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Temporal variability of summer-time ozone and aerosols in the free troposphere over the eastern North Atlantic

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Abstract. In the free troposphere over Tenerife in the summer, O_3 concentrations are anti-correlated with major pollutant aerosols (nss-$SO_4^=$ and NO_3^-) and with ^{210}Pb, a tracer for boundary layer sources. In contrast, O_3 is highly correlated with ^7Be, a product of cosmic ray interactions in the upper troposphere and stratosphere. This suggests that natural O_3 sources (i.e. the stratosphere) might be playing an important role. Nonetheless our results do not preclude the possibility that substantial amounts of pollution-related O_3 could be transported in the free troposphere. However, to be consistent with our results, the transport mechanisms would have to incorporate efficient processes for the removal of pollutant aerosol species and ^{210}Pb.

Introduction

Tropospheric O_3 is both a greenhouse gas and a strong oxidant and is a precursor to the formation of highly reactive radicals such as OH which play a critical role in controlling the lifetimes and fates of many chemical species [*Levy*, 1971; *Thompson*, 1992]. Tropospheric O_3 is principally derived from two sources: episodic injection of air from the stratosphere where most of the Earth's O_3 column inventory resides; and *in situ* photochemical production in the polluted continental boundary layer where most of the nitrogen oxides (NO_x) and reactive organic carbon compounds (VOC's) are emitted. Conversely, there is the potential for net chemical destruction of O_3 in the free troposphere where NO_x levels are low. Results from numerical simulations suggest that increasing anthropogenic emissions of both NO_x and VOC's are leading to higher concentrations of tropospheric O_3 throughout the northern hemisphere [e.g., *Thompson*, 1992]. Direct measurements indicate that O_3 has been increasing at an annual rate of 1-2% per year for the past several decades at some relatively remote European surface sites and may have more than doubled over the last 100 years [*Janach*, 1989; *Volz*, 1993]. In contrast, a recent analysis of two decades of ozonesonde data from a wide range of sites [*Logan*, 1994] finds that, while O_3 appears to have increased in the free troposphere over a number of stations in Europe, it has remained relatively constant in most other regions [*Oltmans*, 1993; *Logan*, 1994], e.g. at Mauna Loa Observatory (MLO), Hawaii (19.53°N, 155.57°W) [*Oltmans and Levy*, 1994].

The export of O_3 from continental regions to the marine atmosphere involves complex meteorological [*Moody et al.*, 1995] as well as chemical [*Jacob et al.*, 1993] processes. This report focuses on data from Izaña, Tenerife, Canary Islands (28°18'N, 16°29'W) where, as a part of the Tropospheric Ozone Research (TOR) program, O_3 has been measured at a Spanish meteorological observatory located on a mountain ridge (elevation 2370 m). This region is affected by a variety of air masses [*Sancho et al.*, 1992], including relatively clean air from the central North Atlantic and more polluted air from Europe or North America. The data from Izaña are interesting because of the strong and coherent temporal changes in species concentration and their clear association with specific meteorological conditions.

Izaña experiences a pronounced orographic flow regime [*Schmitt et al.*, 1988]. At night downslope winds prevail and samples should be representative of free tropospheric air. Night-time O_3 at Izaña exhibits a marked seasonal cycle [*Schmitt et al.*, 1988; *Schmitt and Carretero*, 1995]. From August through February, the composited monthly mean concentrations (1987-1994) are relatively constant, with values of 38-42 ppbv. Mean concentrations increase rapidly in the spring to a maximum of about 57 ppbv in June and then decrease through the summer. The monthly means are similar to those at MLO [*Oltmans and Levy*, 1992] except from June through September when the Izaña means exceed those at MLO by 8-15 ppbv.

The high summer means at Izaña have previously been attributed to the impact of anthropogenic species [*Schmitt et al.*, 1988; *Schmitt and Carretero*, 1995]. Relatively high concentrations of O_3 are generally associated with back-trajectories from north of Tenerife that pass over or close to Europe and North America. In some cases, by backtracking along trajectories, the O_3 concentration measured at Izaña could be matched with good agreement to ozonesonde measurements over continental stations [*Schmitt and Carretero*, 1995]. Indeed, the Izaña monthly mean O_3 concentrations are similar to those at non-urban sites in Europe throughout the year [*Janach*, 1989].

In this paper we use the concentrations of non-sea-salt (nss) $SO_4^=$, NO_3^-, ^{210}Pb, and ^7Be, to more thoroughly investigate the potential sources of the high summertime O_3 concentrations at Izaña. Over the North Atlantic, NO_3^- and nss-$SO_4^=$ are largely derived from anthropogenic sources [*Savoie et al.*, 1992]. Pb-210 ($\tau_{1/2}$ = 22 years) is a decay product of ^{222}Rn ($\tau_{1/2}$=3.8 days) in soils; ^7Be ($\tau_{1/2}$=53 days) is produced in the stratosphere and upper troposphere by cosmic ray interactions. Consequently these nuclides can serve as excellent tracers for the transport history of air parcels [*Brost*

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et al., 1991; *Balkanski et al.*, 1993]. Although PAN (peroxyacetylnitrate), also measured at the site, can help in assessing the influence of anthropogenic sources, its concentrations during summer at Izaña are too low for this purpose, probably due to its dissociation at the typical summertime temperatures [*Schmitt et al.*, 1988; *Schmitt and Carretero*, 1995; *Schmitt*, 1995].

Results and Discussion

Ozone is continuously monitored with a Dasibi UV absorption instrument whose calibration is tied to the U.S. National Institute of Standards and Technology reference O_3 photometer maintained at Gaithersburg, Maryland [*Oltmans and Levy*, 1992]. Daily high-volume (1 m^3 min^{-1}) aerosol filter samples are collected at night (i.e., during downslope wind conditions) as a part of the Atmosphere/Ocean Chemistry Experiment (AEROCE). Samples for chemical analysis are collected on Whatman-41 filters and analyzed in Miami for nss-$SO_4^=$ (total aerosol $SO_4^=$ minus Na^+ times 0.2517, the $SO_4^=/Na^+$ ratio in bulk seawater) and NO_3^- using ion chromatography [*Savoie et al.*, 1992]. The radio-tracer samples are collected on quartz filters and analyzed at Yale using a high-purity germanium well gamma counter [*Turekian et al.*, 1989].

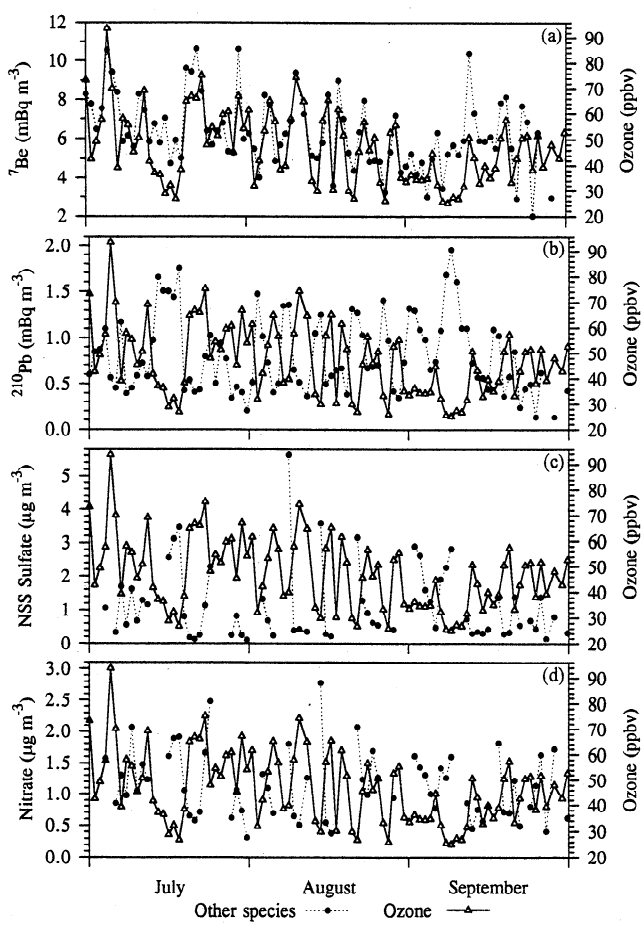

Figure 1. Daily mean night-time concentrations during July-September 1991 of O_3 with: (a) ^{7}Be; (b) ^{210}Pb; (c) nss-$SO_4^=$; and (d) NO_3^-. Data joined by lines indicate contiguous samples.

Our filters quantitatively collect aerosol NO_3^- and also gas-phase HNO_3, a major end-product of PAN decomposition. Thus our NO_3^- measurements should yield a good estimate of the total of aerosol NO_3^-, HNO_3, and PAN that might have been present. At Izaña the NO_3^-/O_3 volume mixing ratio during high O_3 events is typically in the range of 0.004 to 0.008 (i.e., NO_3^- concentrations of 0.5-1 µg m^{-3} and O_3 of 50-60 ppbv). These ratios are in the range of values for the NO_y/O_3 ratios measured in the upper troposphere over northern Europe [*Murphy et al.*, 1993].

A daily time series of O_3 and aerosol (night-time) data from July through September (henceforth, "summer") of 1991 shows that the day-to-day changes in O_3 concentrations are strongly correlated with those of ^{7}Be (Fig. 1a). In every case, the maxima and minima in the O_3 concentration data are associated with corresponding maxima and minima in ^{7}Be. Note the series of sharp one-day changes around mid-July and just after mid-August. In contrast, the O_3 time series is strongly anticorrelated with that of ^{210}Pb (Fig. 1b). Often ^{210}Pb changes by a factor of two or more in a one-day period while O_3 undergoes an equally sharp opposite change. There are also extended periods of low O_3 that are accompanied by high concentrations of ^{210}Pb (e.g., 6 days in mid-July and 12 days in early September).

Lower nss-$SO_4^=$ and NO_3^- concentrations (Fig. 1c and 1d, respectively) are almost invariably associated with peaks in O_3; conversely aerosol maxima coincide with O_3 minima. The temporal changes in nss-$SO_4^=$ are particularly remarkable. Many of the nss-$SO_4^=$ values that are associated with the O_3 peaks are in the range of 0.1-0.4 µg m^{-3} (23-93 pptv), comparable to those at remote South Pacific sites [*Savoie et al.*, 1989]. In contrast, the peak concentrations of nss-$SO_4^=$ (usually associated with low O_3 values) are often a factor of ten or more higher. The NO_3^- data (Fig. 1d) show a pattern that is similar to that for nss-$SO_4^=$. Samples having high concentrations of nss-$SO_4^=$, NO_3^-, and ^{210}Pb usually contained high concentrations of mineral dust as reflected in the aluminum concentrations (e.g. Fig. 2c; *Arimoto et al.*, 1995); these filters also had a very pronounced red-brown coloration that is characteristic of Saharan dust [*Prospero and Nees*, 1986]. Dust from large-scale dust storms, which occur often during the summer months in North Africa, is transported across the west coast of Africa, typically reaching altitudes of 6-8 km and covering large areas of the tropical North Atlantic [*Carlson and Prospero*, 1972; *Prospero and Nees*, 1986].

A series of scatterplots shows that the relationships in the summer of 1991 discussed above are generally valid for the entire data set from Izaña. In these plots, the data are partitioned into two groups, those for which O_3 concentrations are greater than 50 ppbv ("high O_3") and those for concentrations less than 35 ppbv ("low O_3"). The scatterplot of ^{210}Pb versus ^{7}Be (Fig. 2a) shows that high O_3 is associated with high ^{7}Be and low ^{210}Pb and, conversely, that low O_3 is associated high ^{210}Pb and low ^{7}Be. A scatterplot of nss-$SO_4^=$ versus ^{210}Pb (Fig. 2b) shows that nss-$SO_4^=$ is well correlated with ^{210}Pb. Within this distribution, the low O_3 values are tightly clustered at the high end of the nss-$SO_4^=/^{210}$Pb distribution whereas the high O_3 values are clustered at the low end.

As previously stated, high concentrations of nss-$SO_4^=$ and NO_3^- are usually associated with high concentrations of aluminum from mineral dust. Figure 2c shows that nss-$SO_4^=$ concentrations above about 1 µg m^{-3} are usually associated

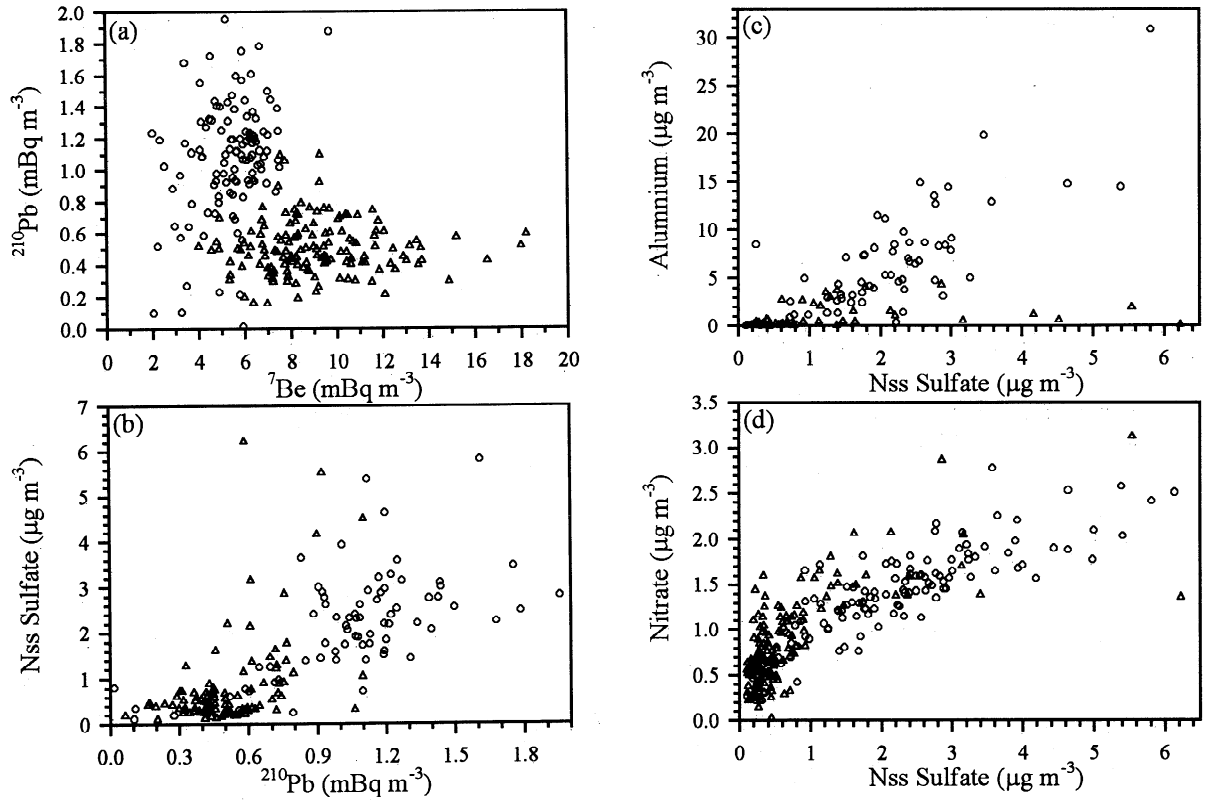

Figure 2. Scatterplot of July-September night-time aerosol concentrations at Izaña. Data are selected and partitioned for O_3 concentrations greater than 50 ppbv (Δ) and less than 35 ppbv (O). (a) ^{210}Pb vs. ^{7}Be, 1 July 1989-31 August 1993; (b) nss-$SO_4^=$ vs. ^{210}Pb, 1 July 1989-31 August 1993; (c) aluminum vs. nss-$SO_4^=$, 2 July 1989-30 September 1992; and (d) NO_3^- vs. nss-$SO_4^=$, 25 July 1987-30 September 1994.

with Al concentrations of several μg m^{-3} or greater (i.e., dust concentrations of 10's of μg m^{-3} or more). These samples are generally characterized by low O_3 concentrations. Conversely, the high O_3 group is primarily associated with extremely low Al concentrations and with nss-$SO_4^=$ concentrations less than 1 μg m^{-3}.

Although the time sequence of high-low aerosol NO_3^- concentrations (Fig. 1d) is similar to that for nss-$SO_4^=$ (Fig. 1c), it differs in one major respect. The low NO_3^- values (associated with O_3 peaks) are typically between 0.5 to 1 μg m^{-3} (180-360 pptv). These values are 5 to 10 times higher than South Pacific values [*Savoie et al.*, 1989] where anthropogenic impacts are minimal. At Izaña the mass ratio of NO_3^- to nss-$SO_4^=$ changes markedly with respect to the O_3 concentration changes. Figure 2d shows the entire July-September Izaña data set for 1987-1994 partitioned according to O_3 concentration. When aerosol concentrations are high (e.g., above about 1 μg m^{-3}), the NO_3^-/nss-$SO_4^=$ mass ratio falls between 0.5 to 1, values that are typical for polluted air masses; these conditions are usually associated with low O_3. When aerosol concentrations are low (less than about 1 μg m^{-3}), the NO_3^-/nss-$SO_4^=$ mass ratio is usually much greater than 1, values that are high compared to typical pollution aerosols; these occasions usually coincide with relatively high O_3 values (in Fig. 2d, over 50 ppbv).

Because of the similarities between the temporal variability of ^{210}Pb and that of nss-$SO_4^=$ and NO_3^- and because of the high concentrations of nss-$SO_4^=$ and NO_3^- during periods of high ^{210}Pb, we conclude that the nss-$SO_4^=$ and NO_3^- are transported from continental pollution sources. This interpretation is supported by isentropic trajectories [J. Merrill, personal communication; see *Moody et al.*, 1995] which, on days when the concentration of nss-$SO_4^=$ and NO_3^- are high, usually track back across North Africa, often hooking north to Europe. These trajectories are consistent with the fact that these samples usually contain very high concentrations of mineral dust as previously discussed. In contrast, the high O_3 (and low aerosol) events were generally associated with trajectories that came from the north in the middle and upper troposphere but which generally do not pass over continental Europe. The tight clustering of high-O_3 events at the low end of the Al versus nss-$SO_4^=$ scatterplot (Fig. 2c) is compatible with this interpretation. Our trajectory results are consistent with the Izaña trajectory climatology [*Sancho et al.*, 1992] which shows that, during July-September, 700 mb trajectories (the pressure altitude applicable to Izaña) fall largely into two classes: one group (26-37% of the cases by month) comes from over the North Atlantic (and possibly North America) north of 28°N (the latitude of Izaña); a second group (23-35%) passes over North Africa (and possibly Europe). At 700 mb, only a very small percentage of the trajectories (2-3%) come directly from Europe or England.

Conclusions

During the summer, high O_3 events at Izaña are associated with air masses that contain very low concentrations of aerosol species that are usually characteristic of "polluted" air masses. Conversely, samples that had high concentrations of pollution aerosols were usually associated with relatively low concentrations of O_3 and with trajectories that had passed over North Africa (and, usually, Europe). If one assumes that

these polluted air masses initially contained high concentrations of O_3, then much of the O_3 must have been subsequently destroyed in transit. The net balance of O_3 production and destruction depends critically on the concentration of NO_x and the concentration of water vapor. Our data suggest that for the cases with high aerosol concentrations, losses of O_3 appear to dominate over production on the time scales that it takes to transport air from pollution sources in Africa and Europe (i.e., a few days). The African-European trajectories generally lie at higher altitudes (e.g., 700 mb [*Sancho et al.*, 1992]) and the air is extremely dry [*Carlson and Prospero*, 1972] so that the water-vapor-related destruction processes for O_3 should be relatively inefficient. The large surface area available on dust might be a factor in the O_3 loss.

While our data can be interpreted to imply a substantial impact from upper tropospheric (and, perhaps, stratospheric) O_3 sources, they do not preclude the possibility that significant amounts of O_3 might be photochemically produced in the free troposphere or transported there from surface sources via convective clouds [*Pickering et al.*, 1992]. If boundary layer sources are playing an important role in free-troposphere O_3, then the transport mechanism from the boundary layer must efficiently remove pollutant nss-$SO_4^=$ and NO_3^- aerosols and their gaseous precursors, especially SO_2 along with the tracer ^{210}Pb. In contrast, O_3, NO_x, PAN, organic nitrates, and VOC's, being relatively insoluble, would be vented to the free troposphere where subsequent chemistry could slowly produce O_3 [e.g., *Liu et al.*, 1987] and oxidize the remaining NO_x to NO_3^-. As the destruction rates of O_3 are also slow in the free troposphere (because of the low water vapor content) the net effect of the production and destruction processes could be to maintain relatively high levels of surface-derived O_3 along with high NO_3^- values. The removal of ^{210}Pb, would obscure the signature for the surface origin of the air parcel [*Balkanski et al.*, 1993].

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