

Airborne observations of strong biogenic NO_x emissions from the Namibian Savanna at the end of the dry season

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Abstract. We report the observation of substantial emissions of NO_x from a several-hundred-square-kilometer region of savanna in northern Namibia in September 1992. The estimated emission rates lie near the high end of the range of values reported from flux chamber studies on various tropical savanna soils and appear to be associated with a light rainfall event which occurred 4 days prior to the observations. If our measurements are typical for this situation, then biogenic emission of NO_x following sporadic rainfall events during and at the end of the dry season may be an important regional source rivaling that arising from savanna burning and may have important consequences for regional scale ozone formation.

1. Introduction

It is widely recognized [Crutzen and Andreae, 1990] that the emission of trace gases (and aerosols) from the burning of biomass in the savanna regions of the world contributes a major proportion of the global source of many trace gases and is expected to result in significant ozone formation in the troposphere [Crutzen and Zimmerman, 1991]. As part of the international Southern Africa Fire-Atmosphere Research Initiative 1992 (SAFARI-92), studying these and related subjects, we instrumented a locally chartered turboprop DC-3 aircraft with a variety of trace gas measurement equipment and carried out several survey flights throughout southern Africa to investigate the regional distribution of trace gases in the boundary layer. Preliminary results of these measurements on biomass burning-related trace gas releases have been reported [Harris *et al.*, 1993a, b], and a complete analysis will be published elsewhere (G. W. Harris *et al.*, paper in preparation, 1996). Following two test flights, a total of 15 measurement flights were carried out between September 18 and October 6, 1992. This paper reports and discusses data obtained during two low-level survey flights on September 27 and 28 (flight numbers SAF10 and SAF11) over a savanna region to the northeast of the Etosha National Park, in Namibia, during which we observed elevated mixing ratios of NO_x which could not be attributed to fire related or anthropogenic sources.

2. Methods

The instrumentation for gas phase measurements of atmospheric composition were shipped to South Africa and installed in a locally chartered turboprop converted DC-3 aircraft at its home base at Wonderboom airport, north of Pretoria. The equipment included two tunable diode laser absorption spectrometers capable of measurement of up to six

species (but used for only five during SAFARI 92). The spectrometers have been used in several airborne and ground-based measurement programs since 1991 and performed satisfactorily during SAFARI, despite the extreme vibration encountered at times, especially when sampling fresh smoke plumes from large savanna fires. Additional equipment was also installed on board the aircraft for the measurement of CO_2 , O_3 , NO , and NO_y . Electrical power for the instrumentation and pumps on board the aircraft was supplied by three 5-kW gasoline-powered generators installed in the rear part of the cabin. The exhaust from the generators was vented outside the aircraft boundary layer, well aft of the intakes for the measurements. Table 1 lists the gas phase species measured from the aircraft; in addition, several aerosol studies were carried out [Le Canut *et al.*, this issue; M. O. Andreae *et al.*, manuscript in preparation, 1996]. The individual instruments for the gas phase measurements are described briefly in the following paragraphs.

2.1. Four-Channel TDLAS

The four laser airborne infrared (FLAIR) spectrometer is a four-channel tunable diode laser absorption spectrometer (TDLAS) in which the four lasers are housed in separate dewars cooled by liquid nitrogen. Three computer-controlled magnetically driven mirrors are used to project the four beams one at a time through a 126-m optical path in a modified 6.4 L White cell [Roths, 1993]. The atmospheric sample is pumped continuously through this cell at reduced pressure (50 mbar) and at flow rates of ~ 5 standard L min^{-1} , which results in an exchange time within the cell of a few seconds. The mirror control is so arranged that each laser in sequence is on line for 2 s. Signal averaging is carried out for 60 s, thereby producing a simultaneous measurement on the four channels each minute. Calibration is carried out by standard addition at the ambient air inlet of gases derived from high pressure gas mixtures (CH_4 , N_2O) or permeation devices (NO_2 , HCHO). The detection limits for NO_2 and HCHO , based on the reproducibility of zero air background spectra obtained regularly during the flights, were determined to be ~ 50 pptv and ~ 75 pptv, respectively, while the precision of the CH_4 and N_2O measurements was usually $\sim 1\%$, (which was insufficient to resolve

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Table 1. Gas Phase Measurements Aboard the DC-3 Aircraft

Species	Measurement Technique	Notes
NO ₂	TDLAS (FLAIR)	a
N ₂ O	TDLAS (FLAIR)	a
CH ₄	TDLAS (FLAIR)	a
HCHO	TDLAS (FLAIR)	a
CO	TTFM-TDLAS	1-s resolution
CO ₂	NDIR (Licor)	10-s resolution
O ₃	Eosin CL (Scintrex)	3-s resolution
O ₃	UV absorption (TE)	20-s resolution
NO	CL (Ecophysics)	b
NO _y	Gold/CO-CL	b, c

TDLAS, tunable diode laser absorption spectroscopy; FLAIR, four-laser airborne infrared spectrometer; TTFM, two-tone frequency modulation; NDIR, nondispersive infrared; CL, chemiluminescence; TE, Thermoelectron; a, time resolution of 60 s shared among four species; b, NO and NO_y were measured alternately by switching inlets every 30 s; c, NO_y converter mounted outside the airframe to avoid losses of HNO₃ on inlet surfaces.

variations in N₂O encountered during SAFARI-92). The accuracy of the determinations depended on the calibration sources and the flow controller calibrations and was estimated to be ~5%. The FLAIR instrument is described in more detail in a forthcoming paper by *Roths et al.* [1996].

2.2. Fast Response TDLAS

The optical subsystem of the second TDLAS instrument is similar to the FLAIR spectrometer, except that only two de-wars are installed, and the beams are combined at a dichroic optical element. They are selected alternately at 20 Hz by a masking chopper arrangement [Wienhold, 1992]. The multiple reflection cell in this compact instrument has a shorter, 45-cm base path and was adjusted for an optical path of 45.9 m through its 2.6-L volume. The gas exchange time in the cell was 0.25 s. The spectrometer is described in detail by *Wienhold et al.* [1994]; the instrument differs from FLAIR in that it employs two-tone frequency modulation (TTFM) [Cooper and Watjen, 1986]. The laser current is modulated at two radio frequencies (330 and 338 MHz), and the detector signal is demodulated at the difference frequency, 8 MHz, where the amplitude noise associated with the laser emission is considerably smaller than at the frequency of 15 kHz used in FLAIR. SAFARI-92 was the first airborne deployment of the system and although an electronics problem prevented dual laser operation the system functioned very satisfactorily in single channel mode, and precisions of <1% at 1 s integration time were achieved for the CO measurement.

2.3. Other Instrumentation

NO and NO_y were measured by an Ecophysics chemiluminescence instrument fitted with two inlets: a direct inlet for NO measurement and an externally mounted, heated, gold-CO converter for reducing NO_y species to NO prior to detection. The NO_y converter was designed to ensure that the first surface encountered by the sampled air was heated gold in the presence of CO. This measure is intended to prevent possible loss of NO_y species, especially HNO₃, to other surfaces before conversion. The measurement was switched automatically between NO and NO_y modes every 30 s. Calibration was performed by addition of NO or NO₂ at the appropriate inlet.

A further inlet was shared by three commercial instruments,

a LICOR model 6262 nondispersive infrared CO₂ instrument and two ozone measurement devices, a Thermoelectron model 49 UV absorption instrument and a Scintrex LOZ-4, which detects ozone through its chemiluminescent surface reaction with solutions of Eosin-Y. The pressure ahead of the three instruments was held constant at 1000 mbar during the flights using servo loop control of a Teflon membrane pump. The LOZ-4 had the faster time response (3 s versus 20 s for the TE49) and operated more reliably, especially in smoke plumes, where the UV instrument gave false positive readings, presumably due to the presence in smoke of large concentrations of (organic?) species which absorb 254-nm radiation.

3. Results and Discussion

3.1. Observations

During one leg of the survey flight in a region to the north-east of Etosha National Park on September 27, 1992 (SAF10), we observed highly elevated mixing ratios of NO₂ at low altitudes in a region where we could visually discern no evidence of current or recent fires. Figure 1 shows the time series of NO₂ mixing ratios measured by TDLAS and the altitude above ground during this low level flight leg near Oshivelo (18.7°S, 17.2°E). As indicated in the figure, the NO₂ rich region extended on the order of 200 km along the flight path. Elevated mixing ratios of NO and NO_y were detected at the same time.

Because of this unexpected observation, we modified our flight planning to allow a second survey of the area (SAF11) on the following day, September 28. Starting from the airstrip at Okaukuejo in Etosha we returned to the area at 0945 local time and performed a profile by flying for ~5 min at altitudes (above ground) of 65, 150, 300, and 450 m so as to register the vertical distribution of the trace gases referred to in Table 1. The temperature and relative humidity profile indicated that the boundary layer was approximately neutral at this time. Strong vertical gradients of several trace gases were observed,

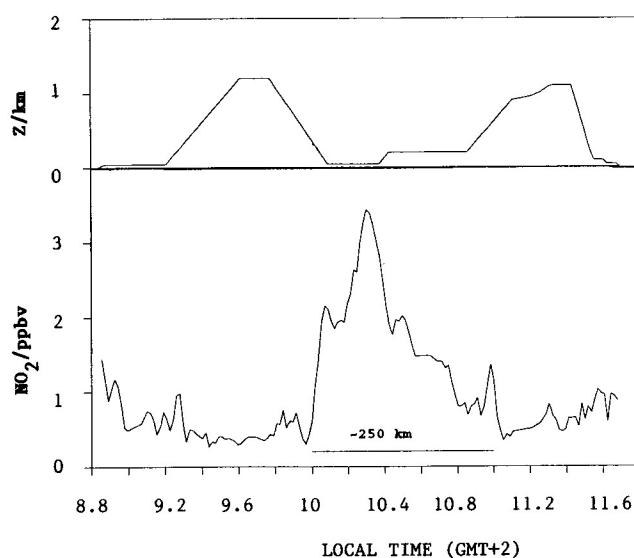


Figure 1. Time series of NO₂ mixing ratios (lower panel) observed during SAF10 on September 27, 1992. The upper panel shows the aircraft altitude measured in kilometers above ground.

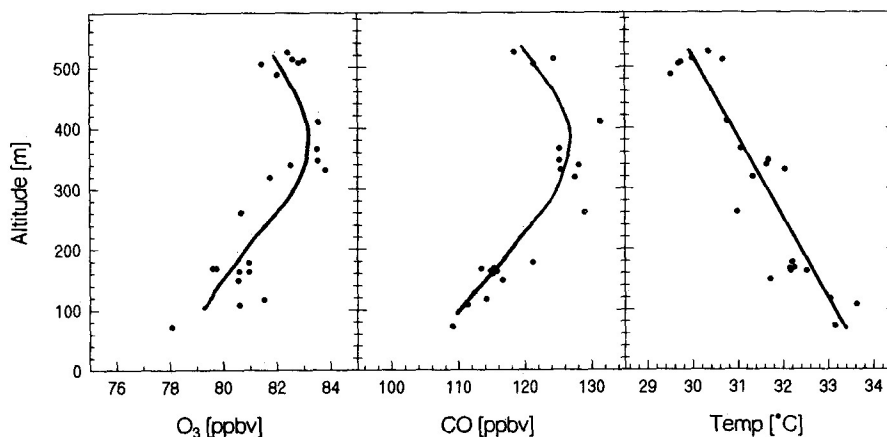


Figure 2. Vertical profiles of ozone, CO, and temperature measured during SAF11 on September 28, 1992.

shown for CO and O₃ in Figure 2 and for CO₂, NO₂, and NO in Figure 3.

The measured O₃ and CO indicated that the air at the upper levels of the profile could be characterized as having been previously impacted by biomass burning; the mixing ratios of ~85 ppbv ozone and ~125 ppbv CO were typical for the southern African boundary layer in regions not directly affected by active fires [Harris *et al.*, 1993a]. Some indication of the history of the airmass can be gleaned from the presence of ~0.5 ppbv of NO_x aloft and from the NO_x/NO_y ratio of ~0.2 (see Figure 3), which suggest a period of 2–3 days had elapsed since the injection of the NO_x. The somewhat lower O₃ and CO mixing ratios below about 250 m probably arise from deposition of these gases to the surface during transport. The mixing ratios of HCHO and CH₄ were quite constant at ~0.45 ppbv and ~1710 ppbv, respectively, over the vertical profile.

The vertical distribution of NO₂ and NO as well as that of CO₂ showed a markedly different characteristic. All three species had a strong gradient toward higher values near the ground, and the CO₂ and NO_x mixing ratios correlated linearly (Figure 4). The anticorrelation of the profiles of these species with that of CO rules out biomass burning as a source of the observed NO_x and CO₂ near the ground, supporting the evidence of the observers (and as recorded on a forward looking video camera) that there were no active fires in the region, and

we conclude that the source of the elevated NO_x mixing ratios near the surface was biogenic emission from the soil.

3.2. Estimates of the Magnitude of the NO Flux

The area, as observed from the aircraft, is characterized by sparse shrub and grass savanna vegetation with large patches of apparently bare soil. Studies of CO₂ evolution from similar savanna soils in Venezuela [Sanhueza *et al.*, 1994] suggest a source strength of 6–12 g CO₂ m⁻² day⁻¹ for both the wet and dry seasons. Similar CO₂ fluxes have been reported from Costa Rican [Schulze, 1967] and South African [Morris *et al.*, 1982] savanna soils. By adopting this range for the present case we estimate from the slope of the NO_x versus CO₂ plot an emission rate for NO_x of 20–40 ng N m⁻² s⁻¹ from the surface at the survey location. If additional sources of CO₂ such as the decay of dry vegetation or emissions from termites were present, the estimate of the soil-derived NO_x fluxes would be higher.

Although the instrument package aboard the SAFARI DC-3 was not designed with flux estimations as a measurement goal, further evidence that the NO_x flux lay near this range can be derived from the measured quantities by applying some simplifying approximations. From the observed HCHO and CH₄ mixing ratios and a simple photostationary state model [Harris *et al.*, 1992] and by using appropriate values for the HCHO

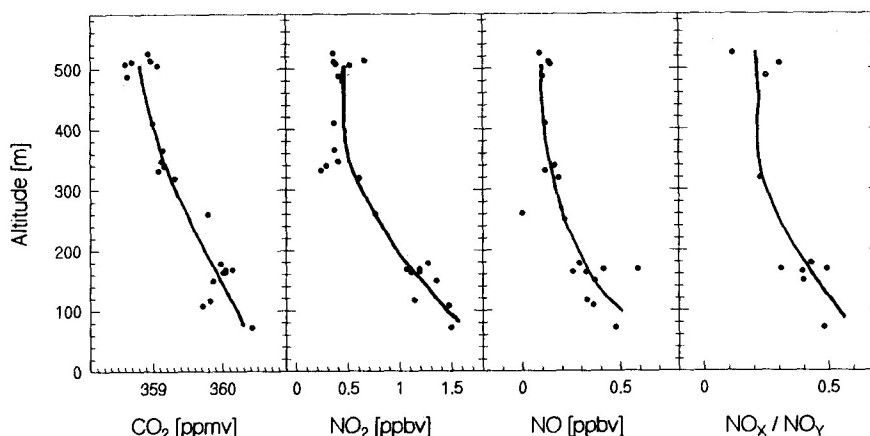


Figure 3. Vertical profiles of CO₂, NO₂, and NO and the ratio NO_x/NO_y measured during SAF11.

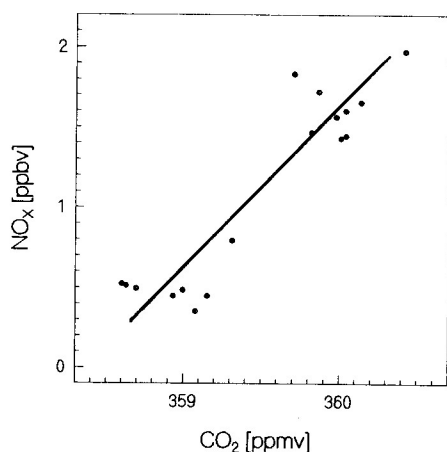


Figure 4. Scatter plot of NO_x and CO_2 mixing ratios determined during the SAF11 profile.

photolysis frequency [Warneck, 1988], we can estimate the OH number density as $\sim 3 \times 10^6 \text{ cm}^{-3}$. Taking into account the (probable) presence of significant amounts of nonmethane hydrocarbon in this airmass would increase the OH concentrations estimated by the calculation. Thus the rate of NO_2 oxidation by OH in the lower layer ($[\text{NO}_x] \sim 2 \text{ ppbv}$) was $\geq 2 \times 10^6 \text{ molecules cm}^{-3} \text{ s}^{-1}$, and the flux from the surface needed to maintain the observed NO_x mixing ratio in the lowest 300 m against this loss is then $\geq 6 \times 10^{10} \text{ molecules cm}^{-2} \text{ s}^{-1}$ ($\geq 14 \text{ ng N m}^{-2} \text{ s}^{-1}$).

A second rough estimate of the NO_x flux can be made by considering the concentration gradients of O_3 and NO_x . Adopting a deposition velocity of $\sim 0.2 \text{ cm s}^{-1}$ for ozone over the mostly bare soil [Warneck, 1988] leads to an estimate of the downward flux of $\sim 4 \times 10^{11} \text{ molecules cm}^{-2} \text{ s}^{-1}$ ozone. This downward flux leads to an observed mixing ratio difference of $\sim 2 \text{ ppbv}$ O_3 between 200 and 100 m altitudes. Assuming the same eddy diffusivity profile for the upward NO_x flux between these altitudes and noting the observed mixing ratio difference of $\sim 0.5 \text{ ppbv}$ leads to an estimate for the upward NO_x flux of $\sim 1.4 \times 10^{11} \text{ molecules cm}^{-2} \text{ s}^{-1}$ ($\sim 32 \text{ ng N m}^{-2} \text{ s}^{-1}$).

If the NO_x flux lies in the estimated range, we may derive an "inverse deposition velocity" for NO_x of $\sim 1 \text{ cm s}^{-1}$; thus the observed depth of the layer of elevated NO_x ($\sim 300 \text{ m}$) implies a transport time over the emitting region of $\sim 3 \times 10^4 \text{ s}$, or ~ 8 hours. At mean wind speeds of 5 m s^{-1} , this suggests that the dimension of the emitting area is on the order of $\sim 150 \text{ km}$ in the mean wind direction, consistent with our observation on September 27 that the source area extended $\sim 250 \text{ km}$ along the flight path. Although at the time of our measurements most of the preceding hours were dark, some conversion of NO_x to NO_y will have taken place, leading to an underestimate of the NO_x flux by some of the above approximate methods.

3.3. Significance of the Estimated Flux

Inquiry revealed that 4 mm of precipitation had been recorded at the Namibian Weather Service station at Oshivelo on September 24, that is, 3 days before our first survey flight in the area and that a further 1 mm was recorded on September 26. Several flux chamber studies have revealed sharp increases in NO emissions from wetted savanna soils. Johansson *et al.* [1988] observed emissions of up $150 \text{ ng N m}^{-2} \text{ s}^{-1}$ from Venezuelan savanna soil following a 3 mm watering during the dry

season. Lower emission increases (up to $25 \text{ ng N m}^{-2} \text{ s}^{-1}$) were observed by Rondon *et al.* [1993] at a trachipogon savanna site. Sanhueza and coworkers [Cardenas *et al.*, 1993] have reported that NO_x emissions from savanna soils are maximized when the soil water-filled pore space lies between 40 and 60% and we speculate that the high NO_x fluxes we observed are associated with the rainfall events on September 24 and 26, which may have brought the soil moisture content into the above range.

The chamber studies of NO_x fluxes from intentionally wetted savanna soils cited above, as well as others, [Sanhueza, 1992; Levine, 1993] have indicated within hours of watering a strong increase in NO emissions which decay quite rapidly by the second and subsequent days. Although we cannot estimate a flux from our observations during the first flight (September 27), the maximum NO_2 (and NO_x) mixing ratios measured at low flight levels were almost double those seen on the next day. Both flights took place at about the same time of day and the general weather situations were similar, presumably leading to similar mixing conditions, so we may qualitatively deduce that the NO_x fluxes were most probably higher on September 27 than on September 28. The fluxes were possibly even higher again on September 25 and 26, if the second, very light, precipitation event played only a minor role, as expected from the results of manipulative experiments involving repeated watering [Johansson *et al.*, 1988; Davidson, 1992]. Very high moisture contents suppress NO emission [Cardenas *et al.*, 1993], but this effect would probably not arise in this case after only light rain onto previously parched soil. Our observations were performed at the end of the dry season after a prolonged drought in Namibia. Under these conditions a large fraction of soil N will be mineralized during the wetting event [Davidson, 1992], and a large pulse of nitrogen will be available to support NO production.

On the very conservative assumption that the lower flux estimate based on the NO_x/CO_2 correlation ($20 \text{ ng N m}^{-2} \text{ s}^{-1}$) for September 28 had been emitted for only the previous 48 hours we calculate that a total of $\sim 4 \text{ mg N m}^{-2}$ had been released as a result of the precipitation event. At the other end of the range of estimates ($40 \text{ ng N m}^{-2} \text{ s}^{-1}$ on September 28, $80 \text{ ng N m}^{-2} \text{ s}^{-1}$ on September 27, and on September 25 and 26), the total amount of NO_x emission would be $\sim 24 \text{ mg N m}^{-2}$.

It is interesting to compare these estimated amounts with the amount of NO_x which would have been emitted if the area had burned. We estimate a biomass loading of $2\text{--}4 \text{ t ha}^{-1}$ dry weight for this savanna type (W. S. Trollope, private communication, 1992), of which $\sim 50\%$ by weight is carbon, and expect a N/C ratio of $\sim 0.3\text{--}0.5\%$ for this nutrient poor, dry savanna. Using an NO_x emission factor of $\sim 20\%$ of fuel nitrogen [Lobert *et al.*, 1991] leads to the conclusion that $60\text{--}200 \text{ mg N m}^{-2}$ of NO_x would be emitted by a savanna fire at this location if all the biomass burned. Thus our observations suggest that between 2 and 40% of the potential NO_x release by burning had been emitted from the site as a result of the rainfall event at the end of the dry season.

Bearing in mind that (at least in normal years) it rains everywhere in the region at least once, whereas the burnin frequency is estimated as once per 2–3 years on average [Menant *et al.*, 1991], it seems likely that the biogenic emission of NO_x as a consequence of sporadic rainfall during the dry season or of the first rains heralding the wet season could be a very significant source from the savanna regions.

In the studied case, where these NO_x emissions were in-

ected into an airmass already loaded with biomass-burning emissions, but in which the NO_x of biomass burning origin had already largely been converted to NO_y, the extra NO_x will lead to enhanced ozone formation during transport. Forward trajectory calculations (M. Garstang, private communication, 1995) for nearby Etosha National Park for the period September 25–30, 1992, predominantly show transport of air masses out over the Namibian coast into the tropical South Atlantic Ocean where satellite observations [Fishman *et al.*, 1990] have documented elevated levels of tropospheric ozone during the September–November period. Our observations suggest investigation of whether the sudden release of NO_x from burning or the steady, slower release over several days from rainfall-stimulated microbiological soil processes has the greater integrated efficiency for ozone production. Also indicated are further studies to investigate the annual emissions from savanna soils with particular regard to the variability connected to sporadic rainfall events as well as with other factors including soil characteristics and denitrification potential, [Le Roux *et al.*, 1995].

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