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, O₃ concentrations are anti-correlated with major pollutant aerosols (nss-SO₂ₓ and NOₓ) and with ²¹⁰Pb, a tracer for boundary layer sources. In contrast, O₃ is highly correlated with ³⁷Be, a product of cosmic ray interactions in the upper troposphere and stratosphere. This suggests that natural O₃ 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 O₃ 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 ²¹⁰Pb.

Introduction

Tropospheric O₃ 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 O₃ is principally derived from two sources: episodic injection of air from the stratosphere where most of the Earth's O₃ column inventory resides; and in situ photochemical production in the polluted continental boundary layer where most of the nitrogen oxides (NOₓ) and reactive organic carbon compounds (VOCs) are emitted. Conversely, there is the potential for net chemical destruction of O₃ in the free troposphere where NOₓ levels are low. Results from numerical simulations suggest that increasing anthropogenic emissions of both NOₓ and VOCs are leading to higher concentrations of tropospheric O₃ through the northern hemisphere [e.g., Thompson, 1992]. Direct measurements indicate that O₃ 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 O₃ 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 O₃ from continental regions to the marine atmosphere involves complex meteorological [Moody et al., 1995] as well as chemical [Jachob 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, O₃ 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. Nighttime O₃ 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 at O₃ 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 O₃ concentration measured at Izaña could be matched with good agreement in ozonesonde measurements over continental stations [Schmitt and Carretero, 1995]. Indeed, the Izaña monthly mean O₃ 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) SO₂ₓ, NOₓ, ²¹⁰Pb, and ³⁷Be, to more thoroughly investigate the potential sources of the high summertime O₃ concentrations at Izaña. Over the North Atlantic, NOₓ and nss-SO₂ₓ are largely derived from anthropogenic sources [Savoie et al., 1992]. Pb-210 (t₁/₂ = 22 years) is a decay product of ²²²Rn (t₁/₂=3.8 days) in soils; Be (t₁/₂=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 (peroxycetyl nitrate), 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 O₃ photometer maintained at Gaithersburg, Maryland [Olmi and Levy, 1992]. Daily high-volume (1 m³ 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-SO₄²⁻ (total aerosol SO₄²⁻ minus Na⁺ times 0.2517, the SO₄²⁻/Na⁺ ratio in bulk seawater) and NO₃⁻ 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].

Our filters quantitatively collect aerosol NO₃⁻ and also gas-phase HNO₃, a major end-product of PAN decomposition. Thus our NO₃ measurements should yield a good estimate of the total of aerosol NO₃⁻, HNO₃, and PAN that might have been present. At Izaña the NO₃/O₃ volume mixing ratio during high O₃ events is typically in the range of 0.004 to 0.008 (i.e., NO₃ concentrations of 0.5-1 µg m⁻³ and O₃ of 50-60 ppbv). These ratios are in the range of values for the NO₃/O₃ ratios measured in the upper troposphere over northern Europe [Murphy et al., 1993].

A daily time series of O₃ and aerosol (night-time) data from July through September (henceforth, "summer") of 1991 shows that the day-to-day changes in O₃ concentrations are strongly correlated with those of ²¹⁰Be (Fig. 1a). In every case, the maxima and minima in the O₃ concentration data are associated with corresponding maxima and minima in ²¹⁰Be. Note the series of sharp one-day changes around mid-July and just after mid-August. In contrast, the O₃ time series is strongly anticorrelated with that of ²¹⁰Pb (Fig. 1b). Often ²¹⁰Pb changes by a factor of two or more in a one-day period while O₃ undergoes an equally sharp opposite change. There are also extended periods of low O₃ that are accompanied by high concentrations of ²¹⁰Pb (e.g., 6 days in mid-July and 12 days in early September).

Lower nss-SO₄ and NO₃ concentrations (Fig. 1c and 1d, respectively) are almost invariably associated with peaks in O₃; conversely aerosol maxima coincide with O₃ minima. The temporal changes in nss-SO₄ are particularly remarkable. Many of the nss-SO₄ values that are associated with the O₃ 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-SO₄ (usually associated with low O₃ values) are often a factor of ten or more higher. The NO₃ data (Fig. 1d) show a pattern that is similar to that for nss-SO₄. Samples having high concentrations of nss-SO₄, NO₃, and ²¹⁰Pb 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 O₃ concentrations are greater than 50 ppbv ("high O₃") and those for concentrations less than 35 ppbv ("low O₃"). The scatterplot of ²¹⁰Pb versus ²¹⁰Be (Fig. 2a) shows that high O₃ is associated with high ²¹⁰Be and low ²¹⁰Pb and, conversely, that low O₃ is associated high ²¹⁰Pb and low ²¹⁰Be. A scatterplot of nss-SO₄ versus ²¹⁰Pb (Fig. 2b) shows that nss-SO₄ is well correlated with ²¹⁰Pb. Within this distribution, the low O₃ values are tightly clustered at the high end of the nss-SO₄/²¹⁰Pb distribution whereas the high O₃ values are clustered at the low end.

As previously stated, high concentrations of nss-SO₄ and NO₃ are usually associated with high concentrations of aluminum from mineral dust. Figure 2c shows that nss-SO₄ concentrations above about 1 µg m⁻³ are usually associated

![Figure 1. Daily mean night-time concentrations during July-September 1991 of O₃ with: (a) ²¹⁰Be, (b) ²¹⁰Pb, (c) nss-SO₄, and (d) NO₃. Data joined by lines indicate contiguous samples.](image-url)
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\(_4^{2-}\) 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\(_4^{2-}\) (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 [Savoe et al., 1989] where anthropogenic impacts are minimal. At Izaña the mass ratio of NO\(_3^-\) to nss-SO\(_4^{2-}\) 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\(_4^{2-}\) 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\(_4^{2-}\) 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\(_4^{2-}\) and NO\(_3^-\) and because of the high concentrations of nss-SO\(_4^{2-}\) and NO\(_3^-\) during periods of high \(^{210}\)Pb, we conclude that the nss-SO\(_4^{2-}\) 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\(_4^{2-}\) 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\(_4^{2-}\) 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\(^\circ\)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$_x$ aerosols and their gaseous precursors, especially SO$_2$ along with the tracer $^{210}$Pb. In contrast, O$_3$, NO$_x$, PAN, organic nitrates, and VOCs, being relatively insoluble, would be vended 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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