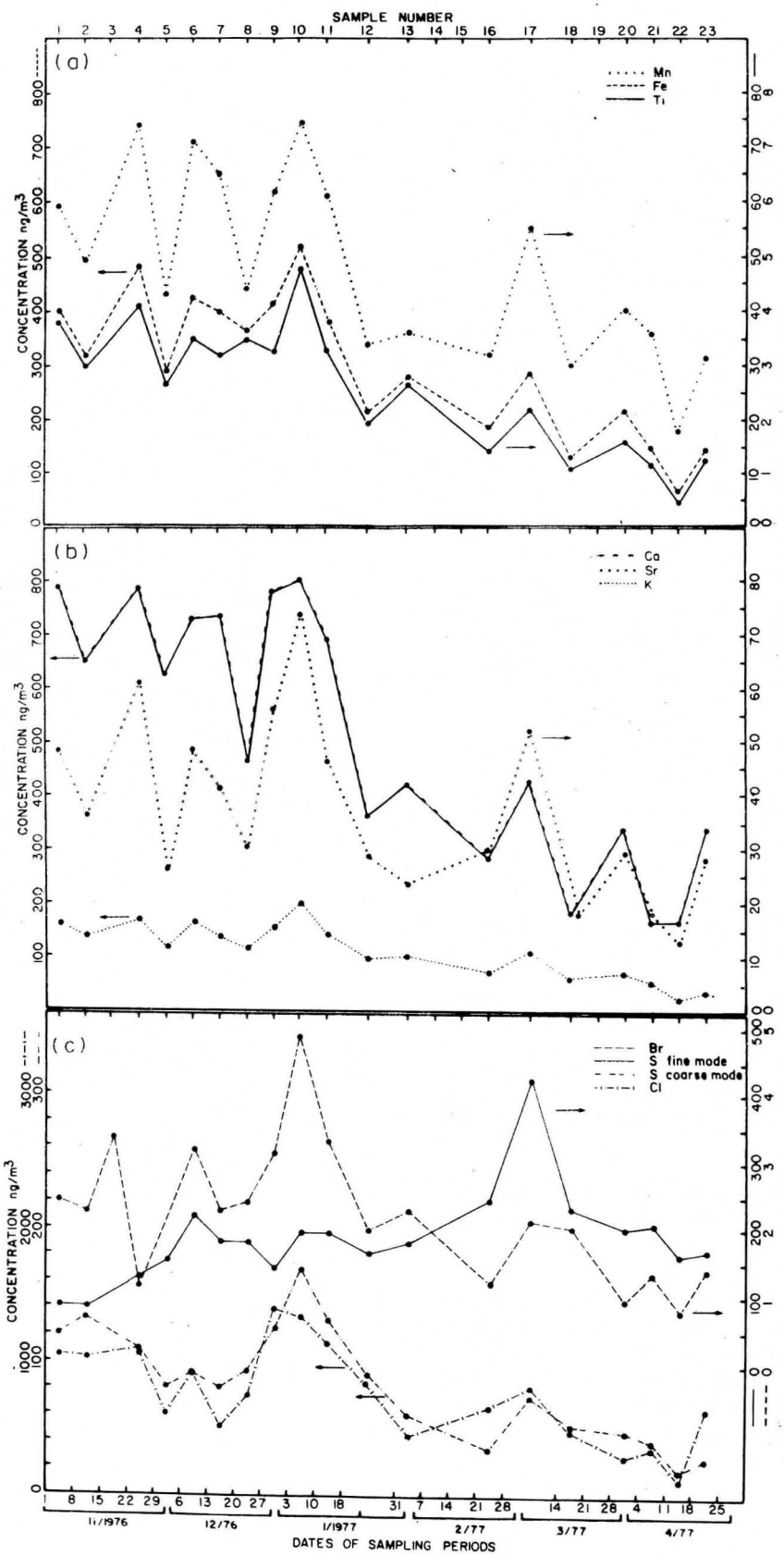
Fig. 2.(a) and (b) Cumulative mass distributions of K, Ca, Ti, Mn, Fe, Sr, Cl, S and Br. The deviation from linearity for all elements except S and Br is an indication of particle bounce-off. The 's' shape of the S and Br distributions is characteristic of bimodal distributions. The mass median diameter is indicated as d_m.

that the S, Cl and Br behave quite differently from the crustal elements, and from each other; the sea surface is the obvious source of the large particle fraction of these elements.

The cumulative mass distributions, plotted on a log-normal scale in Fig. 2, do not show the straight line characteristics expected of a unimodal, stable aerosol. The increasing deviation of the measured distribution from the ideal distribution (broken line in Fig. 2) with decreasing particle size indicates excess mass on the smaller size stages. This effect indicates particle

Table 1. Geometric mean elemental concentrations of 19 size-fractionated aerosol samples taken at Gobabeb

Impactor stage number	50% cut point (μmad)	Geometric mean, ng m^{-3}, (standard deviation)									
		S	Cl	K	Ca	Ti	Mn	Fe	Br	Sr
1	4	33(2.0)	264(1.8)	26(1.7)	104(2.0)	4.9(1.8)	1.0(1.6)	51(1.7)	0.33(2.4)	0.72(1.8)
2	2	38(1.8)	196(2.2)	30(2.1)	162(2.0)	7.0(2.1)	1.5(1.9)	83(2.1)	0.36(2.4)	1.25(2.0)
3	1	23(1.6)	102(2.3)	21(1.8)	99(1.7)	5.3(1.9)	1.2(1.6)	67(1.9)	0.27(2.3)	0.85(1.7)
4	0.5	34(1.8)	34(1.7)	6.9(1.8)	26(2.1)	2.1(2.2)	.39(1.6)	23(2.0)	0.18(2.2)	0.24(1.9)
5	0.25	81(1.8)	2.7(2.7)	3.0(1.8)	7.5(1.8)	0.6(2.1)	<0.13—	5.8(1.9)	0.23(1.7)	<0.07—
6	filter	55(1.3)	17(2.1)	7.3(2.1)	26(2.2)	1.9(1.8)	<0.31—	17(2.1)	0.43(1.6)	<0.20—
Total		264	616	94	425	22	~4.3	246	1.8	~3.2



Figs 3.(a), (b) and (c). Variation with time of the elemental concentrations of the aerosol, summed over all six stages, except for S (coarse mode = stages 1 + 2, fine mode = stages 4 + 5 + 6). The composition of the aerosol does not show a dramatic change from sample 12 onwards, coinciding with a major change in the wind regime.

bounce-off and capture on lower impactor stages. A SEM micrograph of the stage 6 (sample 11) back-up filter stage revealed particles of few μm diameters, confirming that bounce-off had indeed occurred. Stage 5, however, appeared to be free of these artefacts. The heavy loading of the impactor stages after a 1-week sampling period and the extreme dryness of the Namib Desert air during the day might be factors enhancing bounce-off errors. The resulting distortions of apparent size distributions can be minimised by using shorter sampling periods and by using a different impactor slide coating; the paraffin used in this work will be replaced by Vaseline in future sampling under desert conditions.

The relative error due to bounce-off is least for the largest stages; by taking a line through the first three points of the crustal element and chlorine distributions, the mass median diameter d_m (in μm aerodynamic diameter) and geometric standard deviations σ_g of these distributions may be obtained (crustal elements: $d_m = 2.3$ μmad, $\sigma_g = 1.9$; chlorine: $d_m = 3.5$ μmad, $\sigma_g = 2.2$). The uncertainties on the slopes in Figs 2(a) and (b) point to an uncertainty of around 0.4 μmad on the mass median diameters.

The S and Br cumulative mass distributions are indicative of a bimodal aerosol. In principle the parameters for the two modes could be extracted by a least squares fit. However, the distortion due to particle bounce-off makes such a procedure inappropriate in this case. An estimate of the mass median diameters of the two S modes was obtained from a plot of concentration vs size (Annegarn *et al.*, 1978): 0.3 μmad and 3.0 μmad, respectively.

3.2. *Variation with wind direction*

The wind data for the sampling periods were analysed by classifying the directions as maritime, continental–dune sand or continental–gravel plain, corresponding with the three distinct geographic areas surrounding Gobabeb. During periods 1–11, the winds were predominantly maritime in origin; while periods 12–17 were classified as mixed maritime–continental. No marked changes in the aerosol composition were noted with these changes in average wind regime. The long sampling periods used in this experiment were obviously not appropriate for extracting wind-correlated information. Accurately studying the influence of the wind direction on aerosol concentration would require time resolution of 1 or 2 h. Such measurements were initiated subsequently using streaker time sequence samplers (Annegarn *et al.*, 1979).

3.3. *Interelement correlations*

Further information on the sources of the various elemental components of the aerosols was obtained by

Table 2. Interelement linear regression coefficients and adjusted R^2 values for size-fractionated aerosol samples

Model	Eq. No. and coeffs.		Stage 1	Stage 2	Stage 3	Stage 4	Stage 5
$K = aFe + c$	1	a	0.47	0.34	0.24	0.16	—
		c	0.0*	0.0*	5.2	4.1	—
		adj R^2	0.95	0.97	0.93	0.64	0.07
$K = aFe + bCl + c$	2	a	0.36	0.32	0.18	0.16	—
		b	0.025	0.016	0.037	0.0*	—
		c	0.0*	0.0*	5.0	4.18	—
		adj R^2	0.97	0.99	0.95	0.59	−0.03
$K = aCa + c$	3	a	0.19	0.17	0.19	0.19	—
		c	5.45	0.0*	0.0*	3.07	—
		adj R^2	0.94	0.83	0.88	0.84	−0.07
$Ca = aFe + c$		a	2.37	1.76	1.16	0.83	1.02
		c	0.0*	0.0*	19.8	0.0*	0.0
		adj R^2	0.92	0.88	0.93	0.76	0.79
$Sr = aFe + c$	4	a	0.013	0.015	0.011	0.007	†
		c	0.0*	0.0*	0.0*	0.0*	
		adj R^2	0.80	0.91	0.85	0.62	
$Sr = aFe + bCl + c$	5	a	0.0054	0.011	0.011	0.006	†
		b	0.0015	0.0016	0.0*	0.0*	
		c	0.0*	0.0*	0.0*	0.0*	
		adj R^2	0.90	0.94	0.84	0.61	
$Sr = aCa + c$	6	a	0.0053	0.0077	0.0090	0.0085	†
		c	0.0*	0.0*	0.0*	0.0*	
		adj R^2	0.87	0.82	0.77	0.85	
$S = aCl + c$		a	0.126	0.145	0.105	—	—
		c	0.0*	0.0*	11.7	42.8	74.7
		adj R^2	0.83	0.81	0.62	0.04	0.12

* Intercept not significantly different from zero.
† Incomplete data, Regression not attempted.

examining interelement correlations and by comparison of measured ratios with standard crustal and marine element ratios.

The elemental composition of individual particles on various stages of sample 11, obtained from the SEM, was an additional aid in this interpretation.

The high correlation between the elements Ti, Mn and Fe observed in Fig. 3, and ratios of Ti/Fe = 0.097 and Mn/Fe = 0.018 which vary little with particle size and which are similar to the corresponding ratios in average crustal rock (Mason, 1966) and soil (Vinogradov, 1959) (Ti/Fe = 0.088 and 0.12 and Mn/Fe = 0.020 and 0.022, respectively) confirm a common continental source for these elements.

While K, Ca and Sr correlate reasonably well with Fe, close examination of the data suggests that additional sources contributed to these three elements in the aerosol. This shows up most clearly for K in the results of the linear regression analysis (Table 2) of the equations

$$K = a\,Fe + c \quad (1)$$

and

$$K = a\,Fe + b\,Cl + c. \quad (2)$$

The values of adjusted R^2 (coefficient of determination) show that an improved fit is obtained for the data from stages 1 to 3 when a marine component, modelled by Cl, is included. For the marine fraction of the K, the K/Cl ratio [obtained as the coefficient b from the linear regression analysis of equation (2)] for stages 1–3 averages 0.027, compared to the sea water ratio of 0.020. If we assume that no K/Cl fractionation occurred during aerosol formation then these results indicate that Cl losses of the order of not more than 25% occurred either during transportation as an aerosol, or during analysis (see Berg and Winchester, 1977). For the first three size fractions, the K/Fe ratio of Fe-correlated soil component closely matches the world soil average of 0.36 (Aubert and Pinta, 1977). For stages 4 and 6 the correlation of K with either Fe alone, or with Fe and Cl, is worse (Table 2) than the correlation:

$$K = a\,Ca + b \quad (3)$$

indicating a Ca–K-rich soil aerosol distinct from the Fe-rich component. This is discussed further below. For stage 5, the smallest diameter fraction, neither Fe, Cl nor Ca provide a significant prediction for K; however, this small particle K, together with the small particle excess represented by the intercept terms in (1) or (3) amounts to only a few ng m^{-3}. Previous investigations, for example in the sparsely inhabited area of northern Florida (Johansson *et al.*, 1975; Johansson *et al.*, 1976) and in remote locations on the South American continent (Lawson and Winchester, 1978) showed a distinct K/Fe enrichment, probably due to plant emanations or forest fires. In the tropical jungle, Crozat (1979) measured an excess of several hundred ng m^{-3} of small particle K. The absence of any enrichment in the Namib Desert, which is characterised by an extremely sparse vegetation, supports the biogenic origin of the small particle K excess observed elsewhere.

The Ca/Fe ratios observed (Table 2) are considerably higher than the world average soil value (0.36) or rock value (0.73), showing an enrichment of Ca of up to six times. The variations in Ca/Fe ratio with particle size are greater than for any of the other crustal elements and the ratio is the highest for the largest particle sizes. The average analysis results for nearly 200 soil samples collected all over the Namib Desert (Evens, 1978) did indeed point to Ca being high by a factor of 2.4 relative to Fe, in comparison with world average soil. In aerosols generated by the wind, the Ca is even more enriched, by another factor of 2, due to a physical aerosol/soil fractionation effect (Evans, 1978). An obvious explanation for this is that the Namib Desert contains extensive outcrops of limestone (Scholz, 1972) as well as large areas of gypcrete ($CaSO_4$). The SEM pictures did indeed show individual $CaSO_4$ particles on the four largest stages. The marine contribution to Ca is found to be relatively small if one assumes that the sea water Ca/Cl ratio (0.021) exists in the marine aerosol. Even on stage 1, where the highest marine contribution occurs, marine-derived Ca would be less than 5% of the total Ca.

As with K, there is a significant contribution to the amount of Sr found in these aerosols in the larger size fractions. Linear regressions (Table 2) for the equations

$$Sr = a\,Fe + c \quad (4)$$

and

$$Sr = a\,Fe + b\,Cl + c \quad (5)$$

show an improved fit when the marine component is added. It is expected that further amounts of Sr would be contributed by the Sr associated with the Ca-rich minerals discussed above; for fine particle Sr (stage 4), the linear regression

$$Sr = a\,Ca + c \quad (6)$$

shows a significantly better correlation with Ca than with Fe. Sr has been found clearly enriched in the small particle size fraction of Namib soil and the aerosols that are generated from it (Evens, 1978). Due to covariation of the wind-dispersed aerosol components, the Sr cannot be partitioned accurately among the three sources of iron-rich, calcium-rich and marine aerosols by a simple multiple linear regression and the coefficients of Equations (4), (5) and (6) should not be used for quantitative comparisons.

The bimodal sulphur distribution indicates that at least two sources were contributing to this element in the atmosphere. In Fig. 3 the large (stages 1 and 2) and small (stages 4, 5 and 6) sulphur modes are plotted separately as a function of impactor number (time). The large particle S correlates with variations in the Cl concentrations (Table 2) indicating a possible marine source for the large mode sulphur. However, the S to Cl ratio for stage 1 is 0.13, which is enriched by a factor

of 2.6 over the sea water ratio of 0.048. As the Cl loss is only 25 %, inferred from the K/Cl ratio, the high S/Cl cannot be accounted for by a Cl-loss mechanism alone (Berg and Winchester, 1977). The scanning electron microscope examination of sample 11 revealed the presence of individual particles of $CaSO_4$; elemental maps of stage 1 showed a close association of Ca and S, with coincident regions of maximum deposition, which are distinct from the regions of maximum Cl deposition. This evidence, together with the evidence of the excess Ca, indicates unambiguously that the source of the large particle S excess was remobilised gypcrete, a gypsum crust which locally can reach thicknesses up to 4 m (Goudie, 1972). Gypcrete has been described as "soft" (Scholz, 1972) or as "rather puffy, in contrast to the more dense calcrete" (Goudie, 1972), hence remobilization of gypcrete should in principle be relatively easy.

Small particle S does not show correlations with any of the other elements determined here. A small mass median diameter of the order of 0.3 μmad is an indication that the aerosol originated from a condensation process. At this site, the gaseous precursors for this transformation cannot be due to pollution sources. However, there are two mechanisms for transferring gaseous S species across the sea water/air interface which could be the source of this S. Along the coast of Namibia, the ocean supports a heavy phytoplankton bloom, due to the upwelling of the nutrient-rich Benguela current (Hart and Currie, 1960). It has been established (Andreae, 1980; Barnard *et al.*, 1983) that dimethylsulphide, produced by the plankton, can escape into the atmosphere, providing a significant component of the natural sulphur input on a global scale. As a consequence of the peculiarities of the oceanic currents off Namibia, and the rich biomass, the bottom waters over the continental shelf have a highly anoxic layer, supporting a rich fauna of anaerobic bacteria. Off Walvis Bay this layer often reaches within a few m of the surface. On occasions dramatic eruptions of H_2S have been recorded (Hart and Currie, 1960) in this region, while continuous emission on a much smaller scale is known to occur. We consider these processes the likely source of the observed fine particle S. Evidence has been presented by Annegarn *et al.* (1979) that the final step in the oxidation of these S precursors occurs during the night hours when condensed fog droplets provide an aqueous phase which enhances the reaction rates.

The condensation of S-containing gases onto aqueous aerosol particles and ultimate oxidation of the sulphur to SO_4^{2-} will, in the absence of neutralizing NH_3, lead to the production of acidic droplets. Due to the low biomass (the primary source of atmospheric NH_3) in this desert region, it is postulated that the sulfate, formed during the high-humidity night hours, will be incompletely neutralized. During the day, when the relative humidity drops below 15 %, evaporation will concentrate the acidic droplet; if any NaCl was present in the original droplet, the Cl will then be driven off preferentially. This effect would be expected to be most marked in the sub-μm size range. There is some evidence to support such a mechanism from the SEM examination of stage 5 (0.25 μm) of sample 11: X-ray analysis showed regions of 'pure' Na_2SO_4, i.e. only Na and S were seen. There were other areas of the slide, however, where only S was observed, i.e. no cations were found. This S could have been deposited in the form H_2SO_4, $(NH_4)HSO_4$ or $(NH_4)_2SO_4$, indicating a S condensation well in excess of the NaCl content of the original droplet. This is supported by the PIXE data which show much higher levels of S than any other element in the fine stages on all samples, although more complete Na data would be required to confirm this. The atmosphere along the Namibian coast in the region of Walvis Bay is known to be exceptionally corrosive, more so than at other coastal locations; the formation of a natural acidic aerosol as postulated above may be the reason.

Br is another element for which our data suggest both a dispersal and a gas condensation source. Like S, the concentration of Br with particle size is remarkably uniform. In the larger particle sizes Br correlates well with Cl. The Br/Cl ratios in the largest particle sizes (Table 2) are lower than the sea water ratio suggesting that preferential loss of Br has occurred. In the smaller particle sizes (stages 4–6) a marked Br enrichment becomes apparent and the correlation with Cl becomes insignificant. Duce *et al.* (1965) suggest that Br lost from the marine aerosol is captured by rainfall, either in the washout or on condensation nuclei (i.e. aerosol particles). The present data conform to the hypothesis that Br indeed condenses on the smaller particle size fraction, which would, in non-desert regions, act as rain condensation nuclei.

The excess Br in the small particles cannot be attributed to automobile exhaust, as in the case of less remote regions (Johansson *et al.*, 1976), because the detection limits for Pb in the present samples are such that the Pb/Br ratio at Gobabeb is certainly below 0.2, while in automobile exhaust emissions Pb/Br is closer to 3 and tends to rise as the emissions age due to preferential loss of Br (Robbins and Snitz, 1972). The Pb content of the Namib aerosol must be extremely low. The sum of the average detection limits for the six impactor stages implies a Pb level well under 3 ng m^{-3}, far below most Northern Hemisphere levels (Reiter *et al.*, 1976) and comparable with other remote station levels (Rahn, 1976).

The total level of Zn in the Namib Desert air averages 0.7–0.9 ng m^{-3}, the concentrations in impactor stages 1–6 being 0.23, 0.13, 0.13, 0.11, 0.06 and < 0.26 ng m^{-3}, respectively. If one predicts the Zn concentration from the average Fe data and the average Zn/Fe ratio in soil (Aubert and Pinta, 1977), a total value of 0.33 ng Zn m^{-3} is found. The excess Zn is thus only 0.4–0.6 ng m^{-3} (of which 0.2 ng m^{-3} appears to be of large particle size) and the enrichment factor of Zn relative to Fe and to average soil is thus only 2.0–2.8. In the 104 data sets listed by Rahn (1976),

not one Zn enrichment factor value is below 10. The reason for that astonishingly low Zn enrichment in Namib Desert air is not in the extremely high Fe levels, due to high unfractionated airborne soil levels, since the average total of 246 ng Fe m^{-3} is not unusual (Rahn, 1976), nor is it in a strong relative Zn deficiency in Namib soil (Evens, 1978). The average total Zn concentration itself is extremely low. According to Rahn (1976), Zn levels below 3 ng m^{-3} have been reported only for the snow-covered regions of northern Norway (lowest 10% value of 0.98 ng m^{-3} with corresponding enrichment factor, vs Al and average crustal rock, of 170) and the South Pole (0.03 ng m^{-3}, enrichment factor 61) while the lowest Zn enrichment factors were for the north Atlantic (12.2 corresponding to a concentration of 8.5 ng Zn m^{-3}) and Bermuda (15.2, for a concentration of 6.0 ng Zn m^{-3}). At the remote Southern Hemisphere location of Chacaltaya, Bolivia, Adams *et al.* (1977) observed Zn levels of 3 ng Zn m^{-3}, mostly unaccounted for by soil dispersal since the enrichment factors were around 20.

The sum of the detection limits of Cu for the six impactor stages corresponds to 0.83 ng Cu m^{-3}, while from the airborne Fe concentration and the average soil composition one would expect an airborne Cu level of 0.14 ng m^{-3}. The enrichment factor is thus below 6, the Cu excess below 0.7 ng m^{-3}. According to Rahn (1976) the present upper level for Cu is only above reported South Pole concentrations (0.04 ng m^{-3}; enrichment factor of 93) and northern Norway minimal concentrations (0.43 ng m^{-3}; enrichment factor of 95), while hitherto, the lowest reported Cu enrichment factor is for Bermuda (7.91; concentration of 2.4 ng m^{-3}).

V, Cr and Ni were only observed in a few impactor samples, but again, the low detection limits of the PIXE analysis allow some conclusions to be drawn. The upper limit for the Cr concentration is 2.3 ng Cr m^{-3}. The airborne Fe concentrations and average soil Cr/Fe ratios would lead to 1.3 ng Cr m^{-3}. Few data have been reported below both the present Cr concentration detection limit and the resulting enrichment factors of < 1.7 (Rahn, 1976). Similarly low levels must be present for V and Ni. A total maximum level of 2.6 ng V m^{-3} has been calculated, while 0.64 ng V m^{-3} is expected for simple soil dispersal, implying an enrichment factor below 4.0. The upper level for Ni, summed over all particle sizes, is 1.49 ng m^{-3}, instead of 0.26 ng m^{-3} predicted from the Fe levels. Ni and V are usually measured in unexpectedly high concentrations, particularly close to pollution sources (Duce and Hoffman, 1976). The fact that neither V nor Ni, which are abundant in fuel oil, are detected in enhanced concentrations at the Gobabeb station indicates that local pollution from the station's diesel generator is insignificant.

The generally observed enrichment of Zn, Cu and other chalcophilic elements has been attributed to a world-wide contamination with some anthropogenic combustion aerosol (Dams, 1974), selective evaporation from rocks (Goldberg, 1976), and selective emanations from plant material (Beauford *et al.*, 1977). The observed unusually low enrichment at the present remote Southern Hemisphere site with extremely sparse vegetation points most to plant material emanation as the probable source while ruling out selective rock evaporation. The low Zn and fine K concentrations indicate that practically no combustion aerosol, anthropogenic or natural, is present in the Namib aerosol. Future comparative measurements in equally remote Southern Hemisphere locations with abundant vegetation will have to indicate unambiguously whether world-wide anthropogenic combustion aerosol contamination is important relative to natural biogenic emanation.

4. CONCLUSIONS

Gobabeb was chosen as a sampling site for remote aerosol measurements in the Southern Hemisphere. Analysis of size fractionated impactor samples taken under varying wind conditions over a 23-week period indicated an aerosol of combined soil and maritime origin, which was free from local or regional anthropogenic pollution. The measurements have provided valuable baseline values of remote natural aerosol concentrations. K, Ca, Ti, Mn, Fe and Sr showed size distributions with a mass median diameter of 2.3 μmad. Enrichments of Ca, K and Sr relative to average crustal soil or rock were observed, consistent with analysis of soils of the region, and the occurrence of outcrops of gypcrete. Unexpectedly low concentrations of Cu, Zn and sub-μm K may be related to the sparsity of vegetation in the Namib Desert. Br and S had bimodal size distributions. Large particle Br and S were correlated with Cl, indicating a sea spray source. Small particle Br was not derived from automobile exhaust gases, since the Pb levels were too low to account for gasoline as a measurable source.

The mass median diameter of the small particle S was 0.3 μmad, indicating a condensation aerosol. The concentrations of this fine mode sulphur ($\sim$ 200 ng m^{-3}) were four times the averages reported for Southern Hemisphere temperate latitude continental and marine locations, including some sites in forested areas (Lawson and Winchester, 1979; Maenhaut *et al.*, 1981).

The fine aerosol sulphur background concentrations observed in remote areas may be maintained by the oxidation of reduced S gases which emanate from marine or terrestrial biogenic sources (Barnard *et al.*, 1982), although their relative importance is unknown at present. It is noteworthy that the Namib Desert fine aerosol S concentrations are maintained at levels higher than those found at other remote Southern Hemisphere sites. The low Namib concentrations of fine particle K, Zn and other elements expected from biomass or fossil fuel combustion preclude these as sources of the fine aerosol sulphur. The nearest areas of extensive tropical vegetation are several hundred km to

the north. However, the measurement location is 60 km east of the Atlantic coast, near substantial oceanic upwelling, which is known, by odour and chemical measurements, to transfer S-bearing gases to the atmosphere. The results of this study suggest that marine sources are the more important source of natural fine sulphur, a result of potential value in understanding the global cycling of sulphur in the natural atmosphere.

The Namib site, which is essentially free of local vegetation, is ideally suited for measurements which may establish the relative importance of marine and terrestrial sources of gaseous precursors to the natural levels of sulphur. Future work will be oriented towards measuring the sulphur flux from the ocean and determining the acidity of the aerosol and the condensation fogs.

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