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Trace gas measurements during the Oxidizing Capacity of the Tropospheric Atmosphere campaign 1993 at Izaña

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Abstract. As part of the Oxidizing Capacity of the Tropospheric Atmosphere (OCTA) project, an intensive measurement campaign was conducted in July/August 1993 at the high-altitude observatory Izaña, Tenerife. Measurements of NO, NO_2, NO_y, PAN, J_{NO_2}, CO, VOC, HCHO, H_2O_2, O_3, and RO_x were made to study the photochemical processes which control the oxidizing capacity of the remote troposphere. Special attention was paid to the processes controlling the budget of ozone. Diurnal changes in the concentration of the species resulted primarily from the transition between downslope flow (usually free tropospheric air) and upslope flow (a mixture of marine boundary layer air and free tropospheric air modified by island emissions). Median concentrations for downslope and upslope conditions were NO_x (47/76 parts per trillion by volume (pptv)), NO_y (392/519 pptv), peroxyacetylnitrate (PAN) (10/23 pptv), CO (89/92 parts per billion by volume (ppbv), ethane (499/486 pptv), propane (35/40 pptv), ethene (25/31 pptv), isoprene (0/60 pptv), HCHO (1.1/1.4 ppbv), H_2O_2 (2.4/2.1 ppbv), and O_3 (40/38 ppbv). Maximum amounts of RO_x were measured around noon and reached values up to 70 pptv with no observable signal in the night during downslope conditions.

1. Introduction

Ozone in the troposphere originates either from the stratosphere by downward transport to the troposphere at extratropical latitudes, often in connection with tropopause folding events [*Danielsen*, 1968; *Holton et al.*, 1995], or from in situ photochemical production involving NO_x, CO, and hydrocarbons [*Crutzen*, 1973, 1995]. In rural and remote environments an important fraction of the tropospheric ozone is due to photochemical production. It is well established by models and observations that ozone production in remote areas is usually limited by the available NO_x. Photochemical ozone production has been studied extensively in rural environments [*Hirsch et al.*, 1996; *Kleinman et al.*, 1995; *Olszyna et al.*, 1994; *Poulida et al.*, 1994; *Kleinman et al.*, 1994; *Trainer et al.*, 1991; *Volz et al.*, 1988; *Liu et al.*, 1987], while studies in the remote troposphere are less common [*Ridley and Robinson*, 1992; *Atlas and Ridley*, 1996; *Hoell et al.*, 1996].

In this study we present measurements of the concentrations of NO, NO_2, NO_y, peroxyacetylnitrate (PAN), CO, nonmethane hydrocarbons (NMHC), HCHO, H_2O_2, O_3, and RO_x made during the August 1993 Oxidizing Capacity of the Tropospheric Atmosphere (OCTA) campaign at the high-altitude research station Izaña. The purpose of this campaign was to study the photochemical processes which control the budget of ozone and other photooxidants in the unpolluted free troposphere. In this respect, the OCTA campaign is a complement to the series of studies at the Mauna Loa Observatory in 1988, 1991, and 1992 [*Ridley and Robinson*, 1992; *Atlas and Ridley*, 1996]. In this paper a description of the experiment is given together with an overview of the data obtained. Meteorological conditions during the campaign are discussed in detail in an accompanying paper by E. Cuevas et al. (unpublished manuscript, 1997). Instrumental intercomparisons for measurements of NO, NO_2, NO_y, and O_3 as well as an intercomparison of RO_x measurements are given in the paper by *Zenker et al.* [this issue]. A detailed interpretation of the local photochemistry at the site will be given by A. Volz-Thomas et al., (Photochemical budgets of peroxy radicals (HO_2 and RO_2) and ozone during the OCTA intensive, manuscript in preparation, 1997), while long-range transport is dealt with in a paper by *Schultz et al.* [this issue]. The data obtained at Izaña have been published on a CD-ROM [*Stordal et al.*, 1995].

2. Experiment

2.1. Izaña Observatory

The experiment was conducted at the Global Atmospheric Watch (GAW) station Izaña, which lies at an altitude of 2370 m on the island of Tenerife (Canary Islands), about 400

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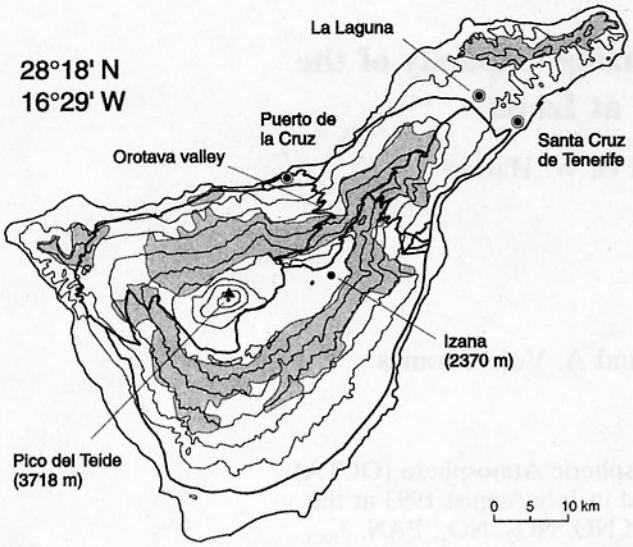

Figure 1. Map of Tenerife with the location of the Izaña observatory. The dark areas are covered with forest.

km west of the African coast (28°18′N, 16°30′W). Figure 1 shows a map of Tenerife.

The region around the Canary islands is characterized by the existence of the trade wind inversion that persists through most of the year. In summer the upper boundary of the inversion layer lies at about 1500 m, that is, significantly below the altitude of the station. This inversion shields the high-altitude observatory from the lower atmosphere and thus from the anthropogenic emissions on the island, especially during the night when downslope flow from the free troposphere is encountered at the station. During the day, thermally and dynamically driven upslope flow brings anthropogenically polluted air to the station.

The station buildings are on the northeastern flank of the Teide, the island's volcanic crater (3700 m). To the north the Orotava valley connects the station with Puerto de la Cruz, a small town on the northern shore of Tenerife. Between 1200 m and approximately 2000 m above sea level (asl) a pine forest covers most of the island. The vegetation in the surroundings of the station is sparse, while the ground is loosely covered with light volcanic material. The road, which leads to the meteorological observatory, the nearby television station, and a military camp, is closed to public traffic. Approximately 10 to 20 cars per day pass en route to or from the observatory. Approximately 500 m to the north a road running from La Laguna to the Teide passes the station. Because the Teide is a major tourist attraction, up to 60 cars and busses per hour use this road, especially in the morning hours and in the late afternoon.

2.2. Instrumentation and Sampling Methods

An overview of the measurements performed during the OCTA campaign is given in Table 1. Regular measurements of meteorological parameters, O_3, NO, NO_2, PAN, NO_y, $J(NO_2)$, CO, and NMHC have been performed by Meteorologie Consult (MC) since 1990/1991 [*Schmitt*, 1994; *Schmitt and Volz-Thomas*, 1996]. The main air intake for these measurements is mounted on top of a four-story tower, 2.5 m above a flat instrumentation platform which is approximately 15 m above the ground (Figure 2). Wind speed and direction are measured 3 m above the platform, while temperature and humidity are measured at 1.5 m. The common air intake is a combination of a stainless steel tube (60 mm ID, 3 m long) and a glass tube (60 mm ID, 30 cm long) extending through the roof from inside the fourth floor of the building. The residence time inside the tube is approximately 1–2 s. The ozone analyzer is installed on the fourth floor close to the air inlet. The systems for NO_x/NO_y, PAN, and NMHC are located on the third floor. The instruments are connected to the main air inlet through perfluoroalkoxy (PFA) tubes (6 mm ID, about 4 m long).

Ozone was measured by UV absorption (Dasibi Model 1008), while an automatic gas chromatographic (GC) system (1 analysis per hour) with cryogenic preconcentration [cf. *Rudolph et al.*, 1987] is used for the measurement of PAN. For this measurement the sample air (total 250 mL) is drawn at a flow rate of 40 mL/min through a 40 cm long glass tube (4 mm ID), which is cooled to −80°C by means of a two-stage immersion cooler. Quantitative collection of PAN was established for air flows up to 50 mL/min. For injection, the sample loop is switched into the carrier gas flow by means of a polytetrafluoroethylene (PTFE)/polyimide multiposition valve, and the sample loop is heated to 20°–25°C after a delay of 30 s. Separation is achieved on a packed column (600 cm long, 1.5 mm ID PTFE tube filled with 10% Carbowax 600/Chromosorb W-HP, 60–80 mesh) at 35°C. Nitrogen (5.0 grade) is used as carrier gas, and an Electron Capture Detector (ECD Dani 3200) operated at 60°C is used for detection. The detection limit is <0.5 parts per trillion (ppt). PAN calibration mixtures were produced by photolysis of acetone in an NO_2 calibration gas [*Zerbach*, 1990]. A 1 L glass flask is filled with an NO_2 mixture (2 ppm, 1100 hPa), and 15 μL of acetone are added with a syringe. After ~20 min equilibration time, the mixture is irradiated for 4 min with a low pressure Hg lamp which is mounted inside the flask. Aliquots of 0.1 mL of the resulting PAN mixture are sampled from the flask with a precision syringe and injected directly onto the column of the GC or into the sample loop. The whole procedure is repeated several times. Each time, two "on-column" and one "loop" injections

Table 1. Trace Gas Measurements Made at Izaña During OCTA in July/August 1993

Species	Technique	Institute
O_3	UV absorption	MC, MPI-C
NO	CL	KFA, MPI-C
NO_2	PC/CL	KFA
NO_2	TDLAS	MPI-C
NO_y	AuC/CL	MC, MPI-C
NMHC	GC/FID	MC
CO	GC/HgO	MC/KFA
PAN	GC/ECD	MC
HCHO	TDLAS	MPI-C
H_2O_2	TDLAS	MPI-C
RO_2 radicals	CA	KFA, IFE, MPI-C
HO_2, RO_2	MIESR	KFA
JNO_2	UV radiometer	MC/KFA
Meteorological parameters	standard	INM/MC

CL, chemiluminescence; PC, photolytic conversion; AuC, gold converter; TDLAS, tunable diode laser absorption spectroscopy; GC, gas chromatography; FID, flame ionization detector; ECD, electron capture detector; HgO, mercury oxide detector; CA, chemical amplifier; MIESR, matrix isolation and electron spin resonance spectroscopy; MC, Meteorologie Consult; INM, Instituto Nacional de Meteorologica; KFA, Forschungszentrum Juelich; MPI-C, Max Planck Institute for Chemistry; IFE, Institute for Remote Sensing, University of Bremen.

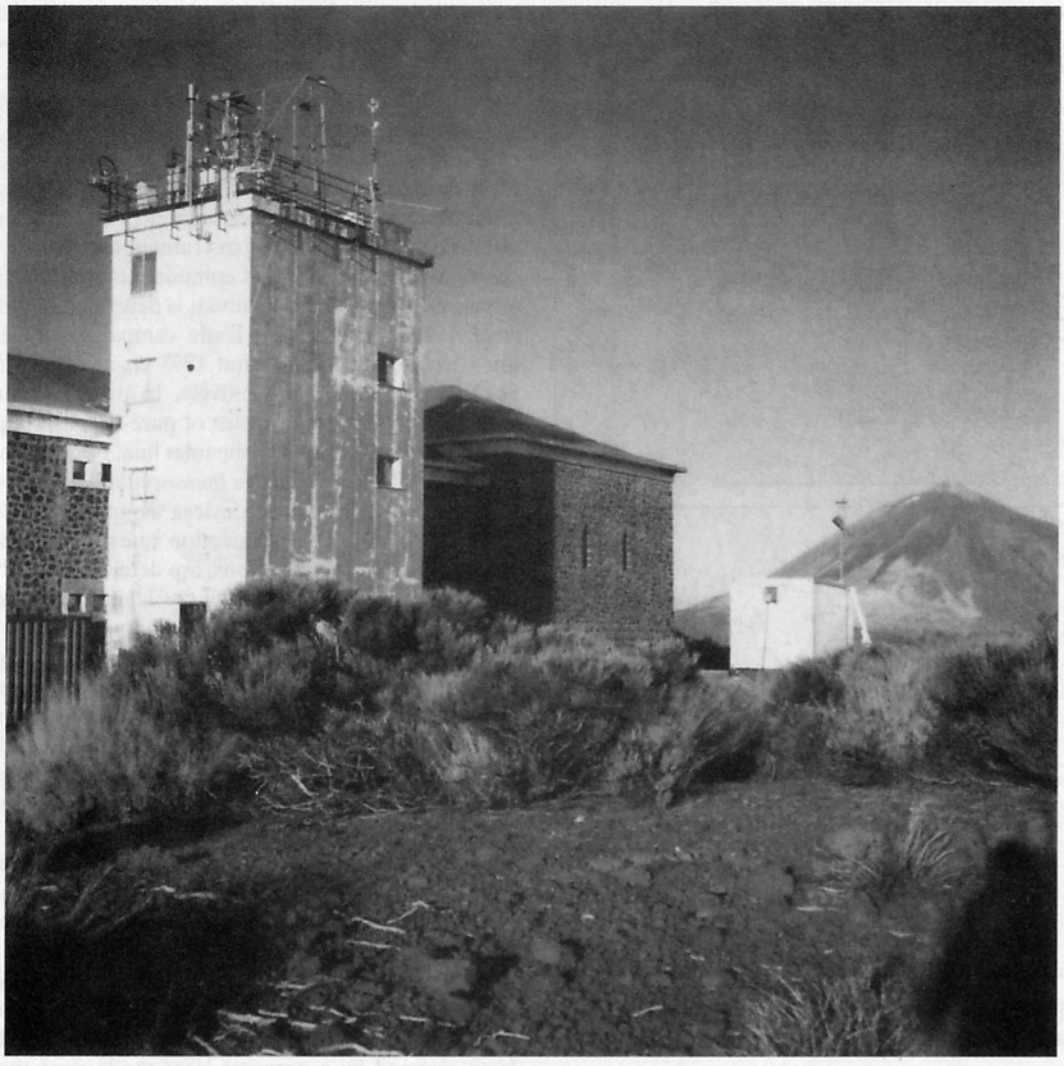

Figure 2. Izaña observatory site view from the northeast, showing (left) the measurement tower and (right) the MPI-C measurement container.

are made at 5 min intervals. The NO_2 concentration of the primary gas mixture was determined by comparison with the NO calibration standard the NO/NO_2 analyzer. The conversion efficiency of NO_2 to PAN was taken to be 80% [*Zerbach*, 1990]. During the campaign at Izaña, PAN measurements were made every hour.

Hydrocarbons (NMHC) were analyzed by an automated GC method built around a dual oven gas chromatograph (Siemens Sichromat 2–8) [*Schmitt*, 1994; *Schmitt and Volz-Thomas*, 1996]. The NMHCs are quantitatively absorbed by passing an air flow of 20–30 mL/min through a 30 cm long stainless steel tube (2 mm ID) packed with 3 cm each of glass wool, Carbopack BHT, and Carbosphere (60–80 mesh), which is cooled to −40° to −50°C by means of an immersion cooler (Cryocool CC65-A). A 10 cm glass tube (0.4 cm ID) packed with Mg $(ClO_4)_2$ is placed in front of the sampling tube for removal of water. The main sampling line (stainless steel tube, inner diameter 0.4 cm) is continuously flushed at a rate of 1 L/min. After thermal desorption, the sample is recollected in a capillary tube, which is immersed in liquid nitrogen. The sample is then injected onto the separation column by rapid heating of the tube. Separation is achieved on a 50 m wide-bore capillary column (0.32 mm ID, 1.2 μm CP Sil-5 CB; temperature program 30°–150°C). Since the C2 compounds are not separated under these conditions, the C2 fraction is passed onto a second column (7 m, 0.32 mm ID, Poraplot U; 55°C isothermal). Helium is used as carrier gas after purification with activated charcoal at −50°C. The performance of the system is checked at monthly intervals with a working standard, which was made by cryogenic collection of 10 bar of local air in a 10 L high pressure cylinder and dilution with synthetic air to a total pressure of 70 bar. The working standard was made in February 1990 and found to be stable after 1 month of storage. For calibration, a National Institute of Standards and Technology (NIST) certified standard (NMS 1660a, sample 13-44-D, 1 ppm propane, 4 ppm methane in air) was used, assuming carbon number response for the other compounds. During the OCTA campaign at Izaña, NMHC were measured every 1.5 hours.

Carbon monoxide (CO) was measured at hourly intervals using an automated GC with a HgO detector (Trace Analytical Model RGA 3). Calibrations were made on a weekly basis by adding a small known flow of a standard mixture (75 ppm CO in air) to the sample air flow. The CO flow was controlled at constant pressure by a quartz capillary, and the sample air flow

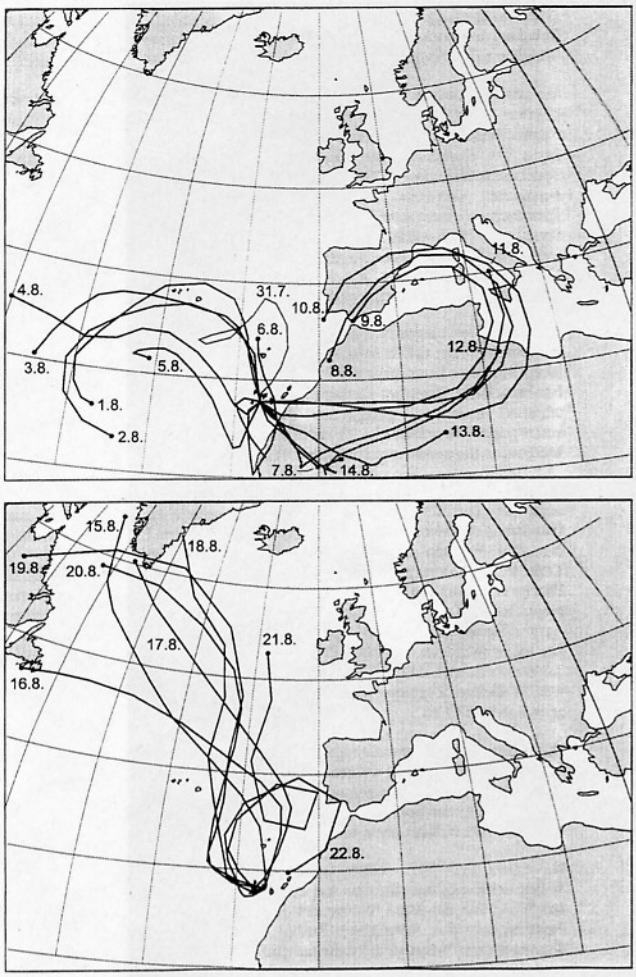

Figure 3. Seven day back trajectories for Izaña during August 1993 (arrival time 0000 UT).

was measured before each calibration. In this way, CO mixing ratios between 100 and 200 ppb above ambient CO were achieved. Calibrations were made at night when the ambient CO concentration does not exhibit large fluctuations.

The photolysis frequency of NO_2 (J_{NO_2}) was measured indirectly with two (upward and downward facing) 2π steradian filter radiometers (Meteorolgie Consult GmbH). An assessment of the instrument and the measurement uncertainties is given by *Volz-Thomas et al.* [1996]. The radiometers were calibrated, via identical instruments that serve as transfer standards, against a chemical actinometer at the KFA-Jülich [*Schultz et al.*, 1995a]. For the OCTA campaign, two additional chemiluminescence detectors (CLD) (modified ECO PHYSICS CLD 770 AL ppt (A. Volz-Thomas et al., manuscript in preparation, 1997) operated by the KFA Juelich were brought to Izaña to allow simultaneous measurements of NO, NO_2, and NO_y. The chemiluminescent reaction of NO with O_3 is used for the detection of NO [*Drummond et al.*, 1985]. NO_2 and NO_y are detected as NO after broadband UV photolysis (TECAN PLC 760 photolytical converter) [*Kley and McFarland*, 1980] and gold-catalyzed reduction in the presence of CO [*Bollinger et al.*, 1983; *Fahey et al.*, 1985], respectively. The additional instruments were installed inside the tower and used the common air inlet. The detection limits for NO, NO_2, and NO_y were 8, 16, and 16 parts per trillion by volume (pptv), respectively, for 10 min integration time, and the precision was 5% (NO), 13% (NO_2), and 19% (NO_y), respectively. For the accuracy of the measurements we add another 5% uncertainty associated with the accuracy of the NO calibration gas standard.

Additional measurements of NO, NO_2, and NO_y were made by the Max Planck Institute for Chemistry (MPI-C). NO_2 was measured together with HCHO and H_2O_2 using a tunable diode laser absorption spectrometer (TDLAS). The four laser airborne infrared (FLAIR) instrument used for these measurements can measure up to 4 components simultaneously within a cycle of 2 min. The instrument is described in detail by *Roths et al.* [1996]. During the Izaña campaign, single absorption lines around 1604, 1254, and 1775 cm^{-1} were used for NO_2, H_2O_2, and HCHO, respectively. In order to determine the spectral background a surplus of pure N_2 gas, supplied from a liquid N_2 tank, is added to the inlet line. For calibration, known quantities of the gases to be measured are added to the N_2 gas stream using permeation devices as gas sources for HCHO, H_2O_2, and NO_2. The permeation rates, which determine the calibration gas concentrations, are determined with a precision of the order of ±10%. During the Izaña campaign the instrument was housed in the MPI-C container which was placed approximately 20 m upwind from the building (Figure 2). The air inlet system was placed on top of the container about 5 m above the ground. Severe problems with the grounding of the container and electrical interference from the nearby television transmitter caused a substantial degradation of the instrument stability. This resulted in reduced precision, and only moderate detection limits of the order of 100–200 pptv for NO_2, ~800 pptv for HCHO, and around 1 parts per billion by volume (ppbv) for H_2O_2 could be achieved at full temporal resolution (2 min). Although tests were performed to check that the absorption lines used in this campaign were free of interference, absolute specificity especially for the HCHO measurement cannot be guaranteed due to multimode operation of the laser. We suspect that a weak absorption due to CH_4 may have been scanned by a parasitic laser mode near the same laser current for which the major mode reached the HCHO line, leading to a positive offset in the HCHO data (see section 3). Except for the case of exact overlap of an interfering absorption, such conditions were usually detected as a change in line shape of the ambient HCHO line; however, the higher than usual noise precluded this diagnosis.

In addition, the MPI-C laboratory container was equipped with instrumentation for NO, NO_y, and O_3 measurements. A TECAN CLD 770 AL pptv and a heated gold converter at 300°C was used for measurements of NO and NO_y in a toggled mode (1 min resolution, 50% duty cycle, mode switching every 5 min). A constant air flow was pumped through the converter for NO_y and, in parallel, through a 6 mm ID PFA tube for NO measurements. For the active channel, either NO or NO_y, the respective air flow was directed through the CL detector, while the other flow bypassed the instrument. A THERMO ELECTRON model 49 UV photometer was used for O_3 measurements. The NO/NO_y and O_3 inlet systems were placed on top of the container close to the TDLAS inlet system. An intercomparison of the different measurements for NO, NO_2, NO_y, and O_3 is given by *Zenker et al.* [this issue]. Excellent agreement within 4 and 10% was found for the NO and NO_2 measurements, respectively, while for NO_y, obvious inlet losses of one of the instruments and missing in situ HNO_3 conversion efficiency calibrations leave some open questions. The O_3 data sets agreed within 7%. This discrepancy was significant, likely

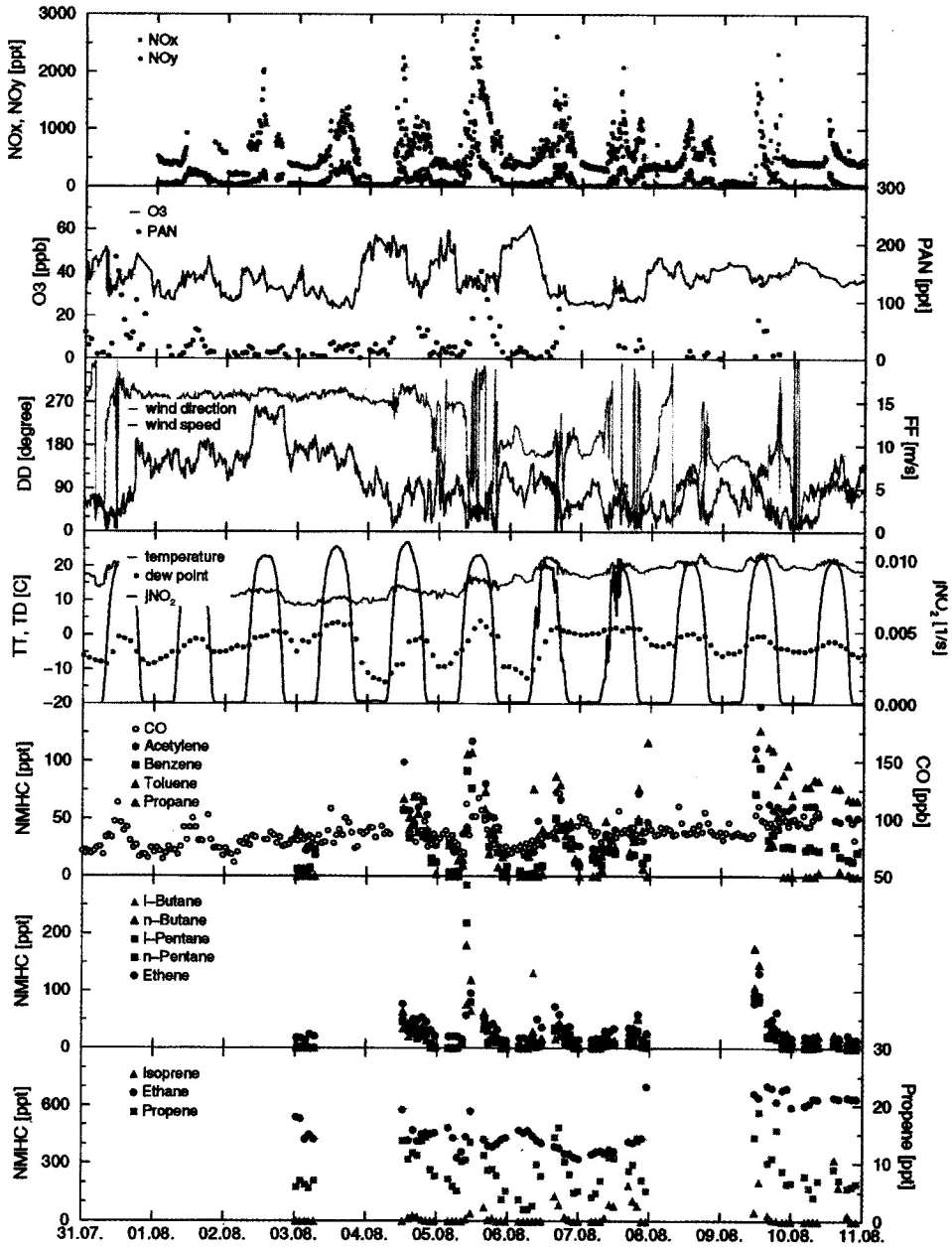

Plate 1. Time series of trace gas measurements, J_{NO_2}, and meteorological parameters measured during the OCTA campaign at Izaña from (a) July 31 to August 11 and (b) August 11–22, 1993.

due to inlet losses in an inlet line which was not protected from dust contamination. Details of the various intercomparisons are given by *Zenker et al.* [this issue].

During the OCTA campaign, three chemical amplifiers operated by MPI-C, the KFA, and the Institute for Remote Sensing of the University of Bremen (IFE) were used for the measurement of peroxy radicals RO_x, which is the sum of HO_2 and RO_2. The basic principle of the technique is that ambient air is mixed with NO and CO which set up a chain reaction with radicals present in the air producing amplified concentrations of NO_2 that can be measured using the chemiluminescent reaction of NO_2 with luminol [*Cantrell and Stedman*, 1982; *Hastie et al.*, 1991; *Heitlinger et al.*, 1995]. Calibrations of the sensitivity of the luminol detector were performed using NO_2 permeation devices (MPI-C, IFE) or an NO_2 calibration gas cylinder (KFA). Calibrations of the sensitivity toward radicals were performed using the thermal decomposition of peroxyacetylnitrate (PAN) in the IFE and MPI-C instruments or the photolysis of H_2O as a source of HO_2 radicals (KFA) [*Schultz et al.*, 1995b]. The IFE and MPI-C PAN calibrations were corrected for inlet losses in the sampling tube. The detection limit of the MPI-C instrument is of the order of 5 pptv. During the Izaña campaign, air sampling inlets of the chemical amplifiers were mounted on top of the TOR station main building about 20 m above the ground.

In addition, cryogenic samples were collected by the KFA for the speciated measurement of HO_2 and RO_2 by matrix isolation electron spin resonance (MIESR) spectroscopy [*Mihelcic et al.*, 1985, 1990, 1993; *Mihelcic and Volz-Thomas*, 1994]. The samples were collected approximately 5 m above the instrument platform of the tower. A detailed intercomparison of the different RO_x measurements is given by *Zenker et al.*

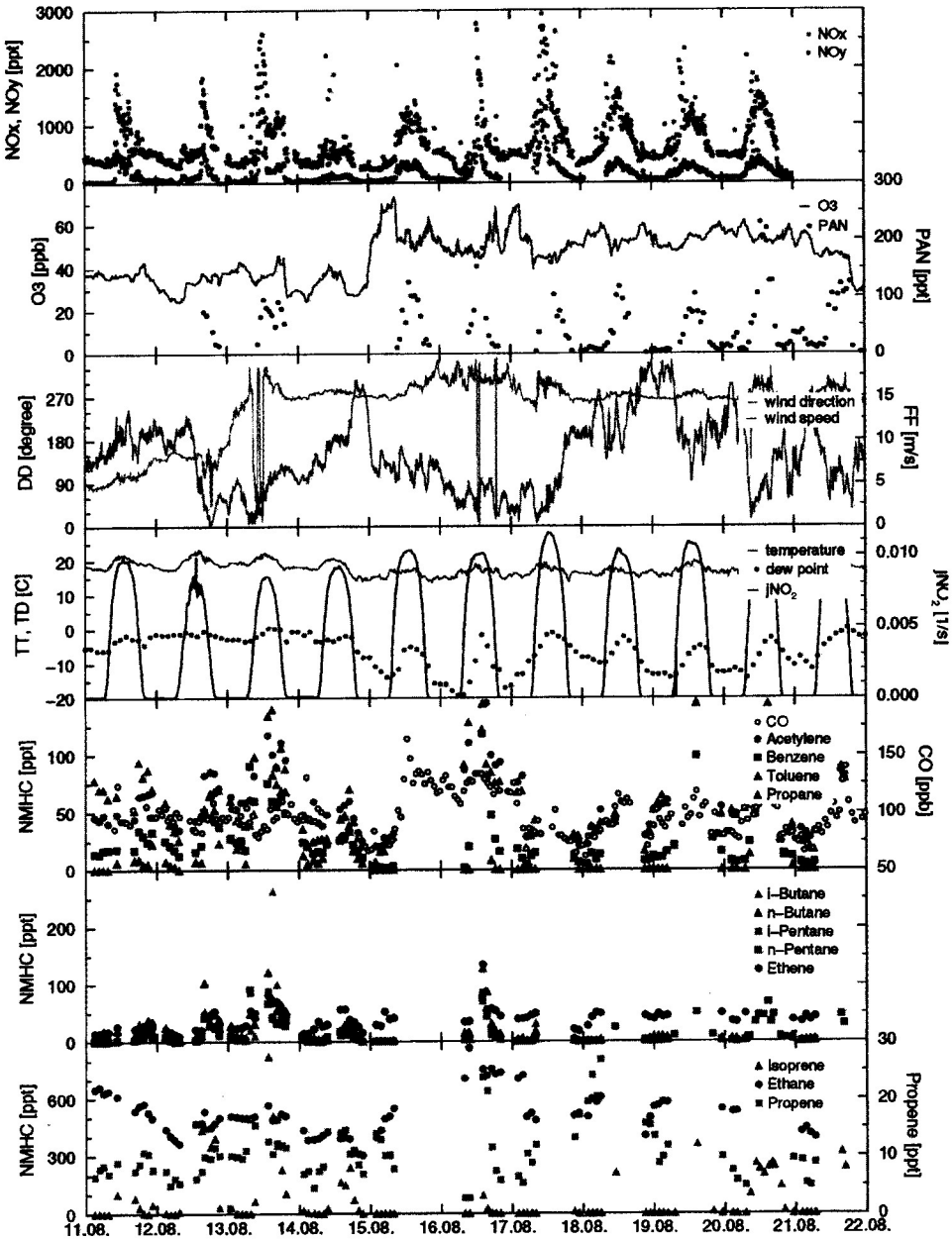

Plate 1. (continued)

[this issue]. In general, all data sets showed a significant correlation to each other. The KFA and IFE chemical amplifier and the MIESR RO_x measurements agree on average within 3–12%, while the MPI-C chemical amplifier is 35–65% low compared to MIESR, most probably due to a nonunderstood calibration bias of the MPI-C instrument.

3. Results and Discussion

3.1. Meteorological Situation

Measurements were performed between July 31 and August 22, 1993, including an intensive period lasting from August 14 until August 21, 1993. HCHO, H_2O_2, and RO_x data were only obtained during the intensive period. Isentropic back trajectories reveal that three different situations with respect to air parcel origin were experienced during the 3 week campaign, each lasting approximately 1 week (Figure 3). During the last day of July and the first 6 days of August the air came from the Atlantic, west of the Canary islands. The trajectories did not pass north of 40° latitude, and the air parcels had no direct contact with anthropogenic sources for at least 9 days. This can be regarded as photochemically well-aged air. From August 9 to August 14 the air had passed over Africa with a residence time of approximately 4 days over the Saharan desert. Five days previously, it had passed over southern Europe. After August 15, transport conditions changed to a rapid flow from northern latitudes. After August 16, air from north of 50° reached the station. Most of the air parcels had crossed the 40th and 50th meridians 4 or 5 days, respectively, before arriving at the station. Some of the air parcels may even have come from polar regions. The trajectories suggest that air from North America passed Izaña between August 16 and 20.

The different air parcel origins were associated with different altitudes from which the air parcels reached Izaña. During

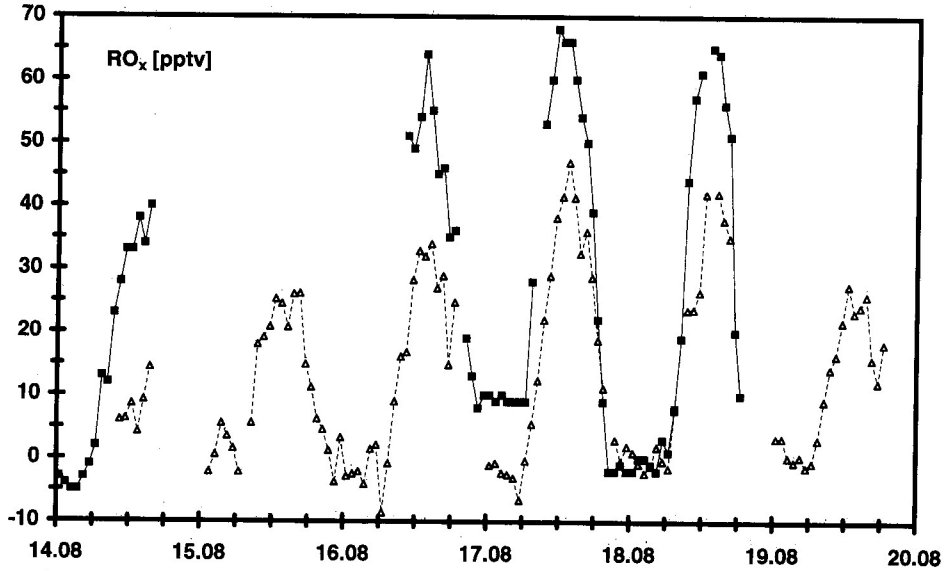

Figure 4. Time series of RO_x measurements obtained from the MPI-C (open symbols, dotted line) and the KFA chemical amplifiers (solid symbols, solid line) during the last week of the OCTA campaign.

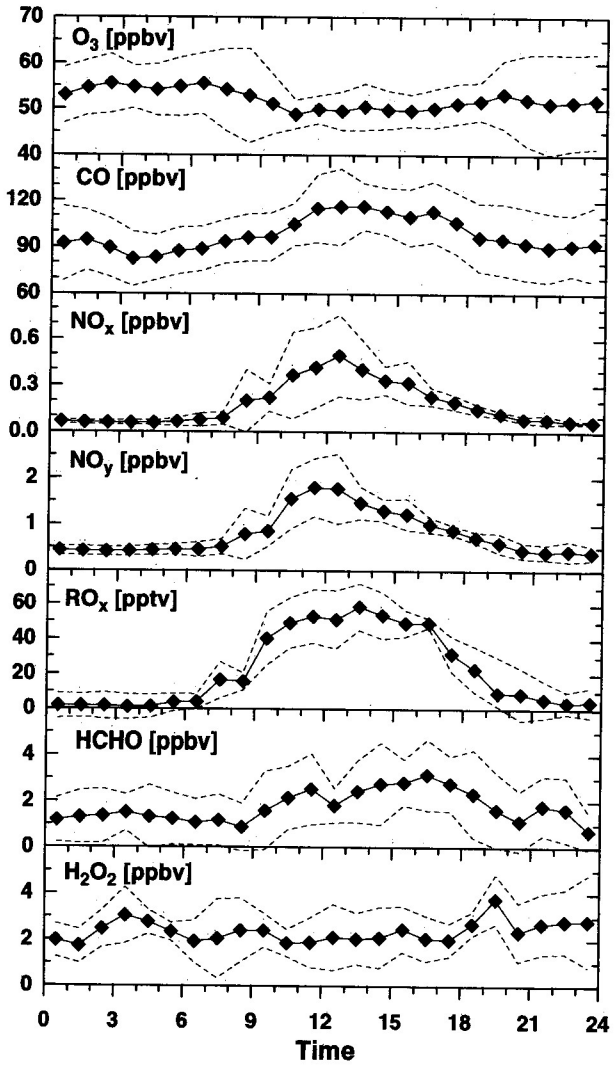

Figure 5. Diurnal variations of O_3, CO, NO_x, NO_y, RO_x, HCHO, and H_2O_2 for the period of August 15–21, 1993. Data points are 1 hour averages, while the dashed lines indicate the standard deviations.

transport from the northern part of the hemisphere the air continuously descended to the altitude of Izaña (770 hPa) from approximately 520 hPa at 50°–60°N to 650 hPa between 40° and 50°N and 720 hPa between 30° and 40°N. During the first period, when the air was coming from west of Tenerife, the average altitude of the air parcel east of 70°W was only 730 hPa, and the air that came from the African continent was transported at even lower average altitudes around 750 hPa.

3.2. Data Overview

Plate 1 gives an overview of the measured trace gases for the period of the OCTA campaign together with some meteorological information. RO_x data obtained by the MPI-C and KFA chemical amplifiers, respectively, are given in Figure 4 for the period between August 14 and August 20, 1993. Although the two data sets are highly correlated, the MPI-C RO_x concentrations are systematically lower. A detailed intercomparison shows that the MPI-C chemical amplifier RO_x mixing ratios are 35–65% low compared to the MIESR samples, while the KFA chemical amplifier shows a rather good agreement with MIESR data [*Zenker et al.*, this issue]. The availability of HCHO and H_2O_2 data is restricted to a few days during the intensive measurement period lasting from August 14 until August 21, 1995. This is due to the instrumental problems described above. Therefore these data are not included in Plate 1. Instead, mean diurnal variations of both species are presented in Figure 5. Tables 2 and 3 give mean, median, standard deviation, range, and number of observations for the measurement period, split into daytime (0900–1800 UT) and nighttime (2100–0600 UT) values, respectively. Table 4 documents mean, median, and standard deviation for NO_x, NO_y, PAN, O_3, and CO for the three different air parcel origins, again for the whole data set as well as split into daytime and nighttime values.

3.3. Chemical Composition for Different Air Parcel Origin

Variations in the chemical composition for the air parcels with different origins can be deduced from nighttime measurements when local influences can be excluded due to downslope flow from the free troposphere. Plate 1 and Table 4 show that

Table 2. Median, Mean, Standard Deviation, Range, and Number of Observations (1 Hour Averages) of the Trace Gas Measurements Obtained During the Whole Period From July 27, 1993, to August 22, 1993, for Upslope Conditions During the Day Between 0900 and 1800 UT

	Median	Mean	s.d.	Range	N
NO_x	0.08	0.16	0.21	0.0–1.5	520
NO_y	0.52	0.71	0.51	0.12–3.21	484
PAN	0.023	0.040	0.045	0.001–0.32	315
O_3	38	40	10	22–71	636
CO	92	94	15	63–160	385
HCHO	1.4	1.7	1	0.2–3.9	72
H_2O_2	2.1	2.2	0.7	0.8–3.9	60
Ethene	0.031	0.035	0.020	0.010–0.135	151
Ethane	0.486	0.501	0.113	0.303–0.865	151
Ethyne	0.047	0.052	0.030	0.018–0.235	151
Propene	0.009	0.010	0.004	0.002–0.026	151
Propane	0.040	0.052	0.038	0.007–0.280	151
i-butane	0.005	0.014	0.030	0.0–0.262	151
Butene	0.0	0.001	0.002	0.0–0.010	151
n-butane	0.010	0.022	0.031	0.0–0.179	151
i-pentane	0.003	0.014	0.030	0.0–0.284	151
n-pentane	0.004	0.014	0.025	0.0–0.219	166
Isoprene	0.0	0.060	0.124	0.0–0.823	166
2-methylpentane	0.0	0.006	0.012	0.0–0.097	151
3-methylpentane	0.0	0.003	0.007	0.0–0.051	151
n-hexane	0.0	0.006	0.011	0.0–0.074	151
Benzene	0.019	0.027	0.024	0.001–0.118	166
Toluene	0.005	0.026	0.038	0.0–0.157	166
α-pinene	0.023	0.028	0.018	0.011–0.102	45

Units are parts per billion by volume (ppbv).

the first episode, which is associated with transport from the Atlantic, is characterized by low ozone and low CO concentrations. The increase in CO thereafter is most likely a consequence of European emissions which the air parcels had been in contact with before passing over the Saharan desert. *Schmitt* [1994] speculates that the low ozone concentrations in these air parcels have been associated with destruction on dust particles of Saharan origin. The increase in ozone on August 15 is associated with the change in advection pattern to northerly directions. Enhanced CO concentrations, in particular on August 16 and 17, are indicative of anthropogenic influences, whereas the extremely low CO concentrations in the night from August 14 to August 15 suggests that the high O_3 on that night was more likely a result of subsidence of air from the middle or upper troposphere. In contrast to CO and O_3, NO_x, PAN, and NO_y exhibit only small variations for the three different air parcel regimes.

3.4. Diurnal Variation

While the nighttime trace gas budgets are characterized by the history of the air parcels transported down from the free troposphere, daytime trace gas concentrations are influenced by local emissions and upslope flow of polluted air from lower altitudes. This leads to the establishment of strong diurnal variations, which is typical for mountainous locations where topographically induced wind systems are involved in the local meteorology [*Anjea et al.*, 1991; *Hahn et al.*, 1992; *Zaveri et al.*, 1995].

The mean and median trace gas concentrations during the day and during the night are given in Tables 2 and Table 3, respectively. In addition, Figure 5 shows hourly averages and standard deviations for O_3, CO, NO_x, NO_y, RO_x, HCHO, and H_2O_2 as measured during the intensive period between August 14 and 21, 1993, while Figure 6 shows hourly averages of some hydrocarbons obtained during the same period. Strong diurnal variations are established for almost all trace gases measured during the whole campaign. In general, higher concentrations of O_3 and lower concentrations of NO_x, NO_y, PAN, CO, HCHO, and NMHC are observed in the night, due to the nighttime transport of clean, unpolluted air to the station above the stable trade wind inversion. This air is characterized by small values of relative humidity and low concentrations of NO_x (50 pptv), NO_y (390 pptv), and most of the NMHC. Only the NMHC with the longest photochemical lifetimes, that is, ethane, ethyne, and propane, have concentrations in the tens to hundreds pptv level. In contrast, moist and anthropogenically polluted air is experienced during the day. In general, these air masses exhibit higher concentrations of NO_x, NO_y, PAN, CO, HCHO, and NMHC due to local pollution sources and transport from lower altitudes, while the O_3 concentrations are smaller than during the night.

A clear diurnal pattern is also established for RO_x with measurable concentrations between 0700 and 2100 UT. Maximum peroxy radical concentrations were reached around noon, correlated with the solar insolation. The highest mixing ratios measured during the OCTA campaign were about 70 pptv (Figure 4) [*Zenker et al.*, this issue]. In general, nighttime concentrations of RO_x are below the detection limit. The radical signal of the KFA instrument in the night of August 16/17 is most likely an artifact, since no signal is observed by one of the other instruments [*Zenker et al.*, this issue]. The concentrations of H_2O_2 were of the order of several ppbv (2–4) with no clear diurnal variation (Figure 5).

3.5. Trace Gas Correlations

In two recent studies by *Prospero et al.* [1995] and *Graustein and Turekian* [1996] the origin of O_3 at Izaña has been dis-

Table 3. Median, Mean, Standard Deviation, Range, and Number of Observations (1 Hour Averages) of the Trace Gas Measurements Obtained During the Whole Period From July 27, 1993, to August 22, 1993, at Night Between 2100 and 0600 UT

	Median	Mean	s.d.	Range	N
NO_x	0.05	0.05	0.02	0.0–0.13	187
NO_y	0.39	0.39	0.1	0.12–0.7	176
PAN	0.010	0.012	0.010	0.001–0.046	76
O_3	40	41	11	25–68	240
CO	89	90	13	65–130	153
HCHO	1.1	1.3	0.6	0.4–3.1	30
H_2O_2	2.4	2.4	0.6	0.9–3.6	16
Ethene	0.025	0.027	0.011	0.012–0.052	72
Ethane	0.499	0.497	0.099	0.303–0.724	72
Ethyne	0.037	0.040	0.016	0.018–0.081	72
Propene	0.008	0.009	0.004	0.002–0.027	72
Propane	0.035	0.041	0.023	0.007–0.116	72
i-butane	0.001	0.003	0.005	0.0–0.023	72
Butene	0.0	0.0	0.0	0.0	72
n-butane	0.004	0.007	0.009	0.0–0.039	72
i-pentane	0.001	0.002	0.004	0.0–0.020	72
n-pentane	0.001	0.002	0.004	0.0–0.024	72
Isoprene	0.0	0.002	0.007	0.0–0.047	72
2-methylpentane	0.0	0.001	0.001	0.0–0.007	72
3-methylpentane	0.0	0.001	0.001	0.0–0.004	72
n-hexane	0.0	0.001	0.004	0.0–0.035	72
Benzene	0.012	0.013	0.008	0.001–0.037	72
Toluene	0.0	0.004	0.008	0.0–0.048	72
α-pinene	NA	NA	NA	NA	NA

Units are ppbv.

Table 4. Median, Mean, and Standard Deviation of the Trace Gas Measurements Obtained During the Different Periods

	All Data			Day			Night		
	Median	Mean	s.d.	Median	Mean	s.d.	Median	Mean	s.d.
				July 27 to Aug. 6					
NO_x	0.08	0.17	0.22	0.07	0.09	0.06	0.05	0.05	0.02
NO_y	0.52	0.75	0.59	0.47	0.52	0.20	0.37	0.37	0.10
PAN	0.02	0.029	0.032	0.022	0.024	0.022	0.011	0.012	0.009
CO	86	87	11	84	84	8	84	83	8
O_3	33	36	8	30	34	7	33	37	10
				Aug. 7–14					
NO_x	0.06	0.13	0.21	0.14	0.26	0.27	0.03	0.04	0.02
NO_y	0.47	0.59	0.35	0.67	0.84	0.44	0.39	0.39	0.06
PAN	0.034	0.042	0.035	0.051	0.051	0.037	0.002	0.006	0.008
CO	93	93	8	92	93	8	94	93	8
O_3	37	36	5	36	36	4	37	36	6
				Aug. 15–22					
NO_x	0.13	0.19	0.18	0.28	0.33	0.19	0.06	0.06	0.02
NO_y	0.60	0.79	0.54	1.16	1.30	0.53	0.45	0.42	0.12
PAN	0.034	0.053	0.055	0.076	0.086	0.055	0.008	0.013	0.011
CO	94	97	20	108	110	18	81	89	18
O_3	52	50	8	50	49	5	54	51	10

Units are in ppbv.

cussed. Both studies pointed out that the ozone at Izaña cannot come from long-range transport in the boundary layer. Instead, ozone either originates from the free troposphere, reaching Izaña by subsidence from higher altitudes, or from polluted boundary layer air, which was lifted by convection and transported downward to Izaña after photochemical processing. In order to distinguish between these two hypothesis, correlations among CO and O_3 can be used [*Fishman et al.*, 1980; *Luke et al.*, 1992; *Doddridge et al.*, 1994a, b]. A detailed discussion of the role of long-range transport on the ozone budget at Izaña is given in the paper by *Schultz et al.* [this issue].

Figure 7 shows the scatterplots between CO and O_3 for daytime (Figure 7a) and nighttime (Figure 7b) measurements at Izaña for the whole campaign. Shown are the individual data points, as well as averages calculated by grouping the data into 10 bins of CO, each bin comprising 10% of the data. Horizontal bars show the range of CO values, while vertical bars correspond to ± 1 standard deviation for O_3. In general, the original data show hardly any correlation between CO and O_3. The grouped data seem to indicate a slightly positive correlation between CO and O_3 during the day and a slightly negative correlation for free tropospheric air parcels experienced during the night. The positive correlation between these two trace gases during the day can be interpreted as resulting from photochemical ozone production. From the grouped data an increase of the order of 0.3 ppbv/ppbv for $\Delta O_3/\Delta CO$ can be calculated, which is comparable to measurements at three sites on the Atlantic coast of Canada [*Parrish et al.*, 1993] and eight different sites in eastern North America [*Chin et al.*, 1994], respectively. In contrast, the negative correlation observed during the night for CO values less than 110 ppbv might indicate downward transport of air from the upper troposphere [*Hipskind et al.*, 1987]. This interpretation is further supported by a strong negative correlation between O_3 and H_2O (not shown). On the other hand, the increase of O_3 at high CO levels in excess of 110 ppbv, which is due to a single episode in the night of August 15/August 16 coincides with extremely low water vapor and thus also points toward high-altitude transport [*Schultz et al.*, this issue].

A plot of O_3 versus NO_y is shown in Figure 8. Data processing is similar to that described above for the CO-O_3 correlation. Both daytime and nighttime measurements show no significant correlation between O_3 and NO_y. Only in the grouped data a slightly positive correlation can be inferred. A plot of O_3 and NO_z (equal to $NO_y - NO_x$) (not shown) is very similar to Figure 8. A positive correlation between O_3 and NO_y (or NO_z) can be expected due to photochemical O_3 production in polluted boundary layer air and has been observed previously in a number of campaigns at rural sites [*Trainer et al.*, 1991; *Olszyna et al.*, 1994]. Downward transport from the upper troposphere would also produce a positive correlation between NO_y and O_3, since both species have an upper tropospheric source and a sink at the ground [*Hübler et al.*, 1992].

3.6. Comparison Between Mauna Loa and Izaña

In Table 5 the trace gas concentrations measured at Izaña are compared with those found at Mauna Loa during the summer intensive measurement campaign Mauna Loa Observatory Photochemistry Experiment (MLOPEX) II between July 15 and August 15, 1992 [*Atlas and Ridley*, 1996]. In general, both data sets show strong diurnal variations for most trace gases as expected from their characteristics as mountainous sites. Similar concentrations for most trace gases are observed during the night when free tropospheric air descends to both stations, while significant differences in the trace gas levels are obvious during the daytime hours between Mauna Loa and Izaña. This is expected because of the geographical location of Mauna Loa in the Pacific (19°38′N, 155°36′W), far removed from anthropogenic emissions and because of the higher altitude of the Mauna Loa observatory (3400 m asl), which provides better shielding from local sources, although the influence of upslope is seen in the data from MLOPEX as well [*Hahn et al.*, 1992; *Atlas and Ridley*, 1996]. Thus the concentrations of NO_x and NO_y at Mauna Loa are lower by a

Table 5. Comparison of Median Trace Gas Concentrations and Other Parameters at Mauna Loa

	MLOPEX II		OCTA	
Averages	Day	Night	Day	Night
Temperature, °C	11.4	7.2	17.8	15.7
Dew point, °C	−2.2	−8.6	−1.4	−7.6
Ozone, ppbv	33.8	35.6	38	40
NO_x, pptv	50	26.8	76	47
NO_y, pptv	223	188	519	392
PAN, pptv	9.5	4	23	10
CO, ppbv	64	66	92	89
Ethane, pptv	410	429	486	499
Ethene, pptv	12	3	31	25
Ethyne, pptv	28	29	47	37
Propane, pptv	20	17	40	35
Isoprene, pptv	6	0	60	0
HCHO, ppbv	0.3	0.15	1.4	1.1
H_2O_2, ppbv	0.9	1.5	2.1	2.4
RO_2, pptv	25.4	0	65	<DL

MLOPEX II: July 15 to August 15, 1992, Mauna Loa, Hawaii, 19°38′N, 155°36′W, 3400 m asl. From *Atlas and Ridley* [1996], *Greenberg et al.* [1996], *Cantrell et al.* [1996], and *Zhou et al.* [1996]. OCTA: July 31 to August 22, 1993, Izaña, Tenerife, 28°18′N, 16°29′W, 2370 m asl. For RO_x median midday, clear-sky data are given. DL, detection limit.

factor of 2 [*Atlas and Ridley*, 1996; *Hübler et al.*, 1992] (G. Hübler, private communication, 1996), indicating much lower pollution levels. The concentrations of PAN at the two sites are comparable (B. Ridley, private communication, 1996). The absolute concentrations of ozone at Mauna Loa both at night and during the day are smaller than at Izaña by approximately 4 ppbv, while the diurnal cycles are comparable.

The measured H_2O_2 concentrations at Izaña with daytime and nighttime median values of 2.1 and 2.4 ppbv, respectively, are much higher than at Mauna Loa (0.9 ppbv during the day, 1.5 ppbv during the night) [*Atlas et al.*, 1996]. The cause of this discrepancy is presently unknown. Instrumental problems of the TDLAS due to interferences cannot be excluded (see section 2.2), but the measurements at Izaña are supported by an airborne H_2O_2 altitude profile measured on August 30, 1993, in the vicinity of Izaña as part of the OCTA program, which indicates an extended layer of H_2O_2 rich air at an altitude of approximately 2000 m with mixing ratios up to 3 ppbv [*McKenna et al.*, 1995]. Above and below this layer, H_2O_2 mixing ratios decrease to values between 1.5 and 2 ppbv, respectively.

The largest difference between Izaña and Mauna Loa is found in the concentrations of HCHO, which differs by a factor 5–10 [*Atlas and Ridley*, 1996; *Zhou et al.*, 1996]. The much higher concentrations of HCHO found at Izaña during the day could be due to the oxidation of isoprene and other short-lived biogenic hydrocarbons emitted from the pine forest which covers most of the island between 1200 and 2000 m altitude. However, the measured HCHO in free tropospheric air at Izaña is also much higher than measurements at Mauna Loa [*Heikes*, 1992; *Zhou et al.*, 1996] and much higher than predictions by a box model [*Schultz et al.*, this issue]. The observed nighttime concentrations around 1 ppbv are only slightly higher than the detection limit of the TDLAS instrument, which was of the order of 0.8 ppbv, because of the degraded operation of the instrument due to grounding problems mentioned above. In addition, due to the multimode operation of the HCHO laser, a spectral interference from CH_4 cannot be completely excluded. Therefore the HCHO data must be regarded as being too uncertain for drawing strong conclusions.

Large differences are also observed for some of the hydrocarbons. While during the night ethane, CO, and ethyne concentrations at Izaña are only 20–30% higher than at Mauna Loa, median mixing ratios of propane are much lower during MLOPEX [*Greenberg et al.*, 1996]. The higher concentrations of short-lived NMHC like ethene during the night at Izaña may indicate the influence of a local pollution source even on the free tropospheric concentrations.

Mean midday clear sky RO_x concentrations at Izaña are 65 pptv, which is significantly higher than RO_x at Mauna Loa, where 25.4 pptv were measured around noon during July/August 1992 [*Cantrell et al.*, 1996]. While at Mauna Loa the measured RO_x concentration is much smaller than the RO_x concentration deduced from photostationary state calculations [*Cantrell et al.*, 1996], the measured RO_x concentrations at Izaña are in rather good agreement with deviations from the

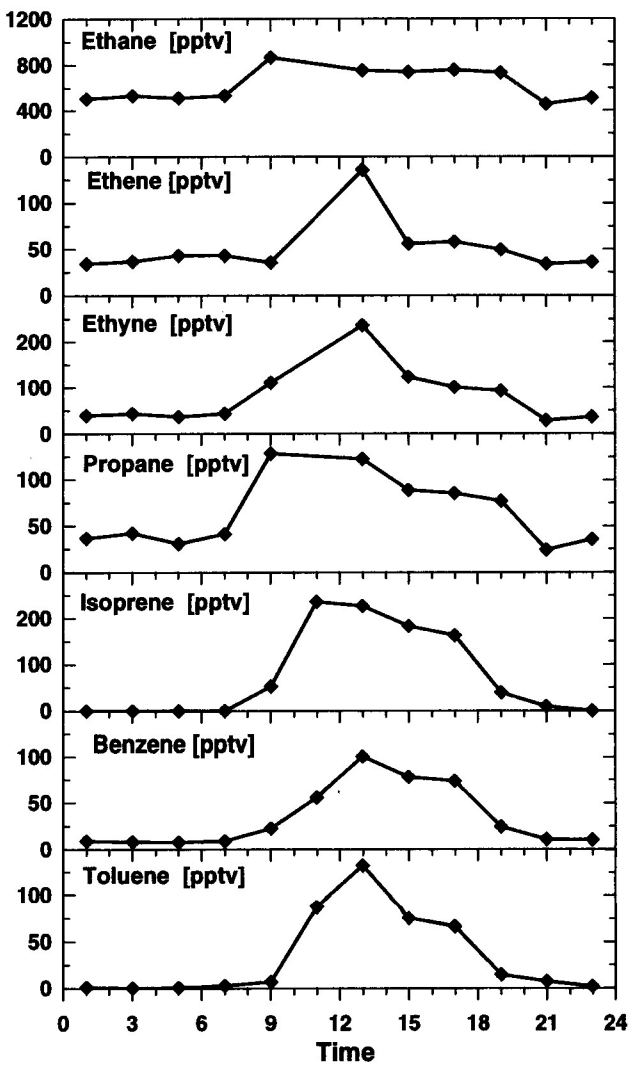

Figure 6. Diurnal variations of ethane, ethene, ethyne, propane, isoprene, benzene, and toluene for the period of August 15–21, 1993. Data points are 1 hour averages. Because of the limited amount of measurements, no standard deviation is shown.

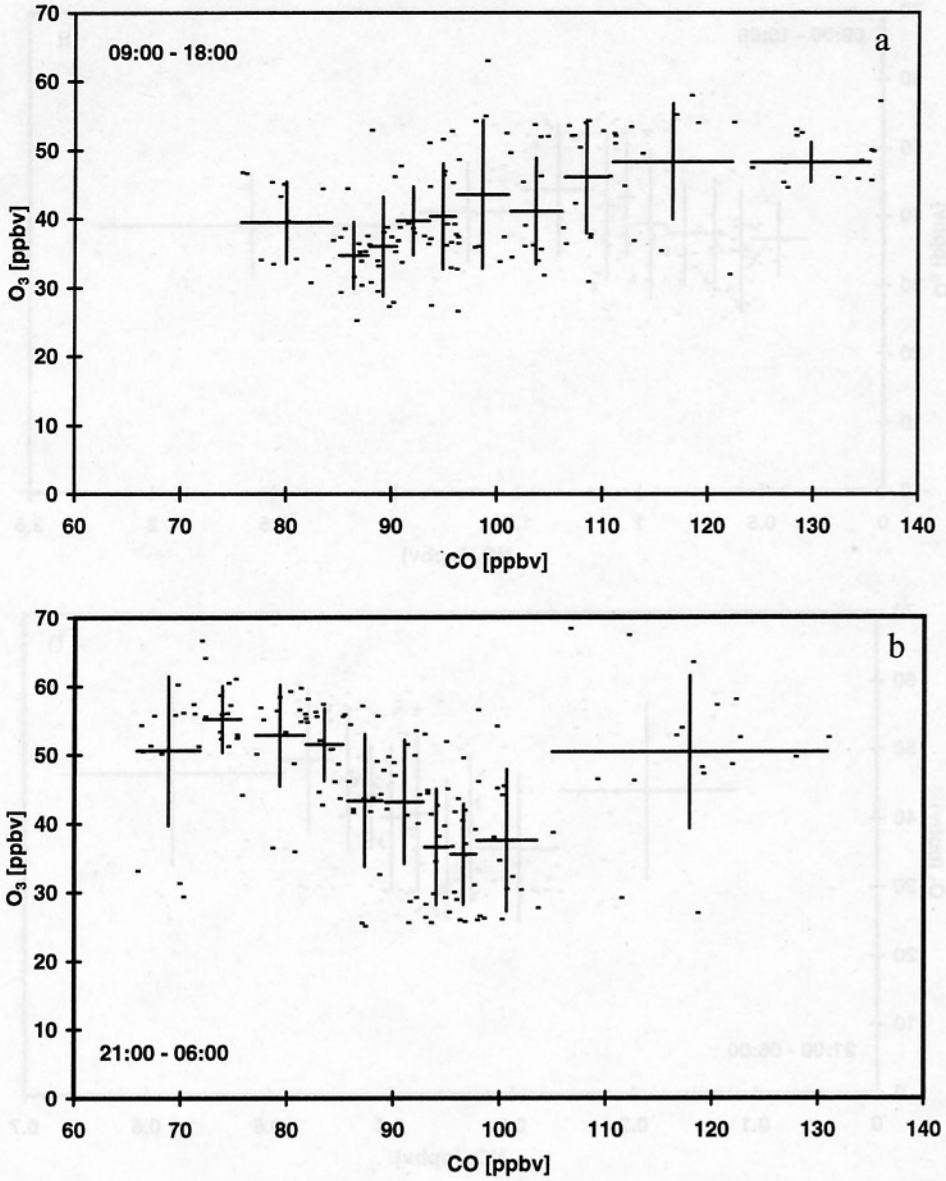

Figure 7. Relationship between O_3 and CO measured during the OCTA campaign for (a) upslope flow during the day and (b) nighttime free tropospheric conditions. The data have been sorted into 10 bins according to the CO concentration and plotted versus the average O_3 level in each bin, each representing 10% of the data. Horizontal bars show the range of CO values, while vertical bars correspond to ±1 standard deviation for O_3.

photo stationary state, deduced from simultaneous NO, NO_2, O_3, and J_{NO2} measurements. Our measurements agree fairly well with peroxy radical concentrations at Mauna Loa obtained from model simulations of the photostationary state if only gas phase chemistry is considered [*Cantrell et al.*, 1996; *Ridley et al.*, 1992]. A detailed discussion of the photochemical budgets of peroxy radicals and ozone at Izaña will be given in a future publication (A. Volz-Thomas et al., manuscript in preparation, 1997). During the night, no significant RO_x concentrations are measured at Izaña, while significant RO_x mixing ratios up to 10 pptv were observed during several nights at Mauna Loa [*Cantrell et al.*, 1996]. At Izaña, RO_x concentrations at or below the detection limit, which is of the order of 5–10 pptv for the KFA instrument [*Schultz*, 1995], are in good agreement with the results of a photochemical box model (M. Schultz, private communication, 1996).

4. Conclusions

In August 1993 a large joint experiment was performed at Izaña (Tenerife), located 400 km west of Africa (28°18′N, 16°30′W, 2370 m asl), to investigate the photochemistry in the remote atmosphere of the North Atlantic. The set of measured species includes O_3, NO, NO_2, NO_y, CO, H_2O_2, NMHC, HCHO, PAN, J_{NO_2}, and peroxy radicals. A strong diurnal variation was observed for most of the species, caused by local meteorology. Nighttime trace gas levels were representative of free tropospheric air, characterized by low concentrations of

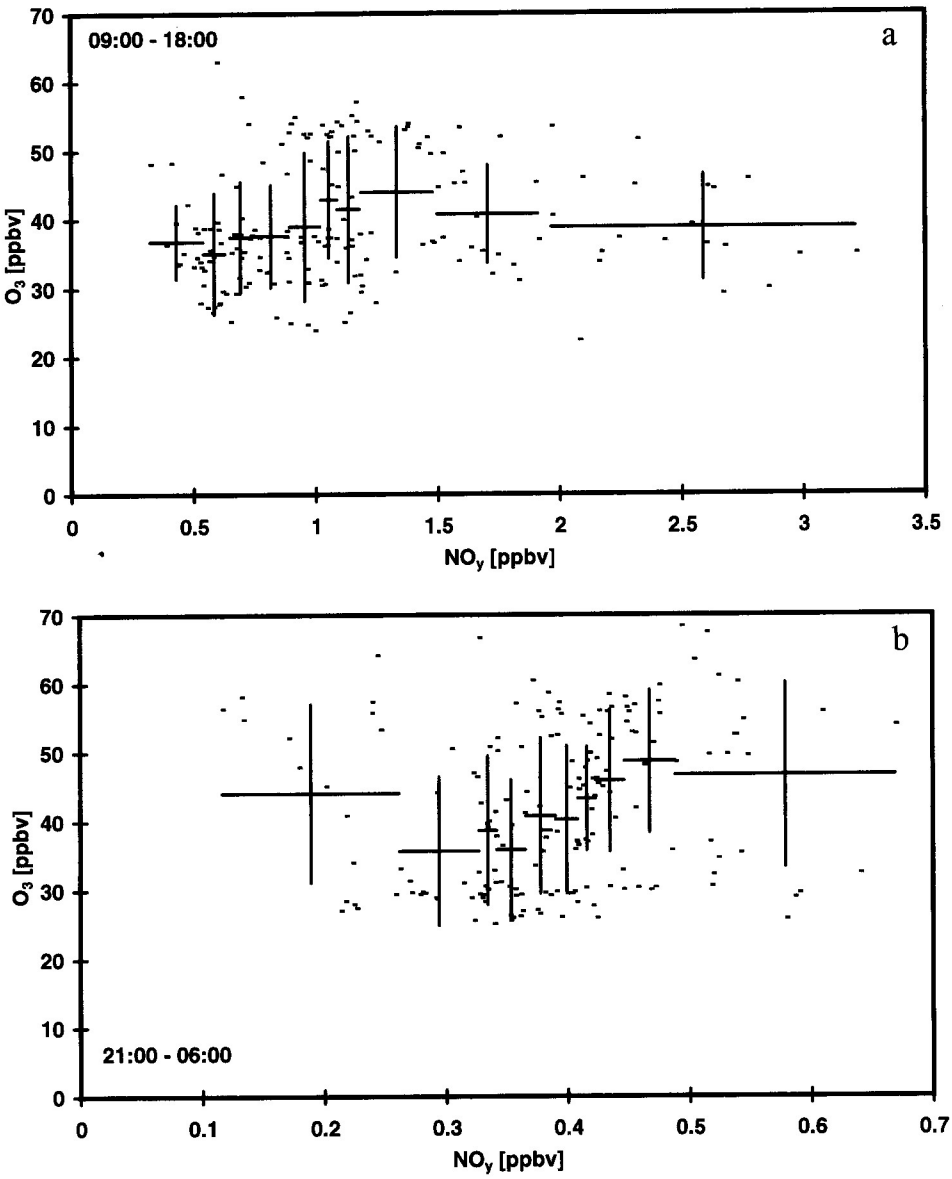

Figure 8. Relationship between O_3 and NO_y measured during the OCTA campaign for (a) upslope flow during the day and (b) nighttime free tropospheric conditions. The data have been sorted into 10 bins according to the NO_y concentration and plotted versus the average O_3 level in each bin, each representing 10% of the data. Horizontal bars show the range of NO_y values, while vertical bars correspond to ± 1 standard deviation for O_3.

NO_x, NO_y, PAN, CO, and NMHC, which indicates low levels of anthropogenic pollution. During the daylight hours, upslope flow conditions were found due to the establishment of catabatic wind systems. Although the station is above the trade wind inversion most of the time during the day, highly elevated concentrations of NO_x, NO_y, PAN, CO, and NMHC indicated that anthropogenically polluted air parcels from altitudes below the inversion layer reached the station. This resulted in higher levels for these trace gases during upslope conditions than those encountered during the series of intensive observation at the Mauna Loa in Hawaii between 1989 and 1992 [*Ridley and Robinson*, 1992; *Atlas and Ridley*, 1996]. A comparison of Izaña and the MLOPEX II summer intensive 1992 (July 15 to August 15) shows that the median free tropospheric trace gas levels are comparable, although the NO_x, NO_y, PAN, and CO concentrations are slightly lower at Mauna Loa. This can be expected due to the larger distance of the Mauna Loa from anthropogenic emissions and the higher altitude compared to Izaña. Unexplained are the differences in free tropospheric levels of HCHO and some of the shorter-lived NMHC, for example, ethene and propene, which are higher by a factor up to 10 at Izaña. While a measurement artifact in the determination of HCHO mixing ratios cannot be completely excluded, the simultaneously observed higher concentrations of the olefines might indicate the influence of a close-by source, even on the free tropospheric data.

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