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Sources of Nitrate and Ozone in the Marine Boundary Layer of the Tropical North Atlantic

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During the period April 1989 through December 1990, O_3 concentrations in the marine boundary layer at Barbados, West Indies, show a pronounced seasonal cycle. Daily averaged values in the winter and spring often fall in the range of 25-35 ppbv for periods of several days, and they seldom fall below 20 ppbv. In contrast, during the summer, values typically fall in the range of 10-20 ppbv. During the winter-spring period, there is a very strong negative correlation between O_3 and a number of aerosol species, including NO_3^-. These anticorrelations appear to be driven by changing transport patterns over the North Atlantic as opposed to chemical reactions involving O_3 and nitrogen species in the atmosphere. Analyses of isentropic trajectories clearly show that high O_3 and low NO_3^- are associated with transport from higher latitudes and high altitudes. Conversely, high NO_3^- and relatively low O_3 are associated with transport from Africa. Our study suggests that North America and the middle troposphere (and stratosphere) are not strong sources for NO_3^- over the tropical North Atlantic. The strong correlation of NO_3^- with ^{210}Pb and the weaker correlation with Saharan dust indicates that NO_3^- is derived principally from continental surface sources, probably in Europe and North Africa, but not from the Saharan soil material itself. During several extended periods, NO_3^- and ^{210}Pb were strongly correlated and their concentrations were high relative to nss $SO_4^=$; these factors, coupled with trajectories originating in Africa, suggest that African biomass burning was a significant source at these times. In contrast, biomass burning appears to be a minor source for O_3 as measured at Barbados, perhaps accounting for an enhancement of about 5 ppbv at most during these periods.

INTRODUCTION

Ozone is one of the primary oxidizing agents in the atmosphere, and it is of critical importance in transformations involving many atmospheric gases, particles, and hydrometeors. Nitrogen oxides also play a critical role in the oxidizing capacity of the atmosphere. Reactions involving the interconversions of the various N_xO_y species play an important role in controlling the concentrations of the H_xO_y radicals that are the primary oxidants for many atmospheric constituents. Both transport and in situ chemistry contribute to the spatial and temporal variations of O_3 in the troposphere [*Chatfield and Harrison*, 1977; *Fishman et al.*, 1979; *Levy et al.*, 1985]. However, there is considerable uncertainty as to which of these processes is most important in the marine boundary layer (MBL). N_xO_y species are produced by several different processes: high-temperature combustion of fossil fuels; biomass burning; lightning; photochemical reactions in the stratosphere; and biological processes in soils. The contribution that each of these sources makes to the total N_xO_y concentrations in a given region is also very uncertain.

During 1988, the Atmosphere/Ocean Chemistry Experiment (AEROCE) was instituted at island locations in the North Atlantic Ocean (Figure 1). A major objective of this program is to characterize the chemical climatology of tropospheric O_3 and a number of other important species, including NO_3^-, and to assess the relative importance of their various sources. In this report, we use the concentrations of chemical tracers, the results from isentropic trajectory analyses, and the regional meteorology as depicted on surface synoptic charts to assess the probable sources of the periodically high NO_3^- and O_3 concentrations observed during the winter and spring at Barbados. In this analysis, we rely on three tracers: mineral dust, ^{210}Pb, and ^{7}Be. Mineral dust at Barbados is derived almost exclusively from the arid and semiarid regions of North Africa [*Prospero and Nees*, 1986]. ^{210}Pb is produced by the radioactive decay of ^{222}Rn for which the overwhelmingly predominant source is continental soils. Hence ^{210}Pb serves as a tracer for material transported from continental sources [*Turekian et al.*, 1989]. Beryllium-7 is a tracer for material originating in the upper troposphere and lower stratosphere where it is produced by the cosmic-ray-induced spallation of nitrogen and oxygen [e.g., *Turekian et al.*, 1989].

SAMPLING AND ANALYSIS

The AEROCE sampling station on Barbados is located on a 30-m rocky promontory at Ragged Point near the easternmost point of the island. The bulk aerosol sampling filters and the sampling intakes for the O_3 monitor are located at the top of a 17-m aluminum walk-up tower.

Ozone has been continuously monitored at the Barbados site since April 1989 [*Oltmans and Levy*, 1992]. The Dasibi UV absorption instrument at the site is calibrated against the NOAA/CMDL standard which is, in turn, tied to the U.S. National Institute of Standards and Technology standard O_3 photometer. Hourly averages are recorded on a computer data system. For this investigation, the hourly averages were averaged over the time periods that the individual bulk aerosol samples were collected.

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Fig. 1. Map of the North Atlantic Ocean showing the locations of the four sampling stations used in the AEROCE program: Barbados, West Indies; Bermuda; Izania, Tenerife, Canary Islands; and Mace Head, Ireland.

For major ion measurements, particles are collected by drawing air through 20x25 cm Whatman-41 filters at a flow rate of about 1 m^3 min^{-1}. The daily sampling protocol yields a sampled air volume of about 1400 m^3. Sampling is controlled by wind sensors that turn the pumps on only when the winds are off the ocean at speeds greater than 1 m s^{-1}. Because Barbados is located in the trade wind belt, winds are very consistent, falling within our sampling specifications more than 90% of the time. Under these conditions, Whatman-41 filters have total mass collection efficiencies greater than 90% for nss $SO_4^=$ and methanesulfonate (MSA), 95% for NO_3^- and sea salt, and 99% for mineral dust [*Savoie et al.*, 1989*a*].

After exposure, the filters are returned to Miami for analysis. Quarter sections of each of the filter samples are extracted with 20 mL of 18 Mohm cm^{-1} Milli-Q water in three separate aliquots of 10, 5, and 5 mL. Na^+ in the extracts is determined within $\pm$2% by flame atomic absorption and Cl^-, NO_3^-, $SO_4^=$, and MSA within $\pm$5% by suppressed ion chromatography [*Savoie et al.*, 1989*a*]. Nonsea-salt (nss) $SO_4^=$ is calculated as total $SO_4^=$ minus Na^+ times 0.2517, the $SO_4^=$:Na^+ mass ratio in seawater. Mineral dust is determined by ashing the extracted filter at 500°C for several hours and weighing the residue. A blank is taken for every sample and is handled in the same way as a sample except that it has had no air drawn through it. The concentrations of the ions in the samples are at least 10 times higher than those in the blanks and average 50 to 100 times higher. The residual ash from the blank sometimes makes a significant contribution to the sample residue. As a consequence of the blanks, the standard error in the mineral dust concentration is essentially constant at $\pm$0.1 $\mu g\ m^{-3}$ for concentrations less than 1 $\mu g\ m^{-3}$; at higher levels, the standard error is $\pm$10%. Because Whatman-41 and other cellulose filters that are coated with NaCl are known to collect HNO_3 vapor with high efficiency [*Appel et al.*, 1980, 1981; *Forrest et al.*, 1980; *Okita et al.*, 1976], we consider our measured NO_3^- concentrations to be those of total inorganic NO_3^-, i.e., particulate NO_3^- plus gaseous HNO_3 [*Savoie et al.*, 1989*a*]. However, the concentration of gaseous HNO_3 in the near-surface MBL is typically around 20% or less of the total NO_3^- [*Savoie and Prospero*, 1982; *Savoie*, 1984; *Hastie et al.*, 1990].

The analyses of ^{210}Pb and ^7Be are performed on high-volume bulk aerosol samples collected on 20x25 cm Gelman glass fiber filters. These filters are changed on the same schedule as those used for the ion analyses. However, because island sources have no significant effect on the concentrations of these species, the samples are collected continuously without regard to wind conditions. Using the glass fiber filters, ^{210}Pb and ^7Be are collected with essentially 100% efficiency [*Turekian et al.*, 1989]. At Yale University, the filters are compressed into pellets which are placed directly into a high-purity germanium well γ detector and counted. Counting times vary from sample to sample depending on the activity levels encountered but are always sufficiently long to yield precisions of $\pm$10% or better for both nuclides. Filter blanks are insignificant.

At the University of Rhode Island, isentropic trajectories are calculated backward in time for potential temperatures corresponding to heights within and above the atmospheric mixed layer at the sampling station. Trajectories are calculated for 0000 UT and 1200 UT of each day. To partially assess the uncertainties that might arise because of strong deformation along the transport path, sets of trajectories for each time and altitude are backcalculated from the four corners of a 1° square that is centered on the sampling site. The analysis technique used and the issue of the adequacy of the required meteorological data are discussed by *Merrill et al.* [1989].

Mean Concentrations

The annual mean concentrations of the species measured at Barbados (Table 1) suggest that this site is heavily impacted by transport from continental sources as are all the other AEROCE sites in the North Atlantic (J. M. Prospero and D. L. Savoie, Aerosol nonsea-salt sulfate and nitrate concentrations over the North Atlantic: Evidence of strong continental impacts, submitted to *Science*, 1992) (hereinafter referred to as Prospero and Savoie, submitted manuscript, 1992). The concentrations of the continental tracers, dust and ^{210}Pb, are much greater than those in tropical South Pacific stations. Mineral aerosol concentrations are about 700 times greater than on American Samoa, while ^{210}Pb concentrations are 7 times greater [*Prospero et al.*, 1989; *Turekian et al.*, 1989]. Of the anionic species, the NO_3^- concentration is about five times higher than the mean values for tropical South Pacific stations while that for nss $SO_4^=$ is about 2 to 3 times higher [*Savoie et al.*, 1989*b*, *c*]. In an earlier study of NO_3^- and nss $SO_4^=$ concentrations at Barbados, *Savoie et al.* [1989*a*] suggest that about 60% of both the NO_3^- and the nss $SO_4^=$ is derived from continental sources.

TABLE 1. Mean Concentrations of Various Species at Barbados

Species	Units	Mean	Period
NO_3^-	$\mu g\ m^{-3}$	0.52	July 1984-June 1991
nss $SO_4^=$	$\mu g\ m^{-3}$	0.77	July 1984-June 1991
Mineral dust	$\mu g\ m^{-3}$	13.	July 1984-June 1991
^{210}Pb	mBq m^{-3}	0.46	Jan. 1989-Dec. 1990
^7Be	mBq m^{-3}	3.6	Jan. 1989-Dec. 1990
O_3	ppbv	21.7	Jan. 1990-Dec. 1990

For O_3, the annual mean concentration at Barbados is 1.6 times greater than the long-term average at American Samoa [*Oltmans and Komhyr*, 1986]. However, in the North Atlantic, the Barbados concentration is somewhat lower than those at the other sea level AEROCE stations. The annual mean concentration at Barbados is 30% lower than that at Bermuda and 40% lower than that at Mace Head, Ireland [*Oltmans and Levy*, 1992; *Simmonds and Derwent*, 1991].

Temporal Variations

The O_3 and NO_3^- concentrations at Barbados (Figure 2) exhibit large variations on a seasonal time scale and also on time scales of days to weeks. On a seasonal basis, O_3 values are highest in winter and lowest during the summer [*Oltmans and Levy*, 1992]. From June through September, values are typically in the range 10-20 ppbv. During winter and spring, the maxima are often factors of 2 higher, 25-38 ppbv. However, the minima are often quite low, frequently comparable to summer-fall levels.

As with O_3, the peak NO_3^- concentrations during the winter and spring are frequently as high or higher than those which occur during the summer and fall. However, in contrast to O_3, the winter-spring NO_3^- minima are frequently much lower than those during the summer and remain so for protracted periods.

For both species, the peaks and valleys in the time series tend to be more clearly defined and of longer duration (of the order of a week or longer) during the winter and spring than those during the summer and fall. In this analysis, we concentrate on the winter and spring seasons. The longer time periods of the peaks and valleys during these seasons permit a closer examination of the relationships between the variations in the concentrations of O_3 and NO_3^- and the concurrent variations in large-scale meteorology and transport patterns. In contrast, during the summer and early fall, there is an almost constant transport of dust and other materials from Africa to Barbados; consequently, the peaks and valleys in the concentrations of the various constituents are densely packed.

In a general sense, the short-term variability in concentrations is understandable in terms of the seasonal climatology of the region. During the summer and early fall, the tropical and subtropical North Atlantic is dominated by flow around the semipermanent Bermuda high-pressure center and Barbados is always located deep in the tradewind regime; hence transport from Africa dominates. In contrast, during the winter and spring, the continuous west-to-east movement of alternating high- and low-pressure systems across the mid-latitude North Atlantic results in dramatic variations in the large-scale meteorology and, consequently, in the air parcel trajectories to Barbados and its environs.

Anticorrelations Between NO_3^- and O_3

In this discussion, "anticorrelation" is used as a descriptive term for those periods when the NO_3^- concentration increases substantially at the same time that O_3 exhibits a sharp decrease and vice versa. The NO_3^- and O_3 data for the periods April-May 1989 and February-May 1990 are shown superimposed in Figure 3 in an expanded scale time series plot. In this figure, the numbered tic marks identify data points that will be discussed in detail in this paper. These points are generally selected because they constitute either maxima or minima in the short-term time series.

The strong anticorrelation between NO_3^- and O_3 is clearly evident from the many cases where the peaks and valleys in their respective concentrations are closely paired: see for example points 1, 4, 5, 6, 7, 8, 10, 11, 12, 13, 15, and 16. Some

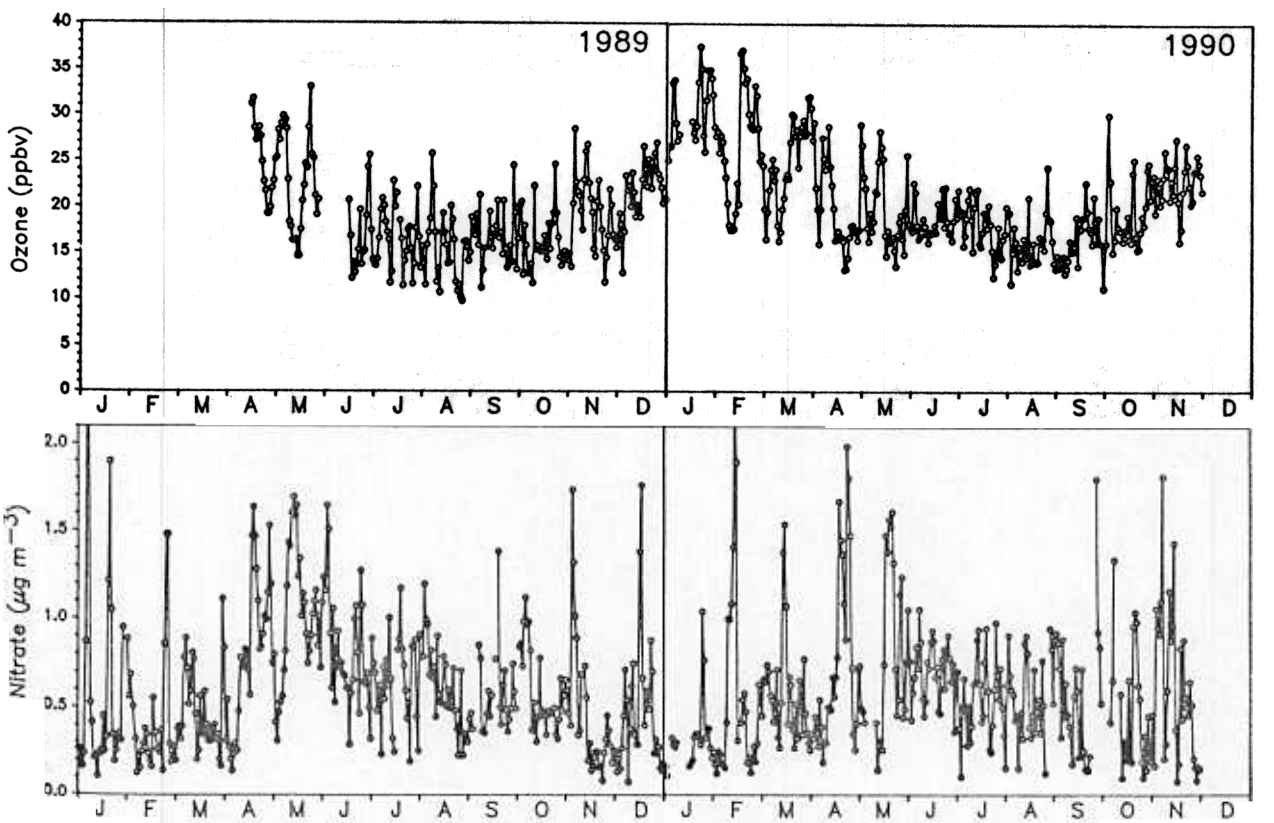

Fig. 2. Time series plots of the daily average O_3 and NO_3^- at Barbados, West Indies, during 1989 and 1990

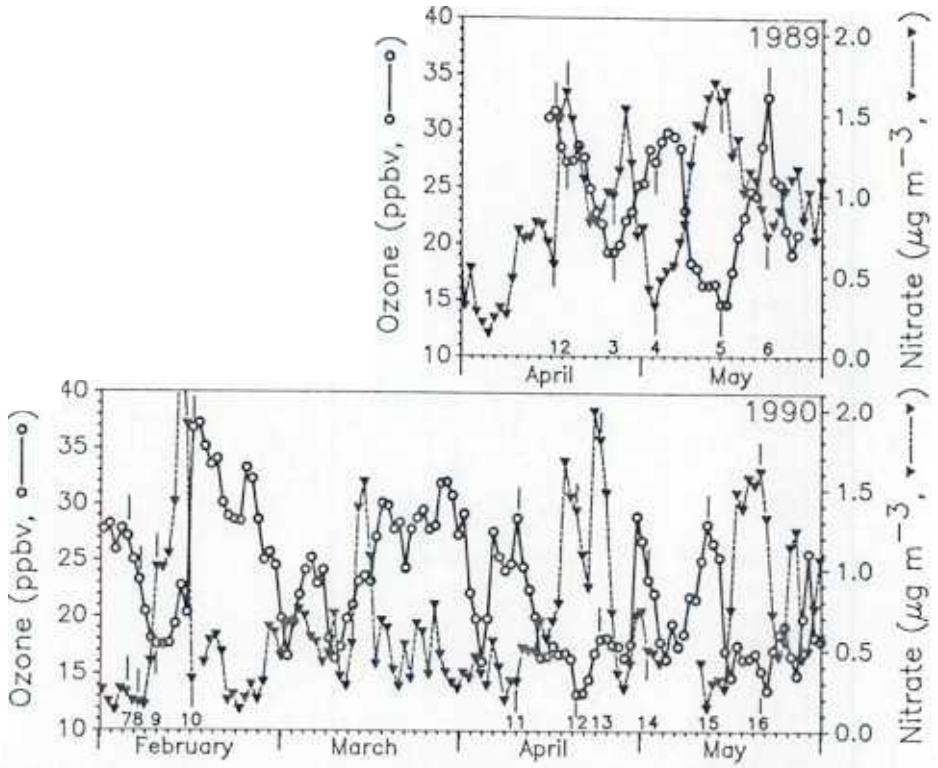

Fig. 3. Time series plots of the daily average O_3 and NO_3^- for April and May 1989 and for February through May 1990. Consecutive daily samples are connected by a line. The tic marks and the numbers at the bottom of the plots identify data for which we present corresponding trajectories (Figures 6, 7, and 8).

exceptions are also noted (e.g., points 2, 3, and 14). However, as we shall show later, these exceptions can generally be rationalized in a way that is consistent with our thesis. In Figure 3, the very sharp counter trends when going from peaks to valleys (or vice versa) are quite impressive. This is true even in many cases where there is not a clear opposition of peaks and valleys. For example, note the sharp reversal between points 3 and 4 and just prior to point 10. Although other examples of each type of interrelationship are evident in the data, we do not discuss them in this report.

While NO_3^- is strongly anticorrelated with O_3, it is strongly correlated with a number of other species in aerosols. This is evident in Figure 4 which presents, for the same time period as Figure 3, data for ^{210}Pb, mineral dust, ^7Be, and nss $SO_4^=$ as well as for O_3 and NO_3^-. It is readily apparent that many of the NO_3^- peaks are accompanied by pronounced peaks in all these species except ^7Be. In the following sections, we shall use these correlations, along with trajectories, to assess the possible sources for these species.

Assessment of the Sources of Nitrate

Strong relationships between NO_3^- and tracers of continental origin, ^{210}Pb and mineral dust, provide compelling evidence that the principal sources for the NO_3^- observed at Barbados are the continental regions in and surrounding North Africa. Even stronger relationships between NO_3^- and nss $SO_4^=$ and several trace elements suggests that these continental sources are anthropogenic rather than natural. The meteorology over and around North Africa indicates that the anthropogenic sources may include those in Europe and in northwest Africa north of the Sahel during the summer and fall. During the winter, they may, additionally, include those in the Sahel and in the savannah and tropical forest regions of North Africa.

The most persuasive evidence of a continental source of NO_3^- is its relationship to ^{210}Pb. The association between these two species is apparent from several perspectives. The strong correlation between NO_3^- and ^{210}Pb is illustrated in Figure 5 which presents all of the data for the entire 2-year period 1989-1990. A linear least squares regression analysis of these data using the maximum likelihood method of *Kendall and Stuart* [1961], which accounts for uncertainties in both variables yields the following equation:

$$NO_3^- = 0.022\ (\pm 0.058) + 1.29\ (\pm 0.11)\ ^{210}Pb \qquad (1)$$

where $\pm$ indicates the 95% confidence interval. The correlation of NO_3^- with ^{210}Pb (coefficient of determination $r^2 = 0.748$) accounts for 75% of the NO_3^- variance. The intercept is less than 5% of the mean NO_3^- concentration and is not significantly different from zero, suggesting that noncontinental sources do not contribute significantly to the NO_3^- concentrations at Barbados. The close correspondence of NO_3^- and ^{210}Pb concentrations on time scales of the passage of synoptic weather systems is illustrated in Figure 4. Throughout the time series, the concentrations of these two species exhibit nearly identical trends.

Figure 4 also shows that periods of high concentrations of NO_3^- and ^{210}Pb occur only in conjunction with significant concentrations of mineral dust. Because mineral dust at Barbados is known to be derived from the Sahara and its environs, this relationship indicates that the transport of high concentrations of NO_3^- and ^{210}Pb occurs by way of North Africa. The correlation between NO_3^- and mineral dust over a broad area of the tropical North Atlantic is well documented. The co-occurrence of high concentrations of NO_3^- and Saharan dust is clear throughout our Barbados aerosol chemistry record [*Savoie*, 1984; *Savoie et al.*, 1989*a*]. This association is also evident from the results obtained by others during aircraft

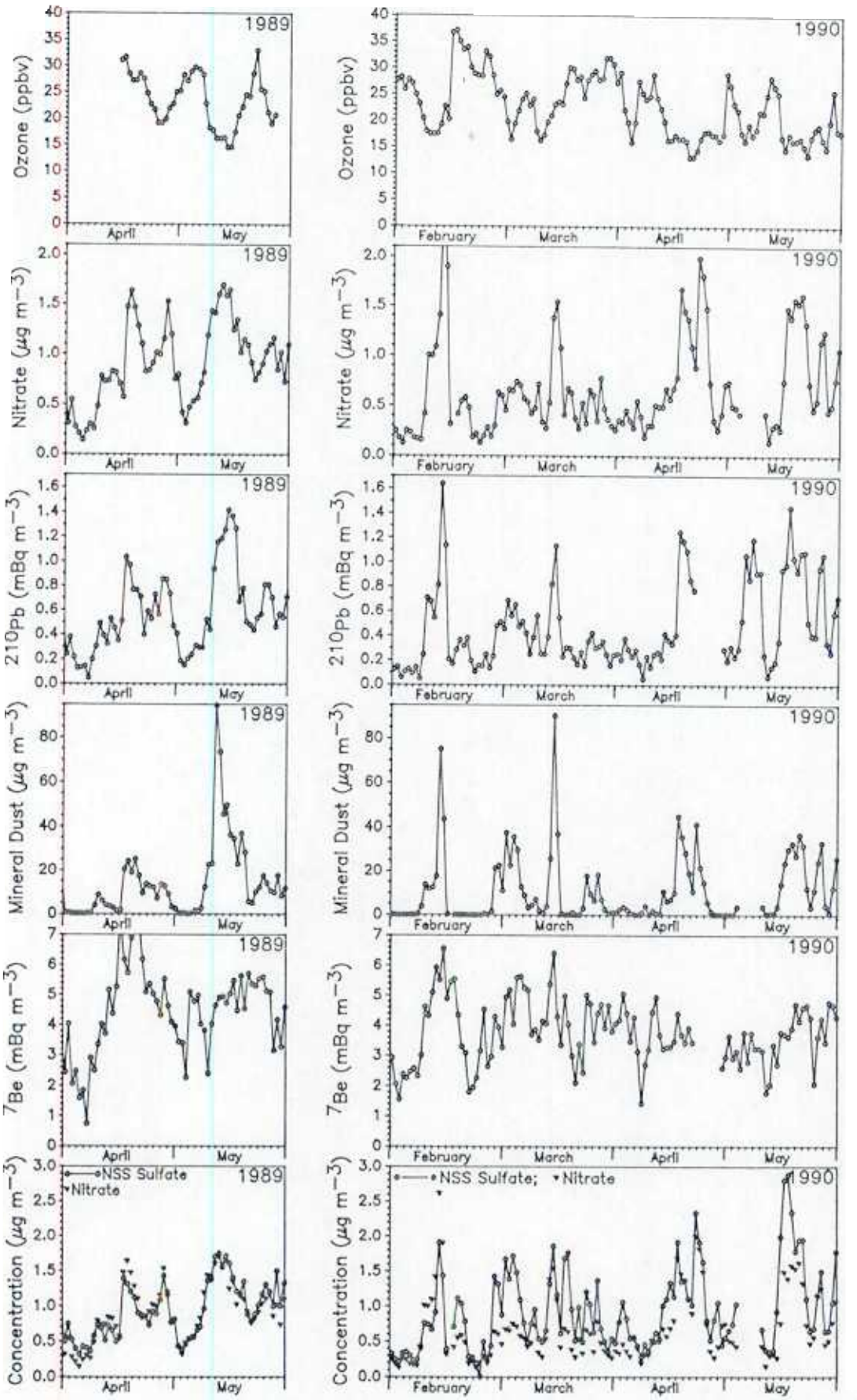

Fig. 4. Time series plots of O_3, NO_3^-, ^{210}Pb, mineral dust, ^7Be, and nss $SO_4^=$ for April and May 1989 and for February through May 1990. Nitrate concentrations are replotted along with nss $SO_4^=$ in the bottom figures to illustrate the varying relationship between these constituents, particularly during the late winter and spring of 1990.

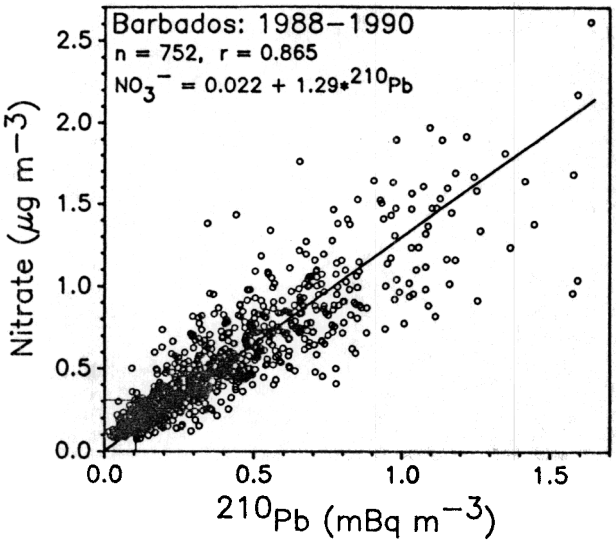

Fig. 5. Scatterplot of NO_3^- versus ^{210}Pb concentrations for all samples collected at Barbados during the period from August 1988 through December 1990: n is the number of independent samples; r is the correlation coefficient.

studies near Barbados [*Talbot et al.*, 1986] and in shipboard samples collected off the west coast of North Africa [*Savoie*, 1984].

We emphasize, however, that a common transport path for NO_3^-, ^{210}Pb, and dust does not necessarily indicate either a common production mechanism or a common source. At ocean islands in both the Pacific [*Turekian et al.*, 1989] and Atlantic, periods of high dust concentration are also periods of high ^{210}Pb. However, elevated ^{210}Pb levels may occur without substantial quantities of mineral aerosol. The production of mineral aerosol is more restricted both spatially and temporally than that of ^{210}Pb. Dust generation requires exposed soil and wind speeds in excess of a threshold level [e.g., *Helgren and Prospero*, 1987] whereas the escape of ^{222}Rn, the precursor of ^{210}Pb, from soils to the atmosphere is relatively insensitive to local vegetation and meteorological conditions. Areas that are major sources of dust to the atmosphere are also sources of ^{222}Rn, but the converse is not necessarily true. At Barbados, the correlation between ^{210}Pb and dust (coefficient of determination $r^2=0.48$, $n=756$) is statistically significant. However, there is considerable variability in the relationship with dust and the correlation is much weaker than that with NO_3^-. Similarly, the correlation of NO_3^- with Saharan dust ($r^2=0.34$, $n=806$) is much weaker than that with ^{210}Pb, suggesting that the NO_3^- is not a component of the soil material itself. Instead, these results support the idea that the NO_3^-, like ^{210}Pb, is principally derived from a gas-phase precursor with a continental source.

Despite the high correlation between NO_3^- and ^{210}Pb, it is unlikely that the Sahara itself is a significant source of a gaseous NO_3^- precursor. Anthropogenic sources in the region are weak and deserts are not believed to be major sources for microbially produced NO. For their model calculations, *Penner et al.* [1991] assumed an NO emission rate of zero for desert-type surfaces.

The NO_3^- is more likely derived from sources in Europe, the Mediterranean coastal region of North Africa (Med-Africa), and sub-Saharan Africa. Dust generation in the Sahara during the summer generally results from high winds associated with the intensification of an anticyclone centered over or off the coast of extreme northwest Africa [*Estoque et al.*, 1986]. In some instances, intensification of a cyclone over the central Sahara occurs concurrently. These conditions generate strong geostrophic flow from the northeast which are conducive to the transport of material from Europe across the Mediterranean and into the Sahara. Comparable flow patterns occur during the winter when cold fronts following cyclones and preceding anticyclones penetrate into the Sahara [*Morales*, 1979]. The southern penetration of this northerly flow, before it turns easterly, to cross the Atlantic is limited by the intertropical convergence zone (ITCZ). During the summer and fall, the ITCZ is located in the region of or to the north of the Sahel. During the winter and spring, the ITCZ is much farther south, frequently well south of the North African savannahs. Consequently, European and Med-African sources can potentially contribute to the concentrations of NO_3^- and other constituents over the Sahara and, subsequently, at Barbados throughout the year. The importance of European sources is supported by the isotopic composition of Pb in aerosols at Barbados [*Hamelin et al.*, 1989]. The transport of additional material from the savannah and forest regions of North Africa, for example, those in the Ivory Coast and Nigeria, to Barbados can only occur during the winter and spring.

Several lines of evidence indicate that the European, Med-African, and sub-Saharan sources of the NO_3^- that is transported to Barbados are probably anthropogenic. Many trace elements at Barbados, most notably Sb and Se which are generally considered to be tracers of anthropogenic input, are usually strongly enriched with respect to the concentrations one would expect from crustal material alone [*Arimoto et al.*, 1992]. The results presented in that study, those presented by *Savoie et al.* [1989*a*], and those from additional studies (D. L. Savoie and J. M. Prospero, University of Miami; R. Arimoto, W. G. Ellis, and J. T. Merrill, University of Rhode Island; and R. A. Duce, Texas A&M University; manuscripts in preparation, 1992) reveal that the concentrations of NO_3^-, nss $SO_4^=$, Sb, and Se at Barbados are all strongly interrelated. The results from the latter studies indicate that the anthropogenic nss $SO_4^=$/Sb ratio at Barbados is similar to those at Izania, Tenerife, and Mace Head Ireland, where pollutants are principally derived from European sources but is a factor of about 2 lower than than at Bermuda where North American sources dominate. Results from other studies clearly suggest that the transport of pollutants from Europe and Med-Africa could be high enough to account for the concentrations measured at Barbados. To be transported to Barbados, material from Europe must first be transported across the Mediterranean and into the Sahara. Results from studies on islands and aboard ship in the Mediterranean [*Bergametti et al.*, 1989; *Dulac et al.*, 1987; *Savoie*, 1984] indicate that such transport occurs frequently. Moreover, the concentrations of the pollutant indicator elements are far higher over the Mediterranean during periods of transport from Europe than those that are measured at Barbados. However, while the data suggest that Europe may be a significant source of pollutants at Barbados, *Dulac et al.* [1987] present substantial evidence that anthropogenic activity in Med-Africa is also a major source of heavy metals to the atmosphere.

As indicated previously, sources in the Sahel, savannah and forest regions of North Africa are likely to contribute additional material that could be transported to Barbados during the winter and spring. There is some evidence which suggests that these sources may include biomass burning which is at its seasonal peak during this time of year. In samples collected leeward of fires at Lamto, Ivory Coast, the NO_3^-

:$SO_4^=$ mass ratios were usually about 1 [*Cachier et al.*, 1991]. Concurrent measurements yielded ^{210}Pb and ^{210}Po activities between 11 and 40 mBq m^{-3} which are significantly greater than usual values in continental air, 2 and 0.2 mBq m^{-3}, respectively [*Lambert et al.*, 1991].

An impact of this biomass burning at Barbados is suggested by the large seasonal variation in the NO_3^-:nss $SO_4^=$ mass ratios. During winter and spring, the ratio is frequently about 1.44 ± 0.19, a factor of 4 higher than that during summer and fall, 0.361 ± 0.043 [*Savoie et al.*, 1989*a*]. *Talbot et al.* [1990] also found comparably high NO_3^-:nss $SO_4^=$ ratios during an incursion of Saharan dust into central Amazonia at the end of April 1987. During the spring seasons of 1989 and 1990, high NO_3^-:nss $SO_4^=$ ratios occurred during several extended periods. In fact, during April and May 1989, the NO_3^- and nss $SO_4^=$ mass concentrations were always about equal when the dust concentrations were greater than about 10 $\mu g\ m^{-3}$ (Figure 4). In 1990, ratios of about 1 or greater occurred during February 9-15, March 15-18, April 18-28, and May 20-June 1. Intriguingly, during the periods of high NO_3^-:nss $SO_4^=$ ratios, ^{210}Pb continues to track NO_3^- reasonably closely. While these results are suggestive of an impact from a biomass burning source, additional research is currently in progress to address this issue more definitively.

Assessment of the Transport Paths of O_3 and NO_3^-

Relation to Meteorology and Trajectories

To look for relationships between meteorological patterns and the concentrations of O_3 at Barbados, we initally used North Atlantic surface synoptic charts. This survey revealed that high O_3 concentrations at Barbados frequently occurred in conjunction with the movement of high-pressure centers eastward off the east coast of the United States. Wind patterns in this situation favor the transport of high-latitude air around the high and into the tropical Atlantic. Conversely, low O_3 concentrations were generally associated with either massive highs that covered a major portion of the North Atlantic or with east-west elongated highs at about 25° to 35°N. In either case, conditions would favor air flow to Barbados from the tropical regions to the east while preventing flow from higher latitudes.

Transport paths were studied by means of isentropic trajectories that were calculated for three different altitudes (potential temperatures) above the island. The 300K trajectories typically arrive over the site between the surface and about 900 hPa. In most transport studies for surface sampling sites, one would normally use 300K trajectories because they represent the transport path directly to the MBL at the station. However, past studies [*Prospero and Carlson*, 1972; *Carlson and Prospero*, 1972; *Westphal et al.*, 1988] have shown that the transport of African dust across the Atlantic occurs primarily in the free troposphere. From this level, dust particles can enter the MBL by settling through the trade wind inversion. However, based on the concurrent increases in ^{210}Pb and nss $SO_4^=$, which exist primarily in submicron particles [e.g. *Turekian et al.*, 1989; *Savoie and Prospero*, 1982], the primary transfer mechanism appears to be turbulent mixing across the inversion, partly as a result of convective activity. This mixing process will affect gases as well as particles, and hence it is potentially important for the transport of gases to the MBL and to Barbados via the free troposphere. Consequently, we also use isentropic trajectories to the free troposphere in our analyses; we chose the 310K trajectories because they frequently coincide with the altitude of the major pathway for the transport of dust [*Carlson and Prospero*, 1972] and other species [*Talbot et al.*, 1986] from Africa. In our investigation, we also included the higher-altitude 315K trajectories. However, in the final analysis, they provided little information that is relevant here, and hence they are not discussed in this report.

Overall, our analyses show that, in the MBL at Barbados, the high surface O_3 concentrations are associated with the transport of air parcels from high altitudes over the mid- to high-latitude regions of North America and/or the North Atlantic Ocean. Conversely, low O_3 levels are consistently associated with 300K trajectories in the tropical MBL. As previously stated, the 300K trajectories provide virtually no information with regard to the transport of material from Africa; in fact, even when they indicate flow from the east, they rarely reach back to Africa within 10 days. In contrast to ozone, as we shall show, the concentrations of the "African" components (e.g., Saharan dust, NO_3^-, ^{210}Pb) are usually highest when the 310K trajectories extend directly back to Africa and are much lower when the 310K trajectories come from high latitudes.

Since we cannot, in this format, provide a discussion of every trajectory that was considered in this analysis, the following examples serve to illustrate the consistency with which the data and the concurrent trajectories fit our overall conclusions. The cited trajectories (Figures 6 to 8) are numbered sequentially in time. The NO_3^- and O_3 data corresponding to a given trajectory are marked with the same number in Figure 2 and also noted on the trajectory figures themselves.

February 1990. One of the clearest cases of the anticorrelation between O_3 and NO_3^- occurs in early-to-mid February, 1990. This case gives a particularly clear indication that the higher latitudes are a strong source of O_3 but not of NO_3^-. During February 4-5, the NO_3^- concentration was very low, 0.234 $\mu g\ m^{-3}$, and the O_3 concentration was high, 27.1 ppbv. During this period, the 300K trajectories were from about 500 to 600 hPa over the northern United States and southern Canada (Figure 7, part 7). Over the course of the next several days, the trajectories indicated a gradual loss of influence from high-altitude and high-latitude locations; concurrently, O_3 decreased to 17.5 ppbv (Figure 7, parts 8 and 9). By February 14, NO_3^-, ^{210}Pb, and Saharan dust increased to their highest levels for winter and spring 1990 with concentrations of 2.61 $\mu g\ m^{-3}$, 1.64 mBq m^{-3}, and 75 $\mu g\ m^{-3}$, respectively. On February 16, the trajectories (Figure 7, part 10) again indicated strong transport from high latitudes and altitudes and O_3 increased sharply to nearly 37 ppbv, its highest level of the year. At the same time, NO_3^- decreased by a factor of 6 from 1.9 to 0.3 $\mu g\ m^{-3}$.

The extreme changes in the trajectory patterns during this period are readily explained by changes in the large-scale meteorology over the North Atlantic. Surface synoptic charts (National Hurricane Center, Coral Gables, Florida) for February 10 showed a massive dome of high pressure (centered at about 40°N, 35°W) which controls the wind patterns over virtually all of the temperate and tropical North Atlantic. Easterly winds prevailed over the entire region south of 30°N. As the high moved toward the east on February 11, one cold front moved off the coast of North America while another moved into North Africa. It is likely that strong winds associated with the North African front were responsible for generating the very high dust concentrations that were seen several days later at Barbados. These same northerly winds would be conducive to the transport of pollutants from Europe and North Africa into the Sahara.

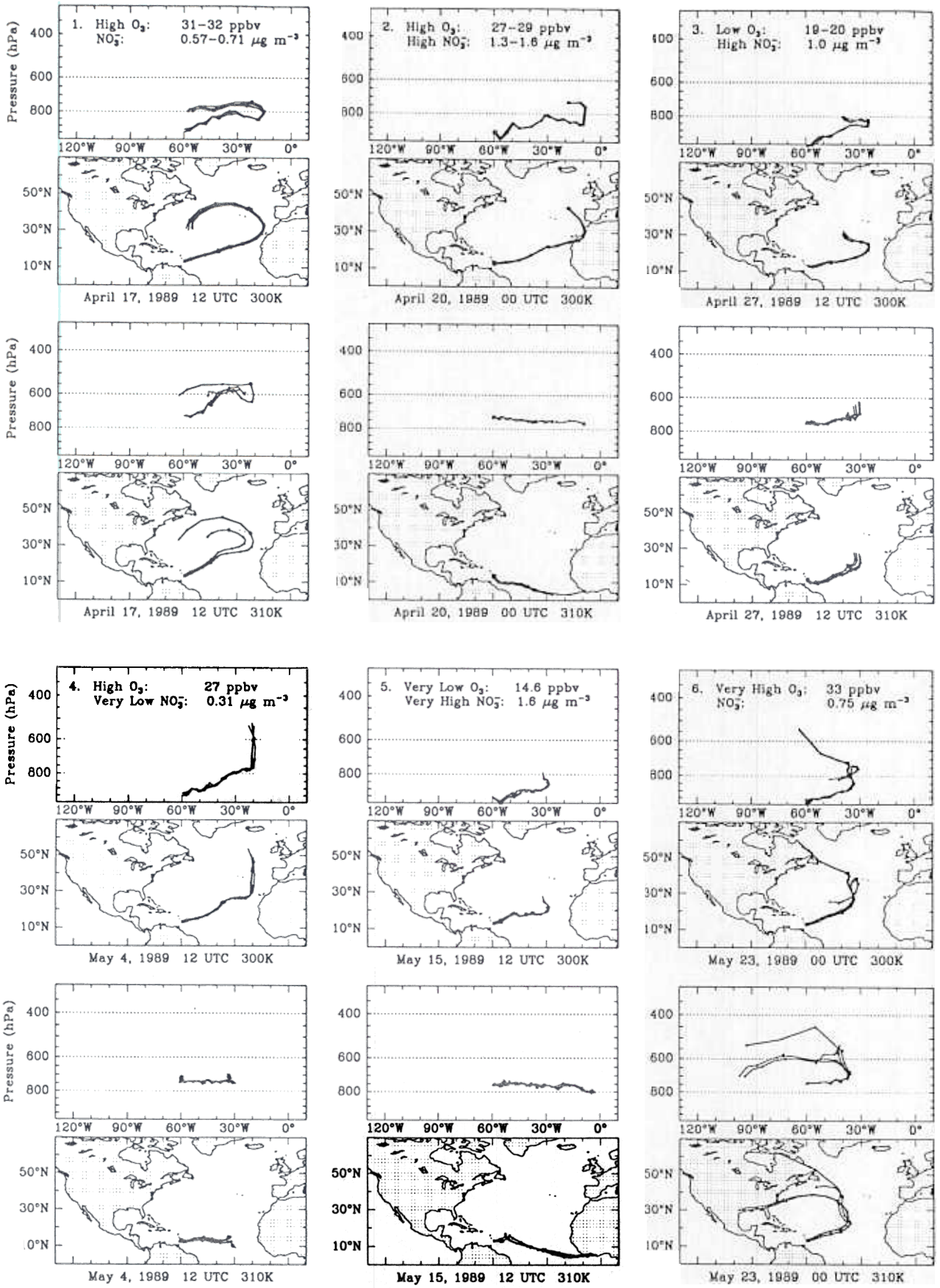

Fig. 6. Selected isentropic trajectories to the MBL between the surface and 950 hPa (300K) and to the free troposphere at about 750 hPa (310K) over Barbados during April and May 1989. The number of the trajectory is the same as for the corresponding daily mean concentrations illustrated in Figure 3. Two displays are presented for each of the trajectories. The upper figure indicates the pressure level (altitude) and longitude of the air parcels and the lower figure displays the latitude and longitude of the parcels for the same period of time. The dots are spaced at 24-hour intervals. The large dots simply indicate the days of the month that are whole multiples of five.

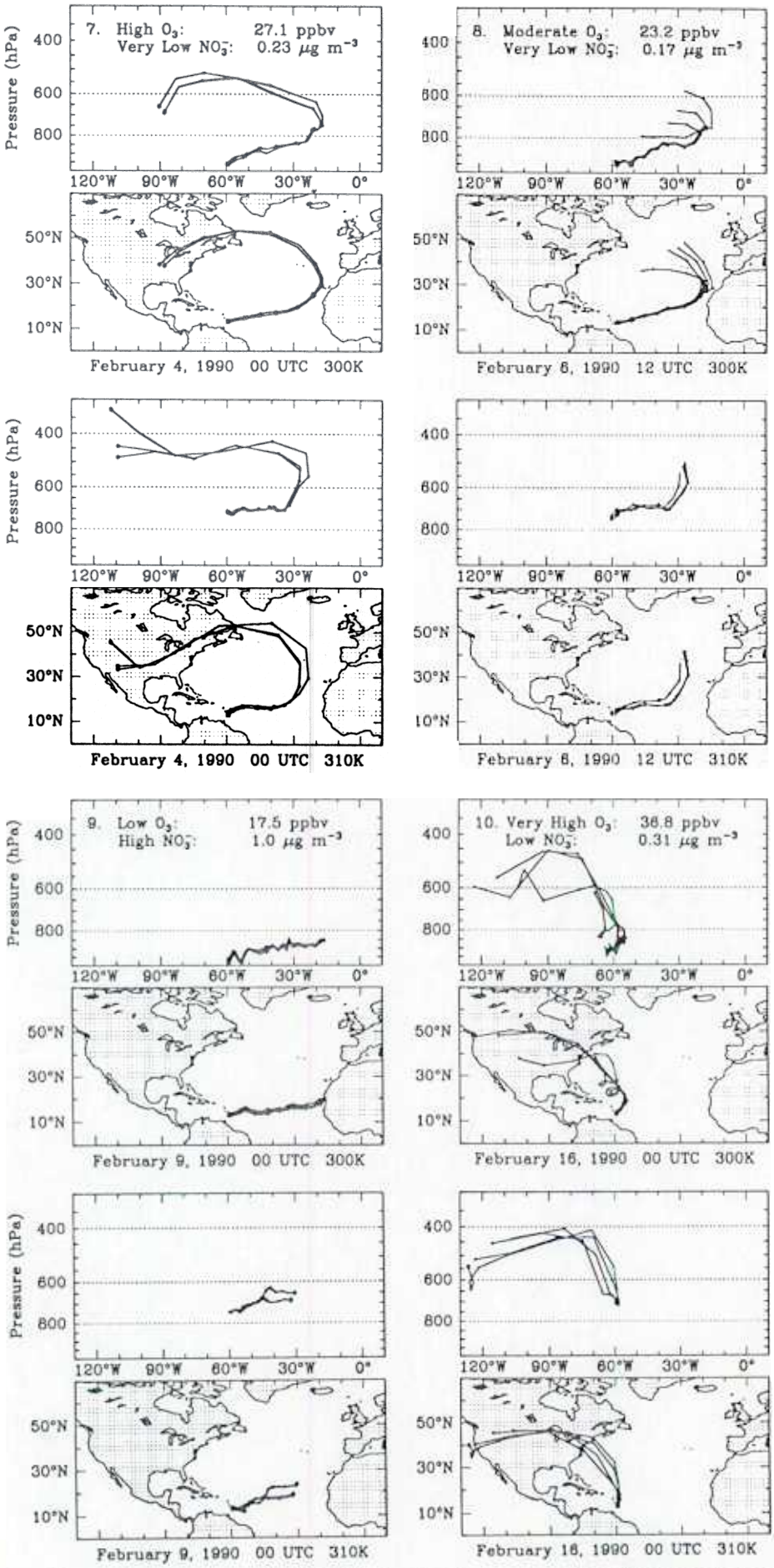

Fig. 7. Selected isentropic trajectories to the MBL (300K) and to the free troposphere (310K) over Barbados during February 1990. See the Figure 6 caption for more detail.

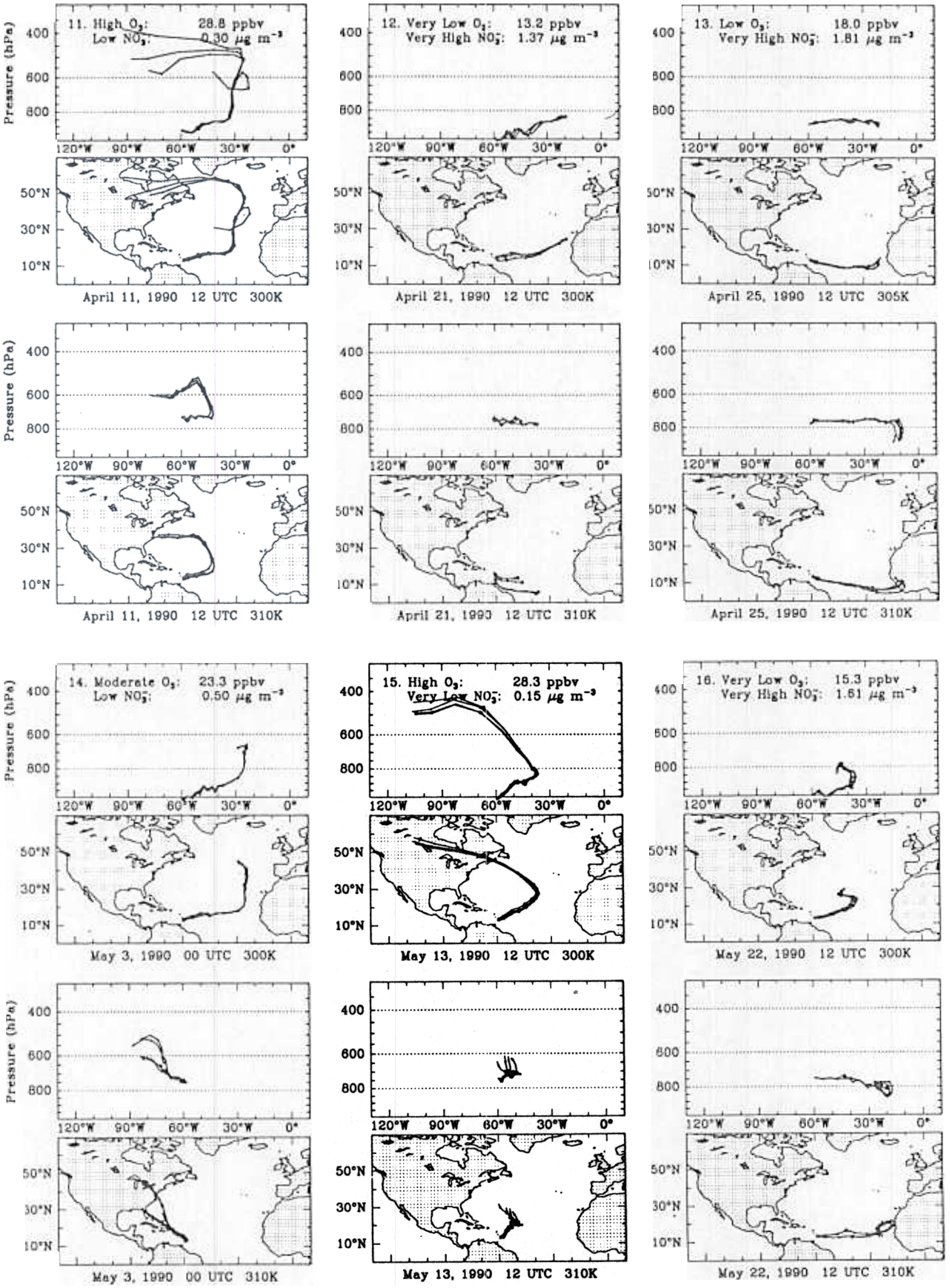

Fig. 8. Selected isentropic trajectories to the MBL (300K) and to the free troposphere (310K) over Barbados during April and May 1990. See the Figure 6 caption for more detail.

Over the course of the next several days, the North American cold front continued to move toward the east followed by another high-pressure system. By February 14, the high was east of north Florida and the cold front extended toward the northeast from south of Puerto Rico. By February 15, the cold front extended almost to Barbados and, on February 16, it was east of Barbados and extended almost into northern South America. The subsiding northerly airflow west of the cold front and east of the high was responsible for the rapid transport of high-altitude air from over the northern United States to the boundary layer at Barbados. As indicated above, this air flow brought very high concentrations of O_3 to Barbados but extremely low quantities of NO_3^-.

April 1990. The period from April 9 to May 3, 1990, provides an excellent example of the association of high NO_3^- and low O_3 levels with strong midtropospheric transport from Africa as well as the low NO_3^- and high O_3 levels associated with transport from high altitudes and latitudes. At the beginning of this period, the NO_3^-, ^{210}Pb, and dust concentrations were near their lowest levels for spring 1990 while O_3 was fairly high. Both the 300K and 310K trajectories indicated transport from 400 to 600 hPa over the central North Atlantic and North America (Figure 8, part 11).

From April 15 to May 1, 1990, all of the daily mean O_3 concentrations were very low, less than 18 ppbv. During most of this period (from April 18-April 28), the concentrations of the "African" constituents were all very high: NO_3^-, 0.73-2.0 $\mu g\ m^{-3}$; ^{210}Pb, 0.41-1.25 mBq m^{-3}; and dust 10-45 $\mu g\ m^{-3}$. The 300K trajectories during this part of the period were all confined below about 800 hPa and to latitudes south of 30°N (Figure 8, parts 12 and 13), while the 310K trajectories indicated strong midtropospheric transport from Africa (Figure 8, part 13).

By April 29-30, the "African" species had dropped to very low levels (NO_3^- to 0.26 $\mu g\ m^{-3}$ and dust to less than 1 $\mu g\ m^{-3}$) and, on May 1-2, the O_3 concentration increased sharply to 29.0 ppbv from 17.6 ppbv on the previous day. During this time, the 300K trajectories showed evidence of transport from high latitudes and altitudes, while the 310K trajectories indicated free tropospheric transport from over the United States (Figure 8, part 14).

May 1990. The data from May 13-29, 1990, also show the strong anticorrelation between O_3 and NO_3^- and provide additional evidence that high O_3 and low NO_3^- concentrations are associated with transport from high latitudes, whereas low O_3 and high NO_3^- concentrations are associated with transport from Africa. From May 13-16, 1990, the O_3 concentrations at Barbados were all greater than 25 ppbv. At the same time, the concentrations of the "African" species were all very low: NO_3^-, 0.15 to 0.32 $\mu g\ m^{-3}$; ^{210}Pb, 0.07-0.18 mBq m^{-3}; and dust, all less than 1 $\mu g\ m^{-3}$. This period was characterized by considerable meteorological activity over the North Atlantic with a combination of several high- and low-pressure centers. The surface weather map indicated northerly winds over portions of the central (east-west) North Atlantic which have the potential for affecting Barbados. Rapid flow from 400 to 500 hPa at 50°-60°N over central Canada was indicated by the 300K trajectories (Figure 8, part 15), whereas nearly stagnant conditions prevailed in the midtroposphere until May 15.

By May 17, a ridge of high pressure extended across 25°N, effectively shutting off transport from the north. From 0000 UTC, May 17, 1990, the 300K trajectories were confined below about 750 hPa and south of 30°-40°N (Figure 8, part 16). At this time, O_3 decreased to about 15 ppbv and remained at that level for about a week. Over the course of a few days the 310K trajectories shifted toward Africa and the concentrations of the "African" constituents increased dramatically: NO_3^- to 0.75 $\mu g\ m^{-3}$ and then to 1.5-1.6 $\mu g\ m^{-3}$; ^{210}Pb to more than 1 mBq m^{-3}; and dust to 20-40 $\mu g\ m^{-3}$.

April 1989. April 18 to 22, 1989, exemplifies the less frequent periods with concurrently high O_3 (27-29 ppbv) and high concentrations of the "African" components: NO_3^-, 1.3-1.6 $\mu g\ m^{-3}$; ^{210}Pb, 0.76-1.03 mBq m^{-3}; and dust, 19-25 $\mu g\ m^{-3}$ concentrations. Although there is no anticorrelation between O_3 and NO_3^- during this period, the trajectories are consistent with our hypothesized sources and transport patterns for both of the constituents. The 300K trajectories, passing through 700-800 hPa between 40° and 50°N, provided for the transport of high concentrations of O_3 (Figure 6, part 2). At the same time, the 310K trajectories, which arrived directly from the southern coast of West Africa, were responsible for the very high concentrations of the "African" components. These results indicate that rare events such as this need not be a consequence of major changes in the sources or transport of the two species. They are rare simply because it is unusual for the large-scale meteorology to concurrently promote transport from high latitudes and altitudes to the boundary layer at Barbados and strong midtropospheric transport from Africa.

Summary 1989. The other 300K trajectories during 1989 support our overall conclusion with regard to the source of the high O_3 concentrations. All of the periods having O_3 concentrations higher than 25 ppbv were associated with transport from high latitudes and altitudes to the boundary layer at Barbados (Figure 6, parts 1, 2, 4, and 6). Conversely, when such transport was restricted, the O_3 concentrations were relatively low (Figure 6, parts 3 and 5).

The 1989 310K trajectories were generally consistent with the concentrations of the "African" components. The NO_3^- concentrations were highest when these free tropospheric trajectories were directly from Africa (Figure 6, parts 2 and 5) and lowest when they were from higher latitudes (Figure 6, parts 1 and 6). However, there were also some periods during which high dust concentrations provide irrefutable evidence for the transport of materials from Africa, but the 310K trajectories did not approach Africa to closer than 10° longitude. Examples of this feature are the data and trajectories for April 27, 1989 (Figure 6, part 3), and May 23, 1989 (Figure 6, part 6). These apparent inconsistencies are important, and their ramifications with regard to the attribution of sources are discussed later.

Sources of O_3 and NO_3^-

Comparisons with other North Atlantic O_3 data. The trajectories during the high O_3 periods at Barbados strongly suggest that the high spring O_3 concentrations are associated with transport from high latitudes and/or altitudes. Comparisons with O_3 data from other regions indicate that this hypothesis is quite reasonable. For example, from February through May, the monthly mean O_3 concentrations at Bermuda (32°N, 64°W) range from about 37 to 50 ppbv, with daily means often in the range of 70-80 ppbv [*Oltmans and Levy*, 1992]. Measurements at the high-altitude (2376 masl) BAPMoN and TOR station at Izania, Tenerife (28°N, 17°W), yield comparable monthly means (70-80 ppbv) throughout the year [*Schmitt et al.*, 1988]. The consistently high concentrations at Izania appear to be characteristic of stations in the free troposphere; comparable levels occur at Mauna Loa, Hawaii [*Oltmans and Komhyr*, 1986]. Allowing for an O_3 destruction rate of 2 ppbv/day under low NO_x conditions [*Oltmans and Levy*, 1992], the O_3 levels measured at Bermuda

and Izania could support the high springtime concentrations measured at Barbados since transport times are typically only several days.

Beryllium 7 as a tracer for stratospheric O_3. The most likely source for the high O_3 concentrations associated with transport from the high altitudes and latitudes is downmixing from the stratosphere. Hence one might expect to see concurrent high ^7Be concentrations. Unfortunately, the use of ^7Be as a tracer for these air masses is complicated by what appears to be an equally strong association of higher ^7Be concentrations with peaks in NO_3^-, ^{210}Pb, and mineral dust. This association may be a consequence of the strong vertical mixing that takes place over the Sahara, typically to altitudes of 6 km or more [*Carlson and Prospero*, 1972; *Prospero and Carlson*, 1972; *Westphal et al.*, 1988]. In the process, large amounts of ^7Be may also be downmixed from the upper troposphere. If this is the case, then one might expect significant amounts of O_3 to be downmixed at the same time. However, O_3 and ^7Be are not strongly correlated during dust outbreaks and, in fact, the O_3 concentrations are usually quite low during these periods. The phenomena which result in these seemingly inconsistent features are clearly important and need to be thoroughly investigated.

The subsidence of high-latitude - high-altitude air around high-pressure centers in the North Atlantic does appear to contribute significant amounts of ^7Be during some periods. This source is particularly notable during several spring periods. For example, during February 1990, the first part of the nearly 2-week long ^7Be peak appears to be associated with the strong peaks in NO_3^-, ^{210}Pb, and mineral dust, i.e., with transport from Africa. However, ^7Be remains high even after the sharp decline in those "African" constituents in mid-February. At the same time that the "African" components decrease sharply, O_3 rises sharply to its maximum for the 4-month period. During the several days following the rapid plunge in the concentrations of the "African" components, much of the ^7Be at Barbados may be associated with the high O_3 concentrations that we believe to be indicative of high-latitude - high-altitude air parcels. The next peak in ^7Be (although only about 2 days long) is also associated with a peak in O_3; the concentrations of the "African" constituents are all extremely low. Clearly, a more detailed analysis will be required to definitively assess the sources of ^7Be at Barbados before it can be used, either alone or in combination with other species, as a definitive indicator of specific atmospheric transport pathways.

Biomass burning as a source of O_3 and NO_3^-. Our results clearly show that the free tropospheric transport of material from Africa appears to have, at most, a minor effect on the O_3 concentration in the boundary layer at Barbados. Unless there is concurrent transport from high latitudes and altitudes, O_3 drops to near summertime levels even when NO_3^- and ^{210}Pb are very strongly enhanced relative to nss $SO_4^=$. If this enhancement is indeed a consequence of biomass burning in Africa [*Savoie et al.*, 1989*a*], these results suggest that the effect of the biomass burning on the O_3 levels in the MBL at Barbados is far smaller than that of transport from higher latitudes. However, there is, at least, some indication that the biomass burning may have a small but significant effect. For example, at the peak of the high NO_3^--^{210}Pb episode in February 1990, the O_3 concentration is about 5 ppbv greater than the levels present during the first few days of the episode. Comparable increases during other periods may also be arguably attributed to the effects of biomass burning.

We can make a rough estimate of the level of O_3 enhancement that we should expect to see at Barbados because of biomass burning in Africa. During the periods that we suggest are impacted by biomass burning, the NO_3^-/nss $SO_4^=$ ratios at Barbados are a factor of about 2 higher than those during the summer and during the non-impacted winter and spring periods. If, on the basis of the NO_3^-/nss $SO_4^=$ ratio, we attribute about 50% of the NO_3^- during the enhanced periods to biomass burning, then the consistency of the $NO_3^-/^{210}Pb$ ratio requires that we also attribute about 50% of the ^{210}Pb to the same source. For many of the enhanced periods, this amounts to about 0.5 mBq m^{-3} of ^{210}Pb which is a factor of 20 lower than the concentrations of about 11 mBq m^{-3} which have been measured in the biomass burning plumes themselves [*Lambert et al.*, 1991]. During transport, O_3 from the fires should be subject to similar mixing and dilution processes. Assuming an O_3 concentration of the order of 100 ppbv in the biomass burning region [*Cros et al.*, 1991], a mixing and dilution factor of 20 would yield a concentration of about 5 ppbv above the background level in the diluted air by the time the products of the plume reach the MBL at Barbados. Implicit in this estimate is the assumption that substantial amounts of O_3 are not generated or destroyed by photochemical processes in the plume during transport. Testing the validity of this assumption, while necessary, is clearly outside the scope of this report.

Implications Regarding Backtrajectories and Source Attribution

The results presented above have several important implications with regard to the use of backtrajectories for assessing the sources of atmospheric constituents. First, it is clear that transport assessments must be based on trajectories that are calculated for several altitudes above the sampling site. The Barbados data shows that, when the concentrations of the "African" components in the free troposphere are substantially higher than those in the boundary layer, vertical mixing can have a tremendous impact on the concentrations measured at the surface [*Carlson and Prospero*, 1972; *Talbot et al.*, 1986].

While there are difficulties in interpreting isentropic trajectories, the situation with isobaric trajectories would be much worse even if they were available for multiple levels. Because isobaric trajectories cannot account for vertical transport, they could never of themselves implicate a high-altitude source.

As noted several times in the preceding discussions, there were occasions when high dust concentrations provided irrefutable evidence of transport from Africa that was not manifested in the isentropic trajectories. There are several possible reasons for these discrepancies. Lateral diffusion (horizontal mixing) during transport across the Atlantic may be an important phenomenon that cannot be adequately addressed even with ensembles of trajectories. In this regard, it is important to remember that downmixing into the boundary layer can occur throughout the period of cross-Atlantic transport, and hence there are a myriad of possible transport paths by which the "African" constituents could reach Barbados.

Moreover, relatively small uncertainties in the locations of trajectories can be critical, especially in regions of strong wind shear and/or of confluence of air masses from widely spaced geographical regions. An example of the latter is presented in Figure 9; in the ensemble of four trajectories, the trajectories to the two northern points are from the north whereas those to the two southern points are from Africa. If the ensemble had been shifted 1° farther south, there would have been no indication of a potential input from the north. Conversely, if

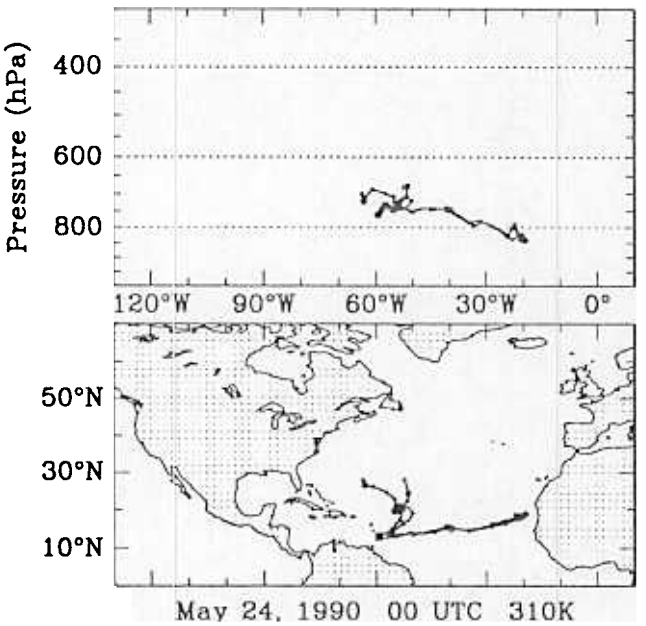

Fig. 9. Isentropic trajectory to the free troposphere (310K) over Barbados at 0000 UTC, May 24, 1990. See the Figure 6 caption for more detail.

the ensemble had been shifted 1° farther north, the potential transport from Africa would have been missed completely. This situation, coupled with uncertainties in the trajectories and short-term north-south movements of the transport paths themselves, probably accounts for the occasional discrepancies between the trajectories and the measured concentrations of the "African" constituents.

In the case of NO_3^- at Barbados, relatively small errors in the trajectories could yield very large errors in the assessment of source region. Reliance on the trajectories alone would have lead to the conclusion that the stratosphere and North America are frequently major sources for NO_3^- at Barbados which is clearly contrary to our conclusion which is based on all of the data collectively. Nevertheless, the isentropic trajectories, when coupled with other evidence (e.g., the consistency of the NO_3^-:^{210}Pb ratio, the concurrency of high NO_3^- and ^{210}Pb concentrations with those of mineral dust, and the fact that the mineral dust originates in Africa), strongly support the conclusions that the majority of the NO_3^- arrives at Barbados via Africa and that the stratosphere and North America are minor sources at most.

Conclusions

The high concentrations of O_3 measured at Barbados during the winter and spring are a consequence of the transport of air parcels from high latitudes and altitudes to the MBL at the site. In contrast, high NO_3^- concentrations occur during periods of strong transport from Africa. Although the meteorological conditions which result in high concentrations of these two species are not mutually exclusive, they usually do not occur simultaneously. Consequently, the dramatic anticorrelations which frequently occur between O_3 and NO_3^- during the winter and spring at Barbados appear to be driven by changes in the major atmospheric transport patterns over the North Atlantic and the large geographical separation between the major sources of NO_3^- and O_3 rather than by any chemical or photochemical interactions between them and/or their precursors.

Taken together, the strong correlation between NO_3^- and ^{210}Pb, the concurrency of their peaks with those of Saharan dust, and the very low NO_3^- concentrations associated with trajectories from the high latitudes form a strong basis for several conclusions concerning the major sources of NO_3^- at Barbados. (1) Lightning, the middle troposphere and stratosphere, and pollution sources in North America are, at most, very minor sources of NO_3^- in the atmosphere over the western tropical North Atlantic. (2) Nitrate concentrations are directly linked to atmospheric transport from Africa, an observation that is consistent with the hypothesis that Europe and/or North Africa are the major source regions. (3) The concurrent enhancement of NO_3^- and ^{210}Pb relative to nss $SO_4^=$ during some winter and spring periods at Barbados is consistent with the hypothesis that these enhancements are actually a consequence of biomass burning in and south of the North African savannahs.

If European and/or North African pollution sources are largely responsible for the NO_3^- and nss $SO_4^=$ concentrations observed at Barbados [*Savoie et al.*, 1989*a*], then the photochemically-produced O_3 associated with those pollutants may account for the fact that the typical summertime O_3 concentrations at Barbados are 5-10 ppbv higher than those at American Samoa in the tropical South Pacific [*Oltmans and Levy*, 1992]. This feature could also result from higher NO_x levels and generally stronger stratospheric input of O_3 to the troposphere in the northern hemisphere as compared to the southern [*Levy et al.*, 1985]. However, our results provide compelling evidence that the European and African sources are not responsible for the much higher O_3 concentrations measured during the winter and spring.

We hypothesize that the concurrent enhancements of NO_3^- and ^{210}Pb relative to nss $SO_4^=$ during winter and spring at Barbados are a consequence of African biomass burning. Burning is also believed to be an important source of O_3 [e.g., *Delany et al.*, 1985; *Fishman et al.*, 1990, 1991; *Watson et al.*, 1990]. Calculations based on the enhancements of ^{210}Pb at Barbados and its measured concentrations downwind of fires indicate that an O_3 concentration of the order of 100 ppbv in the plumes should yield about a 5 ppbv increase in the O_3 level that we measure in the MBL at Barbados. Our evaluation of the O_3 time series indicates that this is roughly the magnitude of increase that does, in fact, occur. We acknowledge, of course, that the effect may be significantly larger in the free troposphere above Barbados where the major transport actually occurs. It is pertinent in this regard that the analyses of satellite data [*Fishman et al.*, 1990, 1991; *Watson et al.*, 1990] indicate that tropospheric O_3 plumes from major biomass burning areas in equatorial Africa south of the intertropical convergence zone (ITCZ) are transported over long distances and have substantial impacts on the O_3 levels thousands of kilometers from the sources. Interestingly, however, the authors find no such major impact from biomass burning in areas of Africa north of the ITCZ, a finding which is clearly consistent with our results. However, the absence of a significant tropospheric O_3 signal in the satellite imagery and in our data raises a question about biomass burning as a source of O_3: Why should the O_3 production be different in different burning regions of tropical Africa?

Atmospheric transport from continental sources appears to play a dominant role in chemistry of the atmosphere over the North Atlantic as reflected in the much higher concentrations of NO_3^-, nss $SO_4^=$, and ^{210}Pb as compared to remote Pacific stations. The results presented here along with others from the AEROCE program provide a substantial data base for testing the ability of general circulation and other three-dimensional

models to simulate that transport. A recent synthesis of field measurements and modeling results [*Galloway et al.*, 1992] indicates that the nitrogen and sulfur transport simulated by the models is far weaker over the open ocean than that indicated by our measurements or those of other investigators. In particular, the models grossly underestimate transport to Barbados. The model estimated means are near the level that, based on the measurements, one expects for periods when there is no significant transport from Africa. However, such periods are comparatively rare, virtually never occurring during the summer and fall and much less than 50% of the time during the winter and spring. Such models are likely to play a major role in predicting how the world's weather and climate will change as a consequence of man's activities. However, to serve that purpose they must first be able to correctly simulate the transport from the major source regions as well as the resulting concentration fields for current conditions.

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