

Electrical discharge source for tropospheric “ozone-rich transients”

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[1] In situ trace gas (O_3 , NO, NO_2 , NO_y) and ultrafine aerosol particle data from a passenger aircraft (project CARIBIC) and the NOAA WP-3D research aircraft are used to identify the origin of “ozone-rich transients” that occasionally appear in aircraft ozone data sets along flight distances of 5–80 km. Evidence of ozone import from the stratosphere, once suggested as the most likely cause, cannot be found. Our data rather reveal that the majority of the recorded ozone transients are artifacts caused by electrical discharges on the aircraft fuselage and the sample air inlet system. These discharges produce not solely O_3 but also nitric oxide (NO) which rapidly reacts with O_3 to form nitrogen dioxide (NO_2). Further evidence is, however, provided showing that some of the less pronounced and broader O_3 -NO- NO_2 -rich transients are of atmospheric origin. We hypothesize that they are formed in an early (i.e., prelightning) phase of thunderstorms due to cold electrical discharges on the surface of charged hydrometeors. Simple considerations suggest that the amount of O_3 and NO produced through these mechanisms is negligible with regard to the global tropospheric budget for the two gases.

INDEX TERMS: 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 3362 Meteorology and Atmospheric Dynamics: Stratosphere/troposphere interactions; *KEYWORDS:* Tropospheric ozone budget, electricity induced trace gas production, stratosphere-to-troposphere ozone

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1. Introduction

[2] Tropospheric ozone (O_3) is a greenhouse gas and plays a paramount role in the chemistry of the atmosphere through photolytic generation of OH radicals. These radicals initiate the oxidative chain reactions responsible for removing numerous trace gases from the atmosphere [Levy, 2000]. Until the early 1970s, tropospheric O_3 was assumed to exist solely due to downward transport from the stratosphere [Regener, 1957; Dütsch, 1971]. Widespread photochemical production of O_3 within the troposphere is now

well documented, but its budget still has significant uncertainties [Lelieveld and Dentener, 2000; Monks, 2000].

[3] In this context, the frequent encounter of ozone-rich transients in the equatorial 10–12 km altitude range (MOZAIC, Measurement of Ozone and Water Vapor by In-service Aircraft) [Suhre *et al.*, 1997] has engendered discussions of their origin [Crutzen and Lawrence, 1997; Cammas *et al.*, 1998; Zachariasse *et al.*, 2001]. During 1/3 of all equatorial MOZAIC flights enhanced O_3 volume mixing ratios in the range of 100–700 nmol/mol compared to the background of 20–40 nmol/mol were recorded over distances of 5–80 km [Suhre *et al.*, 1997; K. Suhre, personal communication, 2000]. Concurrently elevated H_2O concentrations, increased turbulence, and fluctuations in wind speed and direction as well as other flight parameters indicated the likely crossing of clouds and the proximity of deep convection. Three possible explanations for

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the existence of the O₃-rich transients were suggested by *Suhre et al.* [1997]: (a) electrical discharge processes in convection-driven cumulonimbus clouds, (b) direct vertical downward transport from the stratosphere, and (c) horizontal transport of O₃-rich air from the extratropical stratosphere. Stratospheric origin (processes b and c) was suggested as the most likely cause.

[4] In the following discussion, it is important to differentiate the small-scale ozone-rich transients reported by *Suhre et al.* [1997] and discussed here from other ozone-enriched dynamical features that are definitely of stratospheric origin. These stratospheric intrusions are clearly attributed to downward transport of stratospheric air associated with strong tropopause distortions, as indicated by [Danielsen, 1968]. The stratospheric origin of elevated O₃ levels can be demonstrated by trajectory and potential vorticity analysis [e.g., Bithell et al., 2000]. As shown by *Cammas et al.* [1998] based on the MOZAIC data set, in the subtropics they occur as stratospheric filaments having at 10–12 km altitude a horizontal extension of at least ~100 km and ozone mixing ratios as large as 250 nmol/mol. *Cammas et al.* [1998] discuss these stratospheric filaments separately from the smaller scale, tropical troposphere O₃-rich transients.

[5] *Suhre et al.* [1997] strongly suggest that the O₃-rich transients that they report are also of stratospheric origin. If their suggestion is correct, the existence of these transients would imply a considerable, hitherto overlooked source that should be included in the tropospheric O₃ budget. However, there is no strong argument supporting this suggestion. No trajectory or potential vorticity analysis indicating a stratospheric origin has been presented. Indeed, as discussed below it is very difficult to identify a plausible mechanism for transporting stratospheric air in such small features and with such high frequency of occurrence into the tropical troposphere.

[6] In this work, we present additional observations of ozone-rich transients, some of which are associated with measured transients in oxidized nitrogen species as well, and provide strong evidence that they result from discharges in proximity to electrically charged clouds. These observations were made under conditions similar to those of the MOZAIC study (proximity to deep convection), but at varying locations (not only in the upper tropical troposphere, but also in the mid and upper troposphere at mid latitudes). Further evidence suggests that most of the transients are formed in discharges at the aircraft fuselage or sampling inlets and thus are measurement artifacts. In section 2 we describe the instruments and introduce the observations. The stratospheric and electrical discharge origin hypotheses are discussed in sections 3 and 4, respectively, and section 5 discusses the results and presents conclusions.

2. Experimental

[7] Two data sets are analyzed: first, concentrations of O₃, water vapor (H₂O), and ultrafine aerosol particles (4–12 nm diameter) recorded aboard the Civil Aircraft for Regular Investigation of the Atmosphere Based on an Instrument Container (CARIBIC) Boeing 767 from LTU International Airways (Düsseldorf, Germany), and second, concentra-

tions of O₃ and oxidized nitrogen species observed using the National Oceanic and Atmospheric Administration (NOAA, US) WP-3D research aircraft. The measurements that are analyzed in this study represent infrequent, extraordinary observations made in proximity to electrically active clouds. Therefore, in this discussion we will pay close attention to the ability of the instruments to accurately measure rapidly varying, transient levels and to the possibility of measurement artifacts occurring in an electrically active environment.

2.1. CARIBIC Instruments

[8] Ozone was measured using a fast chemiluminescence sensor with a time resolution of 8 Hz (~30 m flight distance). This is a factor of 32 faster than the MOZAIC u.v. absorption O₃ sensor [Thouret et al., 1998], which allows the resolution of much finer spatial features and the measurement of much higher peak values in the O₃ transients (since there is less spatial averaging). The CARIBIC chemiluminescence sensor is calibrated in flight against an u.v. absorption O₃ analyzer that provides spot measurements (integration time: 2.2 sec, or 550 m flight distance) every 17 sec (4.25 km flight distance) [Zahn et al., 2002]. The overall uncertainty is the greater of 4 nmol/mol or 4%.

[9] Particle number concentrations were registered by three condensation particle counters (TSI, 7610) with lower threshold diameters of 4, 12, and 18 nm, and a time resolution of 2 sec. The O₃ and aerosol analyzers share the same stainless steel (SS) inlet tube, in which air enters through a 0.36 cm hole and expands into a 4 cm diameter, 30 cm long tube to slow down to a few m/s [Hermann et al., 2001]. From this tube, air is withdrawn via a 4 mm ID PTFE tube for the O₃ analyzer and via a backward facing 4 mm ID SS tube for the particle counters. In order to prevent static charging the PTFE tube was enclosed in metal tubing that is grounded to the aircraft frame. Particle number concentrations are corrected for sampling efficiency and are transformed to standard conditions (STP, temperature: 273.15 K, pressure: 1013.25 hPa).

[10] Water vapor was measured using a TRANSMET metal-ceramic capacitive sensor (Mitchell Instruments, Cambridge, UK). Its response is proportional to the H₂O vapor partial pressure. A concomitant temperature measurement for inferring the H₂O mixing ratio is thus not required, as in the case of MOZAIC where a hydroactive polymer film capacitive sensor is used [Helten et al., 1998]. The TRANSMET sensor is installed within a 7.5 mm ID SS tube, ~1.5 m downstream of the air inlet system. The air is drawn from a SS inlet located ~15 cm shifted relative to the inlet tip for the O₃ and aerosol particle measurement. During collection of the data presented here, the inlet line had a temperature of ~20°C and was flushed with an air flow of 70 vol-L min⁻¹ (or ~20 L STP min⁻¹). These experimental conditions and the ambient H₂O mixing ratio of ~1000 μmol/mol (which together control the performance of the TRANSMET sensor and the inlet line) led to response times of the H₂O measurement of 30–60 sec at increasing H₂O mixing ratios and of 60–120 sec at decreasing H₂O mixing ratios. The uncertainty of the dew point is ±2 K or ±20% in the relative humidity (at the sampling temperature of –33°C). For further details, see *Brennink-*

meijer et al. [1999], *Hermann et al.* [2001], and *Zahn et al.* [2002].

2.2. NOAA WP-3D Instruments

[11] The measurements reported here were collected during the 1994 Southern Oxidant Study (SOS) conducted in the Nashville/Middle Tennessee area of the U.S. [Cowlings *et al.*, 1998]. The focus of the study was the photochemistry occurring in urban and point source pollution plumes within the continental boundary layer. However, a significant fraction of the flight time was devoted to characterizing the levels of trace species in the free troposphere. The NOAA WP-3D aircraft was equipped with instrumentation for the measurement of oxidants and their precursors. Continuous measurements were made of O₃, carbon monoxide, sulfur dioxide, nitric oxide (NO), nitrogen dioxide (NO₂), and total oxidized nitrogen species (NO_y). On board gas chromatographs measured non-methane hydrocarbons and peroxy acyl nitrates. Only the O₃, NO, NO₂, and NO_y data will be used here. Those measurements will be described in some detail below. A complete suite of meteorological, radiation and aircraft parameters were also recorded.

[12] The O₃ data reported here were measured using a chemiluminescence instrument with a time resolution of 1 sec (100 m flight distance). Before each flight this instrument was calibrated against an u.v. absorption O₃ analyzer in variable O₃ levels produced in clean, dry air. The u.v. absorption instrument also measured ambient ozone with a time resolution of 20 sec during flight (not shown). The overall uncertainty of the chemiluminescence data is better than 2%.

[13] NO, NO₂ and NO_y were measured by 3 independent O₃-NO chemiluminescence instruments that were identical, except for the pretreatment of the sample. NO was measured based upon the reaction with added reagent O₃ (time resolution: 1 sec), NO₂ after its (partial) conversion to NO in a photolysis cell (time resolution: 5 sec), and NO_y after its conversion to NO by gold catalyzed reduction by CO at 300°C (time resolution: 1 sec). The absolute accuracy of the NO, NO₂, and NO_y levels may be no better than a factor of 1.5 due to calibration uncertainties. Relative changes are quantified to better than 10%. Further details of the O₃, NO and NO₂ measurements are given by *Ryerson et al.* [1998].

[14] Three separate inlets brought ambient air to the instruments. O₃ was sampled through a Teflon tube contained within a stainless steel tube. A second, similar inlet was used for sampling NO and NO₂. Both of these inlets sampled in a rearward direction. The NO_y inlet was side-ward facing and mounted within the shroud of a standard Rosemount temperature sensor with the sensing element replaced with a heated, gold-plated stainless steel tube. Thus, charged particles entering the inlets cannot have contributed to the detected trace gas spikes.

2.3. Consideration of Possible Instrument Malfunction

[15] For the purposes of the discussion in this paper, it is essential that the instruments were functioning properly. In particular, we must exclude the possibility of spurious signals possibly caused by electrical discharges on the aircraft in the electrically active regions where the measure-

ments of interest were collected. One general argument indicates that spurious signals from electrical interference are unlikely. On both aircraft, the many state variables of the instruments (such as temperatures, pressures, and flow rates) recorded by the different data logging devices did not indicate any spurious signals or irregularity in the instrument parameters or operating sequence. Likewise, on the NOAA WP-3D aircraft, none of the continuous instruments (other than O₃ and the oxidized nitrogen instrumentation) and neither of the chromatographs displayed transient signals.

[16] There are anecdotal reports that Teflon tubing can produce transients in chemiluminescence instruments by static charging. Outside the skin of both aircraft, any Teflon tubing in the inlet lines to the ozone and nitrogen oxide instruments was completely enclosed in metal tubing that was grounded to the aircraft frame. There was never any indication that vibrations or motion of the tubing generated either ozone or NO in the inlet lines within the aircraft. Except for those discussed in this paper, no unexplained transients have been observed in the ozone or nitrogen oxide instrumentation.

2.3.1. CARIBIC Measurements

[17] Simultaneous transients were recorded by altogether six CARIBIC instruments (2 O₃ sensors, 3 aerosol sensors, and 1 H₂O sensor) that rely on different analytical techniques with correspondingly different response times (and thus time shifts) and sensitivities. Nonetheless, the structure, coincidence, and relative strength of the transients that appeared in the different data sets agreed (Figures 1 and 2). This indicates that the transients do indeed reflect high frequency changes in the concentrations of the species sampled by each instrument.

[18] During the 68 CARIBIC flights (~10 hours each) conducted between November 1997 and January 2002, altogether five O₃ spikes series were recorded, i.e., on 2 July 1998 (20:08 UT at 45°N, 29°E, pressure altitude H_p = 10.0 km), on 7 July 1999 (07:36 UT at 8°N, 71°E, H_p = 9.5 km), on 28 July 2000 (11:06 UT at 8°N, 14°E, H_p = 10.7 km, and 15:21 UT at 48°N, 11°E, H_p = 5.7 km), and on 8 July 2001 (21:55 UT at 25°N, 70°W, H_p = 10.0 km). This frequency of occurrence (7%) roughly agrees with MOZAIC where during 1/3 of all equatorial flights (which accounts for 1/5 of all flights) O₃ transients were recorded, that is also ~7%.

[19] The July 1999 O₃-rich transient analyzed here, is representative for the other four. All were detected in July, at longitudes between 70°W (Caribbean) and 71°E (Indian Ocean), and at latitudes between 8° and 48°N. In contrast to the MOZAIC results, some of these transients were observed outside the tropics. The peak O₃ mixing ratios were always between 500 and 2000 nmol/mol.

2.3.2. NOAA WP-3D Measurements

[20] On June 28, 1994 the NOAA WP-3D flew over central Tennessee. Transients were observed in O₃, NO, NO₂ and NO_y mixing ratios. All of the observed spikes series (i.e., ten strongly pronounced and clearly identified ones, see section 4) are consistent with the measurement of ozone and oxidized nitrogen species sampled through the inlets. The large magnitude O₃ spikes were recorded by both O₃ instruments, with the signal from the u.v. absorption instrument delayed by the expected 10 sec. It is very

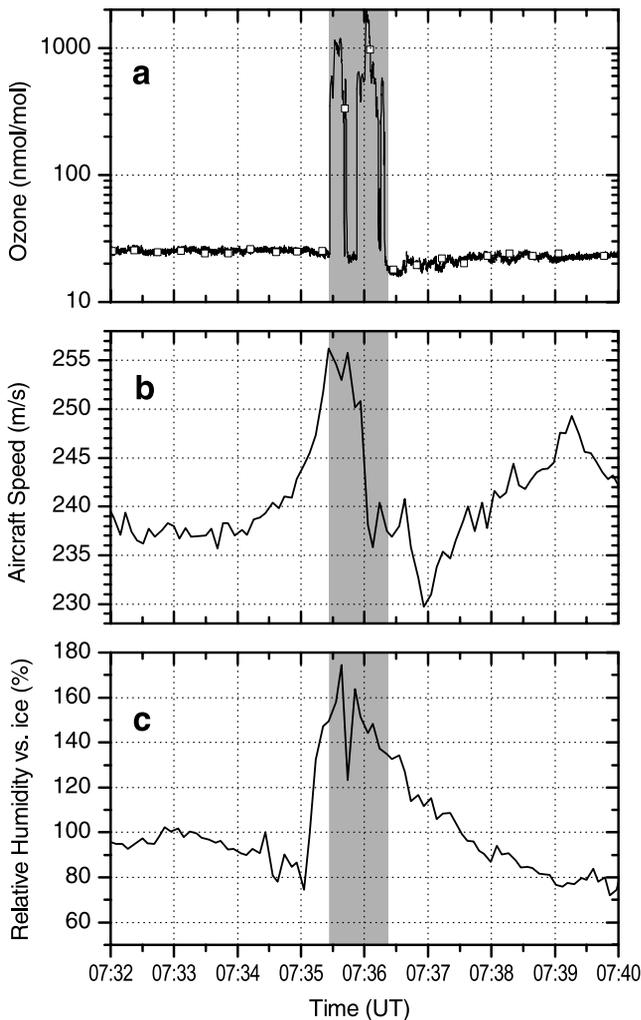


Figure 1. Time series of (a) O_3 mixing ratio (on log scale) detected by the fast (line) and the slow sensor (light squares, their width agree with the measurement time), (b) the aircraft speed recorded from the aircraft, and (c) relative humidity versus ice, as obtained during a CARIBIC flight on 7 July, 1999, at $\sim 8^\circ N$, $\sim 71^\circ E$, and a pressure of ~ 288 hPa. The time axis of the humidity data is shifted by 60 sec, the estimated mean response time of the humidity sensor (see section 2.1).

difficult to envision a source of signal noise that could mimic real signals in both of these very different O_3 instruments simultaneously, with the corresponding 10 sec time delay, and in all of the observed spikes. During all peaks and the entire flight, the O_3 data from both instruments were consistent. During all spike periods the NO_x signals are also consistent with measurement of NO and NO_2 sampled through the inlet. The NO_2 signals were delayed (by ~ 5 sec, see above) and smoothed relative to the NO signals as expected due to the volume of the photolysis cell in the NO_2 sample line (Figure 4).

[21] In the course of NOAA Aeronomy Laboratory research, such pronounced transients in ozone and oxidized nitrogen species have been observed on only one of 105 research flights, all conducted at northern mid latitudes,

although similar but smaller trace gas spikes have been seen in the vicinity of thunderstorms on three other flights.

3. The Stratospheric Origin Hypothesis

[22] Of the five O_3 -rich transients observed during CARIBIC (see section 2.3.1), one is analyzed in detail here. On 7 July, 1999 a high resolution cross-section of an O_3 -rich transient was recorded near the Maldives at ~ 9.5 km altitude (Figures 1 and 2). The structured profile and peak mixing ratios of 2000 nmol/mol are striking, exceeding background levels by a factor of 100. The MOZAIC ozone-rich transients were encountered under similar conditions (high humidity, vicinity to convection cells); however, peak values (300–700 nmol/mol) were lower. This is likely to be primarily due to the slower O_3 sensor used, which cannot resolve details less than 1 km wide (see section 2). Our goal in this section is to critically evaluate the hypothesis that such O_3 -rich transients are due to transport of stratospheric air to the mid to upper tropical troposphere where they are observed.

[23] The maximum levels of O_3 observed within the O_3 transient of 2000 nmol/mol (Figure 2) are typically present

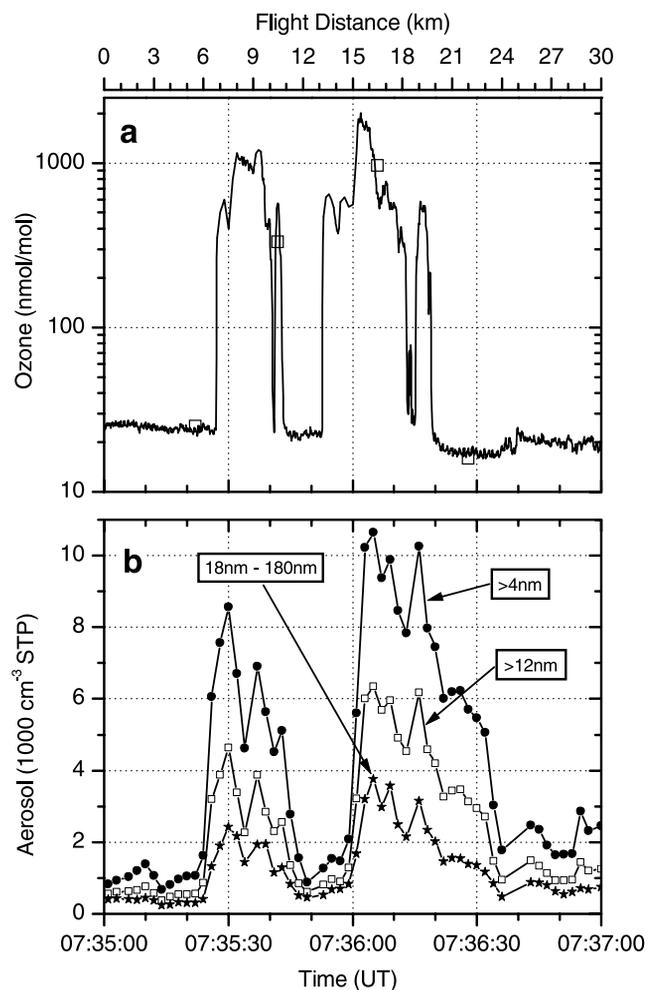


Figure 2. Two-minute section of the flight part shown in Figure 1. Depicted are (a), the O_3 mixing ratio (identical with Figure 1), and (b) the aerosol number concentration for three particle size ranges.

deep in the stratosphere, in the tropics at ~ 20 km altitude and potential temperatures of ~ 480 K. No transport mechanism is known that can bring such O_3 -rich air down to 9.5 km within a short time (hours) while cooling the air to the 340–345 K at 9.5 km (see below). Slower transport, however, cannot retain the fine structures as observed, for instance, the abrupt jumps from ~ 25 nmol/mol to ~ 265 nmol/mol and ~ 332 nmol/mol along less than 50 m in the horizontal at 07:35:27 UT and 07:35:53 UT, respectively.

[24] High concentrations of ultrafine aerosol particles (UFP, Figure 2b) and water vapor (of up to 1200 $\mu\text{mol/mol}$, shown as relative humidity versus ice in Figure 1c) in the O_3 -rich transient are also inconsistent with stratospheric origin. High UFP levels indicate recent formation of aerosol particles, a process occurring in upward moving air such as in convection cells [Ström *et al.*, 1999]. The observed H_2O mixing ratios exceed stratospheric levels by a factor of 100–200 and indicates oversaturation versus ice pointing to the presence of cloud particles. Moreover, detailed meteorological analyses based on ECMWF data (diabatic 5-day back trajectories ending at different distances below and above the flight path, humidity fields, and vertical winds) demonstrate widespread upward flow and vast deep convective activity around the sampling site. This analysis is supported by Meteosat-5 satellite images that indicate extensive areas of high clouds (Figure 3). In summary, no meteorological evidence for air import from the stratosphere was found.

[25] Even the more modest O_3 values of 300–700 nmol/mol reported from the MOZAIC flights can (under the given conditions) hardly be explained by import from the stratosphere. In the tropics, O_3 values of 300–700 nmol/mol are found typically at 18–19 km and potential temperatures of 400–430 K. Downdrafts do occur adjacent to convective cells, but only cooling by evaporating cloud particles can cause the necessary reduction in potential temperature. This process results, however, in cooling rates of only ~ 1 K per 600 $\mu\text{mol/mol}$ evaporated ice and only works efficiently at temperatures above the melting point of ice (0°C), i.e. below ~ 5 km. A continuing supply by ice particles falling from the cumulus anvil of the convection cell into the adjacent downdraft would not lead to additional evaporative cooling, because evaporation stops as soon as saturation versus ice is achieved, e.g., at ~ 900 $\mu\text{mol/mol}$ at -33°C .

[26] Moreover, cooling of the air due to temperature equalization with the colder ice particles from the cumulus anvil cannot cause the necessary cooling effect, either. Let us assume ice particles that fall from 15 km (~ 131 hPa, -70°C , US Standard Atmosphere data for the tropics) down to 9 km (~ 333 hPa, -30°C). How much ice is necessary to cool an air parcel that is transported from 18–19 km down to flight level and that has there (as a conservative estimate) a vertical extension of (only) 1 km? A simple calculation using the specific heats of ice and air yield a mass of more than a half ton ice per square meter. This is a very unrealistic number when assuming that the strongest rain showers can lead to only ~ 100 liter precipitation $\text{m}^{-2} \text{day}^{-1}$.

[27] Another possible ozone carrier is a stratospheric streamer that reaches from the subtropical stratosphere quasi-horizontally into the equatorial troposphere. The high water vapor concentrations and the extremely sharp transitions from tropospheric background levels into the ozone spikes (in the present case below 25 m) unequivocally

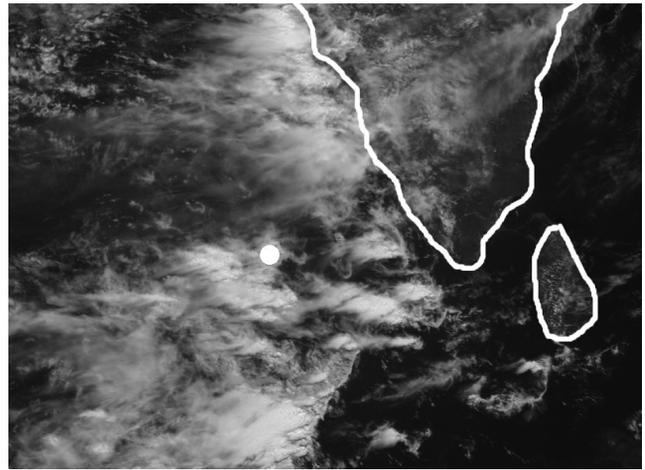


Figure 3. Visible wavelength range ($0.5\text{--}0.9\ \mu\text{m}$) image between $\sim 3^\circ\text{N}$ $\sim 64^\circ\text{E}$ and $\sim 15^\circ\text{N}$ $\sim 83^\circ\text{E}$ (Indian Ocean) from the Meteosat-5 satellite on 7 July, 1999, 06:00 UTC, © EUMETSAT 1999, Darmstadt, Germany. The region of encounter of the O_3 -rich transient is marked as white point.

contradict the intersection of stratospheric streamers. The presence of such a streamer above the aircraft followed by vertical downward motion due to a downdraft disagrees, as before, with the encountered potential temperatures. Namely, as the subtropical summer stratosphere is confined to potential temperatures above 340 K, equatorward transport of subtropical stratospheric air showing ozone mixing ratios above 400 nmol/mol can only occur above 360 K. As before, the process that causes the necessary cooling by at least 20–30 K is missing. In the case of the CARIBIC observations, the 5-day diabatic back trajectories do not indicate any signs for a stratospheric streamer. Additionally, if such a process, i.e., the coincidence of a stratospheric streamer and a tropospheric updraft-downdraft system, exists at all, it would be much too unlikely to occur with the reported probability of 1/3 of all equatorial MOZAIC flights [Suhre *et al.*, 1997].

[28] In summary, the addition of the CARIBIC observations, with finer spatial resolution and larger O_3 maxima, to the MOZAIC data set, makes the stratospheric origin hypothesis much less tenable. Further, the more extensive meteorological analysis presented here can find no support for any stratospheric influence.

4. The Trace Gas Formation in Electrical Discharge Hypothesis

[29] As transport from the stratosphere cannot be responsible for the ozone-rich transients, they must have been produced within the troposphere. There are two processes that can produce ozone in the troposphere: photochemistry and electrical discharges. Since all of the transients have been observed in the vicinity of deep convection, conditions conducive to electrical activity but not photochemistry, the latter mechanism deserves serious consideration. Furthermore, the highest O_3 mixing ratios ever attributed to tropospheric photochemistry are ~ 400 nmol/mol at heavily polluted urban sites [National Research Council, 1991] within the continental boundary layer. The CARIBIC data

do not indicate any signs of strong pollution in the vicinity of the sampling locales, and even severe photochemical O_3 production cannot yield O_3 mixing ratios above 150–200 nmol/mol in the tropical free troposphere. Measurements of photochemical precursors during the NOAA WP-3D observations also indicate that photochemical production was not important; e.g. carbon monoxide levels did not exceed 180 nmol/mol in the vicinity of the transients of O_3 and oxidized nitrogen species. Only the electrical discharge mechanism will be considered further.

[30] Electrical discharges can produce high O_3 mixing ratios, as high as the per cent range in the laboratory. After discovery of this O_3 formation process by *Schönbein* [1840], *von Siemens* [1857] developed the “electrical gas discharge” or “silent or cold discharge” technique for large-scale industrial ozone production. Electrical discharge in the atmosphere was proposed [*Sisteron and Kumar*, 1986] to explain the first observation of an O_3 -rich transient over the US in 1980 [*Clarke and Griffing*, 1985]. *Suhre et al.* [1997] discussed this hypothesis, but concluded it was less likely than stratospheric origin. In the following, we discuss the observed transients in the context of the electric discharge hypothesis to determine where, in the atmosphere and/or at the aircraft, and under what atmospheric conditions the transients are formed.

[31] Convection is the dominant process in the troposphere that produces electrical fields. The CARIBIC aircraft’s own instruments recorded a weak downdraft beginning at the aerosol increase (07:35:20 UT) and turning into an updraft exactly at the O_3 peak (07:36:00 UT), as illustrated by the aircraft speed (Figure 1b). Such convection induced updraft-downdraft transition zones (“squall lines”) are known to be accompanied by high space charge densities [*Dye et al.*, 1988]. This is explained by charge separation between ice - supercooled water particles lofted in the updraft and graupel pellets brought down in the adjacent downdraft [*Paluch and Sartor*, 1973]. Indeed, multifaceted evidence from laboratory measurements [*Peyroux and Lapeyre*, 1982], model studies [*Bhetanabhoita et al.*, 1985], and ground-based observations [*Orville*, 1967; *Shantla and Moore*, 1972; *Atmannspacher and Hartmannsgruber*, 1973; *Griffing*, 1977; *Borra et al.*, 1997; *Winterrath et al.*, 1999] indicate that silent electrical discharge induces generation of trace gases such as O_3 and NO. The trace gas formation occurs during charge transfer (micro sparks) between pointed objects and ambient air, e.g., on tree tops [*Borra et al.*, 1997] or ship masts, the famous blue St. Elmo’s fire.

[32] There are two surfaces which may carry the electrical charge that causes the ozone-transients:

(a) hydrometeors, which loose charge by corona discharge. Although corona currents are tiny compared to lightning bolts, their globally integrated charge transfer is assumed to carry a major fraction of the electrical current flowing in the global circuit [*Williams and Heckman*, 1993].

(b) the airplane itself, which gains charge from ambient hydrometeors and emits charge by electrical breakdown on extremities. Measurements at ground and in the air using three different aircraft by *Jones* [1990] indicate that the presence of cloud particles is a prerequisite for aircraft to collect sufficient charge to trigger electrical discharges from the aircraft fuselage.

[33] Besides O_3 , also oxidized nitrogen species are produced by the discharges (see below). Analysis of their relative concentrations provides two tools to help distinguish whether the O_3 producing discharges occur on the aircraft fuselage or within the atmosphere. Both tools are chemical clocks that give a measure of the time elapsed between the discharge and the detection of the species formed. The first tool is to check if the three trace gases O_3 -NO- NO_2 have reached a photostationary state (PSS), and the second is to determine if the ratio NO_x/NO_y has deviated significantly from unity. As discussed in the following sections, the first provides information on the first minutes after discharge occurrence, the second on the time period of some hours.

4.1. Analysis of Photostationary State (PSS) of O_3 , NO, and NO_2

[34] Silent discharges at low currents solely produce O_3 , NO, and N_2O [*Eliasson et al.*, 1984]. NO_2 is only subsequently formed by the reaction $NO + O_3 \rightarrow NO_2 + O_2$. At the same time, sunlight photolyzes NO_2 to reform NO and O_3 . A photostationary state is quickly established. The approach of O_3 , NO, and NO_2 to the PSS acts as a clock indicating the time elapsed between the species’ production and measurement. As the time constant to approach PSS, τ_{equil} , is on the order of a minute, this clock distinguishes O_3 formed in discharges on the aircraft (out of PSS, as the air transit time from the inlet to the instruments is seconds or less) from O_3 formed in the atmosphere before sampling, i.e., on hydrometeors (in PSS).

[35] The above trace gas triplet (as well as NO_y) was measured by the NOAA WP-3D research aircraft over central Tennessee (experimental details in section 2). Electrically active convection was noted and satellite imagery confirms the close proximity of a thunderstorm. Transients in O_3 , NO, NO_2 , and NO_y were recorded during sampling in the region closest to the storm. They were observed during two flight segments, ~ 90 min apart but at similar altitudes in that region. Figure 4 shows two (of ten total) of the more pronounced transients, each consisting of a series of spikes in each species. O_3 reached at least 320 nmol/mol (the upper limit of the instrument) and NO_y reached 60–70 nmol/mol. All transients document real trace gas variability; instrument artifacts have been ruled out (see section 2.3).

[36] Two types of transients can be distinguished. Type I transients are out of PSS. For example in spike series A (Figure 4), the observed NO_2 averaged $\sim 5\%$ of the NO_2 expected at PSS. Of the ten transients recorded on this flight, nine were type I. These transients cannot reflect atmospheric discharges, but must be due to trace gas formation by electrical discharges on the aircraft fuselage. In contrast, type II transients are in PSS. The broad transient B (Figure 4b) is the single example that we encountered. The ratio of NO_2 observed to NO_2 expected at PSS averages ~ 1.7 in transient B, which is consistent with PSS considering the experimental uncertainties involved in the measurement of NO, NO_2 , and the NO_2 photolysis rate, and the neglect of the role of peroxy radicals in the PSS analysis.

[37] Figure 4 suggests the discharges responsible for type I transients occur on the inlet tubes themselves, because each inlet generates its own characteristic spike signature. The three species O_3 - NO_x - NO_y were measured through

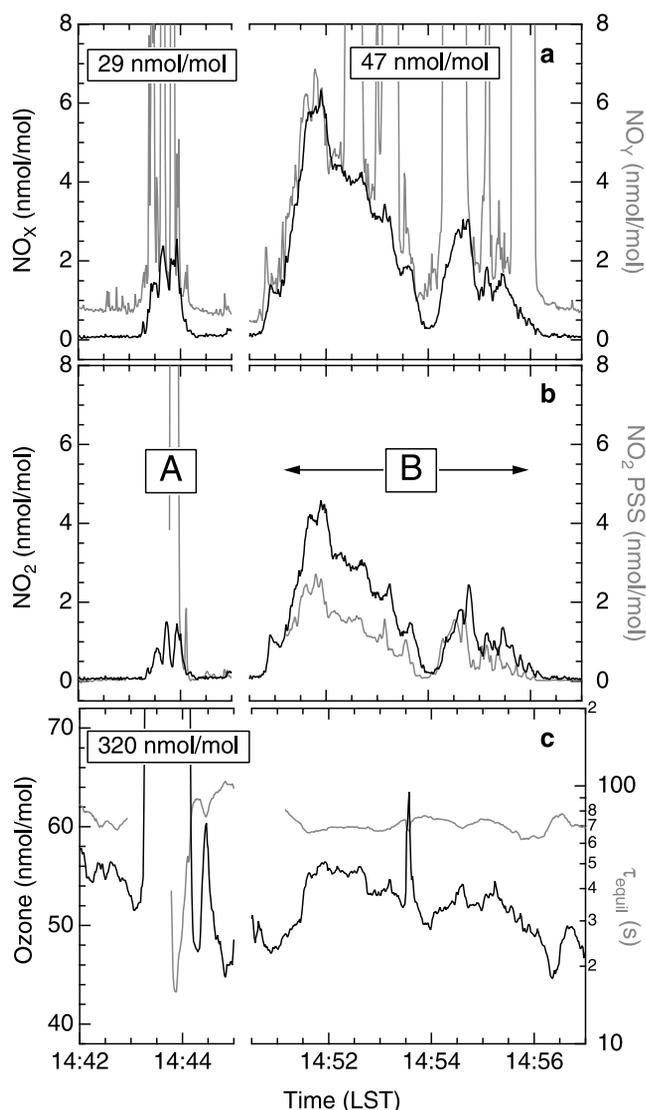


Figure 4. Time series of mixing ratios of (a) NO_x and NO_y , (b) NO_2 measured compared to NO_2 inferred from photostationary state (NO_2 PSS), and (c) O_3 and the time constant (τ_{equil}) for approaching PSS, observed on-board the NOAA WP-3D aircraft on 28 June, 1994 at ~ 5 km altitude near 36°N , 85°W . NO_2 PSS and τ_{equil} were deduced from the measured O_3 , NO , and NO_2 photolysis rate, and the rate constant for the reaction $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$. Off-scale maximum NO_y and O_3 observed in each spike period are given in the boxes in a and c.

three separate inlets on both sides of the aircraft. Their concentrations are poorly correlated in time, suggesting sporadic variation in the discharges on each inlet. In spike series A the shapes of the independent transients of the three species are quite different. Similarly poor correlation was present in all nine type I transients. During the period of transient B several very large spikes in NO_y were not present in the NO_x and O_3 measurements, and one spike in O_3 was not present in the NO_x record. The NO_y inlet was mounted within the shroud of a Rosemount temperature sensor, a metal housing with sharp edges. Such edges are particularly susceptible to electrical discharge. This likely accounts for

the stronger and more frequent spikes present in the NO_y record. In conclusion, the type I transients are simply measurement artifacts.

4.2. Analysis of the Ratio NO_x/NO_y

[38] In transient B, the concentrations of O_3 (slightly elevated over background levels) and NO_x (comparable with levels frequently observed at surface sites in the Eastern U.S. [Parrish *et al.*, 1993]) might characterize a boundary layer air mass that was convectively lofted to the flight altitude, not affected by electrically induced trace gas formation. Figure 4b, however, shows that NO_x and NO_y in transient B are approximately equal (excluding the superimposed type I spikes), i.e., neither peroxyacetyl nitrate (PAN) nor nitric acid (HNO_3) made significant contributions to NO_y . This implies, even when considering the possible partial scavenging of NO_y on cloud droplets, that the NO_x was formed recently (within 1 hr), since the characteristic time to convert NO_x to other NO_y species is only a few hours under June daytime conditions. During summer afternoons, NO_x on average accounts for only about 30% of NO_y in the U.S. boundary layer [Parrish *et al.*, 1993].

[39] It is conceivable that freshly polluted boundary layer air under cloudy conditions (present in regions of the boundary layer on this day) could have been lofted without photochemical conversion of NO_x to other NO_y species. However, carbon monoxide (CO) measurements also made on the NOAA WP-3D aircraft provide some evidence that transient B was not due to lofting of boundary layer air. The average CO concentration from 14:54:11 to 15:56:11 (during the second part of transient B) was (164 ± 5) nmol/mol (2σ confidence limit; the CO instrument was in a calibration and background test during the first part of transient B). The following two-minute period, after the transient ended, the average was again (164 ± 5) nmol/mol. Therefore no enhancement of CO can be discerned during transient B. For average U.S. emissions [U.S. Environmental Protection Agency, 2000], the 1.3 nmol/mol average enhancement in NO_x would be expected to be accompanied by a 9 nmol/mol average enhancement in CO. Also, in the absence of photochemistry, ozone would not be positively correlated with NO_x . In transient B (14:51:30–14:56:00) O_3 and NO_x were linearly correlated ($r^2 = 0.81$) with a slope of 1.01 ± 0.06 (1σ , excluding the small type I spike in O_3 at $\sim 14:53:30$).

[40] Also lightning possibly could be responsible for transient B through two mechanisms. First, the WP-3D aircraft could have passed through a dissipating channel of a lightning flash. However, this would imply an unreasonably intense flash. The first part of transient B covers more than 3 min flight time corresponding to a flight distance of ~ 19 km. Assuming that the aircraft passed directly through the center of a lightning channel of that diameter, then (following the analysis of Stith *et al.* [1999]) a one meter length of this flash must have produced $\sim 10^{25}$ molecules of NO. This is 3 orders of magnitude larger than the upper limit of the per flash generation rate found by Stith *et al.* [1999]. Thus it is unlikely that a single or even multiple flashes could have generated such a channel. It could be hypothesized that the WP-3D happened to fly down the length of a much narrower channel. However,

given the torturous geometry of lightning flashes, this is also unlikely. The second possible mechanism could be outflow of a thunderstorm. We cannot definitively exclude this possibility, but it is not a particularly attractive hypothesis. The primary outflow of thunderstorms is in the anvil at much higher altitudes than the 5 km flight altitude of the WP-3D, and the observed levels of lightning generated NO_x are generally no higher than 1–2 ppbv [Ridley *et al.*, 1996; Stith *et al.*, 1999] compared to the 6 ppbv observed here. Finally, if NO and not O_3 were generated as expected in lightning, O_3 and NO_y would be negatively correlated due to the product NO reacting with ambient O_3 . In contrast, we observe significant positive correlation of O_3 and NO_y in transient B (see above).

[41] Considering all of the evidence, we hypothesize that the elevated levels of NO, NO_2 , NO_y , and O_3 during the transient B episode were caused by corona discharges on cloud particles shortly before sampling.

5. Discussion and Conclusions

[42] The data presented here provide substantial evidence that the very short-term transients in ozone occasionally recorded by aircraft in the free troposphere (having a horizontal extension of 5–80 km) are in the majority artifacts. We suggest that the ozone is formed by electrical discharges on the aircraft fuselage, most likely on the inlet system itself, when flying through electrified air masses. Importantly, besides ozone other trace gases, notably NO, also are formed. Supported by the analysis by Jones [1990], we expect that most and perhaps all of these trace gas transients are linked to the presence of cirrus clouds (neither the MOZAIC nor CARIBIC sensors are able to detect cirrus clouds, but they indicate supersaturation versus ice hinting to the presence of cloud particles). Thus the presence of charged cloud particles is presumed to be a prerequisite to sufficiently charge the aircraft that electrical discharge occurs at the aircraft skin. During CARIBIC, O_3 transients were recorded outside the tropics as far as 48°N, and the WP-3D measurements were recorded in the mid troposphere at northern mid-latitudes. This is in contrast to MOZAIC, which detected such transients only in the tropical troposphere at 10–12 km altitude.

[43] One final consideration further supports our conclusion that the transients are artifacts associated with the aircraft itself. All of the transients reported by MOZAIC [Suhre *et al.*, 1997], CARIBIC and the WP-3D were found only in the immediate vicinity of the active convection and in the presence of updrafts. All the transients are characterized by strong spatial gradients, in general limited by the instrumental resolution. There are no reports of transients that are in the process of dissipating, i.e. away from the immediate vicinity of the convection with much weaker spatial gradients. If the transients actually represent ambient species, then the encounter of dissipating transients would be much more frequent than the encounter of fresh transients for two reasons. First, the initial stage of dissipation of a transient that reduces strong spatial gradients is much more rapid than the gradual mixing of highly elevated concentrations of trace species into the nearly uniform background. Second, the dissipating transients would gradually broaden and come to occupy a progressively larger

fraction of the volume of the troposphere. Schlager *et al.* [1997] have presented an analysis of aircraft emission plumes in the upper troposphere that quantitatively treat such dissipation processes. The lack of observations of dissipating transients strongly supports our conclusion that they are indeed artifacts.

[44] The production of O_3 and NO in discharges on aircraft flying in the vicinity of electrically active clouds is apparently a common phenomenon. We will now estimate the net O_3 and NO sources that may arise from these discharges. At any time ~ 2000 jet aircraft are in the air [IPCC, 1999]. Let us assume that 3/4 of them fly at 250 m/s in the 8–12 km altitude range. The average aircraft frontal surface is $\sim 20 \text{ m}^2$. Thus, aircraft pass a volume per second of $dV/dt = 2000 \cdot 3/4 \cdot 250 \text{ m/s} \cdot 20 \text{ m}^2 = 7.5 \cdot 10^6 \text{ m}^3 \text{ s}^{-1}$. Let us further assume that of the aircraft frontal surface, as an upper estimate, 0.1% or 200 cm^2 will be active for electrical discharges. Let us finally assume that during 10% of all flights (on average 8 h or 7200 km each) O_3 and NO spikes are formed and that their average horizontal extent is 50 km (based on the MOZAIC data). This results in a frequency of encounter of $F = 10\% \cdot 50 \text{ km}/7200 \text{ km} = 0.07\%$. Therefore, a volume per second of $dV/dt \cdot 0.1\% \cdot F = 5.3 \text{ m}^3 \text{ s}^{-1}$ is activated by aircraft for electrical discharges. Based on the CARIBIC and WP-3D data, the average excess in O_3 and NO is estimated as 1000 nmol/mol and 20 nmol/mol, respectively. The gases will be emitted in the NH 8–12 km between 0° and 60°N, i.e., in a volume of $\sim 8.9 \cdot 10^{17} \text{ m}^3$. For inferring the global mean excess of O_3 and NO, we must consider the mean residence time of the two gases. The concentration of NO is determined by the chemical lifetime of NO_x of ~ 7 days in this altitude/latitude range, but the relatively long-lived O_3 is set by the local turnover time estimated to be ~ 30 days. This results in average excess values for NO of $7.5 \cdot 10^{-8} \text{ pmol/mol}$ ($5.3 \text{ m}^3 \text{ s}^{-1} \cdot 20 \text{ nmol/mol} \cdot (8.9 \cdot 10^{17} \text{ m}^3)^{-1} \cdot 7 \text{ days}$) and for O_3 of $1.5 \cdot 10^{-8} \text{ nmol/mol}$. This is negligible for the tropospheric budgets of NO and O_3 . The contribution of this aircraft-induced O_3 and NO source remains negligible when considering local regions, e.g. over the northern Atlantic, where the frequency of aircraft can be 1 or 2 orders of magnitude higher.

[45] The NOAA WP-3D data provide one example of a less pronounced and broader trace gas transient that represents ambient atmospheric species. They were most likely produced by corona discharge on the surface of hydrometeors in an environment with high space charge density, and thus restricted to regions near active convective cells. Thunderstorms in an early or pre-lightning stage might correspondingly form O_3 and NO, a hypothesis supported by various earlier observations [Orville, 1967; Shanila and Moore, 1972; Atmannspacher and Hartmannsgruber, 1973; Griffing, 1977; Borra *et al.*, 1997; Winterrath *et al.*, 1999]. Estimates of the frequency of occurrence of such transients and the possible magnitude of trace gas sources from corona discharges on clouds will require a more extensive observational data base combined with a determination of the electrical currents responsible for the production of the species.

[46] These observations of the small-scale ozone and nitrogen oxide transients serve as a caveat for all measurements made in the vicinity of electrically active clouds. It is

possible for such artifacts to occur. This possibility should be considered in the interpretation of observations of rapidly changing, high levels of ozone and nitrogen oxides.

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