Impact of the Manaus urban plume on trace gas mixing ratios near the surface in the Amazon Basin: Implications for the NO-NO_2-O_3 photo-stationary state and peroxy radical levels

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Abstract

We measured the mixing ratios of NO, NO_2, O_3, and volatile organic carbon (VOC) as well as the aerosol light scattering coefficient on a boat platform cruising on rivers downwind of the city of Manaus (Amazonas State, Brazil) in July 2001 (LBA-CLAIRE-2001). The dispersion and impact of the Manaus plume was investigated by a combined analysis of ground based (boat platform) and airborne trace gas and aerosol measurements as well as by meteorological measurements complemented by dispersion calculations (HYSPLIT model). For the cases with the least anthropogenic influence (including a location in a so far unexplored region ~150 km west of Manaus on the Rio Manacapuru) the aerosol scattering coefficient, σ_s, was below 11 Mm^{-1}, NO_x mixing ratios remained below 0.6 ppb, daytime O_3 mixing ratios were mostly below 20 ppb and maximal isoprene mixing ratios were about 3 ppb in the afternoon. The photo-stationary state (PSS) was not established for these cases, as indicated by values of the Leighton ratio, Φ, well above unity. A change of the synoptic wind direction from east-northeast to south-southeast in the afternoon, due to the influence of river breeze systems and other thermally driven mesoscale circulations, often caused a substantial increase of σ_s and trace gas mixing ratios (about threefold for σ_s, fivefold for NO_x and twofold for O_3), which was associated with the arrival of the Manaus pollution plume at the boat location. The ratio Φ reached unity within its uncertainty range at NO_x mixing ratios of about 3 ppb, indicating "steady state" conditions in cases when radiation variations, dry deposition, emissions, and reactions mostly involving peroxy radicals (XO_2) played a minor role. The median midday/afternoon XO_2 mixing ratios estimated using the PSS method range from 90 to 120 ppt for the remote cases ($\sigma_s < 11$ Mm^{-1} and $NO_x < 0.6$ ppb), while for the polluted cases our estimates are 15 to 60 ppt. These values are within the range of XO_2 estimated by the atmospheric chemistry box model CAABA/MECCA-3.0.

1. Introduction

The chemistry of nitrogen oxides (NO_x, the sum of nitrogen monoxide, NO, and nitrogen dioxide, NO_2) within the planetary boundary layer was studied in detail during the last decades in many regions of the globe. It is well known that NO_x acts as a key catalyst in the formation of tropospheric ozone (O_3) [*Crutzen and Lelieveld*, 2001]. In the absence of competing reactions, a dynamic equilibrium between NO, NO_2 and O_3 (also called photo-stationary state) may be established during daytime in the troposphere:

$$NO_2 + h\nu\ (\lambda < 420\ \text{nm}) \rightarrow NO + O(^3P) \qquad \text{R1}$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \qquad \text{R2}$$

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad \text{R3}$$

R2 is much faster than R1, and therefore R1 and R3 determine the overall conversion rate. The photo-stationary state (PSS) parameter, or Leighton ratio, Φ [*Leighton*, 1961], is defined by:

$$\Phi = \frac{j(NO_2) \times [NO_2]}{k_3 \times [O_3] \times [NO]} \qquad (1)$$

where $j(NO_2)$ is the photolysis frequency of NO_2 and k_3 is the rate constant of R3 [*Atkinson et al.*, 2004]. When Φ is unity, no additional O_3 is produced and the reactions R1-R3 represent a null cycle. The PSS approach is only valid under "steady state" conditions, i.e., in the absence of (a) rapid changes of light intensity and fluctuations of mixing ratios, (b) significant influence of dry deposition or fresh emissions of the involved compounds, and (c) other competing reactions.

Particularly, the oxidation of NO by peroxy radicals constitutes a major net O_3 production pathway in the troposphere [e.g., *Warneck*, 2000]:

$$HO_2 + NO \rightarrow NO_2 + HO \qquad \text{R4}$$

$$RO_2 + NO \rightarrow NO_2 + RO \qquad R5$$

where R is an organic functional group (e.g., CH_3 or C_2H_5). HO_2 and RO_2 radicals (their sum hereafter referred to as XO_2) are formed from the oxidation of carbon monoxide (CO) and hydrocarbons by OH radicals. Most previous studies reported that PSS is readily established under polluted (high-NO_x) conditions [*Carpenter et al.*, 1998; *Griffin et al.*, 2007; *Parrish et al.*, 1986; *Volz-Thomas et al.*, 2003]. It was found, however, that under cleaner (low-NO_x) conditions, XO_2 may substantially perturb PSS, resulting in values of $\Phi >> 1$ and measured NO_2 mixing ratios exceeding those predicted by eq. (1) [*Bakwin et al.*, 1994; *Hauglustaine et al.*, 1996; *Ridley et al.*, 1992]. Some authors [e.g., *Mannschreck et al.*, 2004; *Volz-Thomas et al.*, 2003] suggested that other unknown oxidation processes may cause an additional conversion of NO to NO_2 leading to values of $\Phi >> 1$. This was recently confirmed by *Hosaynali Beygi et al.* [2011] for background conditions in the remote marine boundary layer.

Only few studies have investigated the NO-NO_2-O_3 triad in the Amazon Basin. These either focused on the surface-atmosphere exchange fluxes of individual compounds [*Bakwin et al.*, 1990; *Ganzeveld et al.*, 2002; *Gut et al.*, 2002; *Jacob and Wofsy*, 1990; *Rummel et al.*, 2002; *Rummel et al.*, 2007; *Trebs et al.*, 2006], on airborne studies, and modeling activities [*Andreae et al.*, 1988; *Crutzen et al.*, 1985; *Harriss et al.*, 1988; *Kuhn et al.*, 2010; *Lelieveld et al.*, 2008; *Torres and Buchan*, 1988]. In the Amazon, mixing ratios of the NO-NO_2-O_3 triad are substantially enhanced during the dry (biomass burning) season from June to September. However, the plume of pollutants originating from the city of Manaus (currently about 1.7 million inhabitants) is known to have an additional significant impact on atmospheric chemistry in the region west of Manaus [*Kuhn et al.*, 2010]. Furthermore, high emissions of hydrocarbons have recently been shown to sustain high radical concentrations above the above the Brazilian rainforest close to

Manaus [*Kuhn et al.*, 2007] as well as above other tropical South American rainforest locations [cf. *Lelieveld et al.*, 2008; *Martinez et al.*, 2010], thereby affecting the cycling of NO_x and the production of O_3 in this region. The influence of anthropogenic activities and mixing conditions on atmospheric chemistry within the boundary layer in the Amazon Basin is not well understood, and no direct measurements of prevailing XO_2 radical mixing ratios have been reported so far. Likewise, an investigation of the PSS of the NO-NO_2-O_3 triad has not yet been performed in this region. A thorough understanding of the NO-NO_2-O_3 chemistry and the role of peroxy radicals is required for an assessment of future chemistry-climate interactions in tropical regions with increasing anthropogenic impact [cf. *Ganzeveld et al.*, 2010].

In this paper, we investigate the PSS for the first time at unique (including very remote) measurement locations in the Amazon Basin, based on field measurements made during the Large-Scale Biosphere-Atmosphere Experiment in Amazonia - **C**ooperative **L**BA **Ai**rborne **R**egional **E**xperiment (LBA-CLAIRE-2001). We used a boat platform cruising on rivers in the downwind region west of Manaus, at a distances ranging from ~20-150 km. We sampled clean air at remote locations as well as air masses affected by the Manaus plume, which had interacted with the rain forest and water surfaces of rivers west of Manaus. We infer XO_2 mixing ratios and we show that the PSS approach is not valid in the low-NO_x regime of remote tropical air masses, in agreement with results obtained in other remote regions of the globe. Furthermore, our analysis provides information about the impact of anthropogenic emissions and mesoscale circulations on the pristine tropical forest photochemistry and radical formation near the surface downwind of Manaus.

2. Experimental

2.1 Description of measurement sites and implementation

The measurements were made within the framework of LBA-CLAIRE-2001 from 10 to 27 July 2001 (wet-to-dry season transition) on a boat cruising downwind of the city of Manaus (Figure 1). Manaus had a population of about 1.2 million human inhabitants in 2001; major emission sources in and around Manaus comprise thermoelectric power plants, vehicles, saw mills, charcoal kilns, brick factories and small-scale burnings [*Kuhn et al.*, 2010].

The average annual rainfall in Manaus is ~2200 mm with two marked seasons (November-May wet; June-October dry). The rainforest ecosystem characteristics of the Manaus area are described in detail by *Kuhn et al.* [2007]. The air flow is typically dominated by easterly trade winds transporting humid oceanic air masses from the Atlantic more than 1000 km over the almost undisturbed rain forest of the northeastern Amazon Basin, before reaching the urban area of Manaus.

Three boat trips were performed on Rio Manacapuru (10-11 July) and on Rio Negro (18-20 and 25-27 July) (see Figure 1). During weekends the boat was located at the main station in Manacapuru (Paraiso D' Angelo: 3.297°S, 60.604°W), where instruments were maintained and calibrated. Two boat platforms were used during our experiment. The first boat was equipped with an automatic weather station, and the trace gas and aerosol measuring instrumentation, while the second boat carried a diesel generator providing a power of 15 kW for operation of the instruments. A power cable was connected to an electrical manifold onboard of the first boat and was kept on the water surface using floating devices. The second boat was pulled by the first boat using a 5 mm steel cable and was kept always downwind of the first boat to minimize the risk of local contamination.

2.2 Meteorological measurements

Meteorological quantities were monitored with a time resolution of one minute on a mast at a height of 8 m above the water surface. These comprised wind speed (cup anemometer A101ML, Vector Instruments, UK), wind direction (wind vane, self-referencing, SRW1, Vector Instruments, UK), solar global irradiance (pyranometer, LI-1000, LI-COR, USA), air temperature and relative humidity (Hygromer® IN-1 & Pt100 sensor in aspirated housing, Rotronic Messgeräte GmbH, Germany) and barometric pressure (pressure analog barometer, PTA 427A, Vaisala, Finland). Rainfall was measured using a tipping rain gauge (ARG 100-EC, Campbell Scientific, UK) on the edge of the boat. The position of the boat was tracked continuously using a Global Positioning System unit (GPSHAND, ESYS, Berlin, Germany).

2.3 Trace gas and aerosol measurements

The inlets for trace gas and aerosol measurements were located at a level of 3 m above the water surface. The reactive trace gases, nitric oxide (NO), nitrogen dioxide (NO_2) and ozone (O_3) were measured with a time resolution of one minute using sensitive commercially available analyzers located in the interior of the boat. NO was measured by red-filtered detection of the chemiluminescence produced during the reaction of NO and O_3 (CLD 780 TR, ECO Physics, Switzerland). Excess O_3 was continuously added in a pre-reaction chamber to account for the cross sensitivity by other gases. NO_2 was photolytically converted to NO by exposure of the sample air to a high-pressure xenon lamp (Tecan PLC 760 photolytic converter) and then detected by the chemiluminescence analyzer. The analyzer was calibrated four times during the experiment (on 8, 13, 22 and 25 July 2001) by diluting a 5.32 ppm NO standard gas. The efficiency of the photolytic conversion of NO_2 to NO was 0.52, determined by a back titration procedure involving the reaction of O_3 with NO using a gas phase titration system (SYCOS K-GPT, ANSYCO GmbH, Germany).

The climatic conditions in the Amazon Basin and the absence of air conditioning on the boat caused higher detection limits and uncertainties of the CLD 780 TR analyzer than typical for controlled conditions [cf. *Mannschreck et al.*, 2004; *Volz-Thomas et al.*, 2003]. The limit of detection (LOD) (2σ-definition, 10 min averages) for NO and NO_2 determined during the experiment by sampling synthetic (zero) air that had passed an active charcoal filter were 75 ppt and 135 ppt, respectively. The correction applied for the systematic offset of the CLD 780 TR analyzer determined when sampling zero-air was on average 50 ppt. This value was confirmed by sampling clean air with ambient NO levels near zero during nighttime at the remote locations [cf. *Kley and McFarland*, 1980]. The precision of the chemiluminescence analyzer determined from the signal noise during the calibrations was on average 4% (2σ). The variation of the spans of the individual calibrations made on the boat platform was 20%. The influence of ambient temperature and humidity variations on the sensitivity of the chemiluminescence analyzer are about 1.3% K^{-1} and -0.27% per hPa H_2O [see *Volz-Thomas et al.*, 2003]. The temperature in the boat ranged from 25 to 35°C. Since the calibrations were made at temperatures covering this range, the temperature effect is included in the span variation stated above. Data were not corrected for the humidity effect since it applies to both NO and NO_2 measurements, and would thus not affect the value of Φ (see eq. 1).

O_3 was measured with a UV absorption analyzer (Thermo Instruments, TE49C, USA), which has an accuracy of 5% and a precision of 1% at mixing ratios ≥ 20 ppb. The offset of the analyzer was checked by sampling synthetic air that had passed an active charcoal filter. Grab samples for the determination of VOCs (50 min sampling interval) were collected on fusedsilica-lined stainless steel cartridges (89 mm length, 5.33 mm I.D., Silicosteel, Restek, USA) with 2-bed graphitic carbon adsorbents (130 mg Carbograph 1, followed by 130 mg Carbograph 5; Lara s.r.l., Rome, Italy) using customized constant-flow sampler devices (*courtesy* Jim Greenberg, NCAR). The samples were analyzed off-line in the laboratory using a thermal desorption gas chromatograph with a flame ionization detector (GC-FID) as described in *Kuhn et al.* [2002, 2004]. Calibration was accomplished by different gaseous standards containing isoprene, several n-alkanes, methyl vinyl ketone (MVK), and methacrolein (MACR). The detection limit was determined from the standard deviation of the blank values and was typically 30 ppt for isoprene and 10 ppt for monoterpenes. Overall uncertainties were 10 % for isoprene at 1 ppb and ranged from 5 to 30 % at 100 ppt for monoterpenes [cf. *Kuhn et al.*, 2007]. Additionally, aerosol light-scattering measurements were made with a single-wavelength (λ = 545 nm) nephelometer (Model M903, Radiance Research, USA) at ambient RH.

2.4 Companion measurements

Kuhn et al. [2010] reported on airborne measurements of trace gases and aerosols in the region west of Manaus, which were part of LBA-CLAIRE-2001. In this study, we use data (O_3 and aerosol number concentrations) measured during crosswind transects in the urban outflow at a longitude of ~ 60.41°W (~ 43 km downwind of Manaus) on 19 July (Flight #18: 10:00-14:00 LT, Flight #19: 15:45-18:00 LT). O_3 was measured with a time resolution of 10 s using the same type of instrument as on the boat platform and the aerosol number concentrations (CN) were measured at 1 Hz time resolution with a condensation particle counter (CPC, Model 3762 and 3010, TSI, USA) [cf. *Kuhn et al.*, 2010].

In addition, meteorological measurements (temperature, relative humidity, wind speed, wind direction) were made on a 52-m high walk-up scaffolding tower (K34, ca. 20 m above the forest canopy) [see *Kuhn et al.*, 2007]. The tower is located in the National Institute of Amazon Research (INPA) forest management area (Reserva Biológica do Cuieiras) in undisturbed primary forest about 60 km NNW of Manaus (2.6091°S, 60.2092°W) (see Figure 1).

2.5 Data evaluation

The one-minute time series of all measured quantities on the boat platform were combined into arithmetic averages for 10-minute intervals. However, as recommended by *Yang et al.* [2004], geometric averages of all input quantities were used for the calculation of Φ and XO_2 mixing ratios to minimize the possibility of bias caused by measurement imprecision. Data were excluded from our analysis when the boat was moving or when pollution from the diesel generator was present. About 43% of the remaining numbers of data points were below the detection limit for NO (6% for NO_2). These data were not eliminated from the time series, but are treated with caution for the PSS calculations (see below).

The PSS approach should not be applied under "non-steady state" conditions, i.e., when rapid changes of light intensity or mixing ratios occur. In order to exclude these cases, we calculated the time required to establish the photo-stationary state, τ_{PSS} (1/e-definition), according to:

$$\tau_{PSS} = \frac{1}{j(NO_2) + k_3 \times [O_3]} \qquad (2)$$

The calculated τ_{PSS} values ranged between 60 and 300 s during daytime. When analyzing the one-minute time series we found that trace gas mixing ratios typically remained fairly constant within these short time periods. Similar to previous studies [e.g., *Yang et al.*, 2004] we ensured adequate stability of $j(NO_2)$ by excluding data from the PSS evaluation during periods when the standard deviation of the solar global irradiance of the 10-min averaging interval was higher than 5% of the average value. Since radiation also strongly varies during sunrise and sunset, these periods were automatically removed from the PSS evaluation based on this criterion. Thus, our analysis is confined to clear-sky periods with low radiation fluctuations (see below).

Moreover, we estimated the prevailing XO_2 mixing ratios under "steady state" conditions for cases when $\Phi > 1$, expressing their role in the conversion of NO to NO_2, by assuming that NO_2 is produced via R3, R4 and R5 and re-arranging eq. (1) to [*Carpenter et al.*, 1998; *Volz-Thomas et al.*, 2003]:

$$[XO_2] = \sum_i [R_iO_2] + [HO_2] = (\Phi - 1)\frac{k_3[O_3]}{k_{eff}} \qquad (3)$$

Since the rate constants k_4 and k_5 are nearly identical [*Atkinson et al.*, 2004; 2006] we used an effective rate constant $k_4 \approx k_5 = k_{eff} = 3.6 \times 10^{-12}\, e^{(270/T)}$ cm^3 $molecule^{-1}$ s^{-1} for our analysis. It should be noted that eq. (3) only holds in case no other processes convert NO to NO_2 (i.e., it ignores the potential role of e.g., NO_3 and halogens).

2.6 Measurement uncertainties

Photolytic converters which emit radiation in a very narrow spectral band, making the conversion of NO_2 to NO more specific (e.g., Blue-Light Converters) were unfortunately not yet available in 2001. However, the high-pressure xenon lamp of the Tecan PLC 760 photolytic converter was equipped with an optical filter with a maximal transmittance at 360 nm. As discussed in *Ryerson et al.* [2000] this minimizes interferences from other species (e.g., HONO). Under clean conditions the HONO mixing ratio is about 50 ppt during daytime in the Amazon Basin [*Trebs et al.*, 2004]. The residence time of the air in the converter was 8 seconds (52 % conversion efficiency) and with j(HONO) = 0.3 x j(NO_2) the potential maximal HONO interference is thus ~ 8 ppt. The thermal decomposition of PAN at 30°C for a residence time of 8 seconds is < 1 %. Assuming an upper limit of 500 ppt, the maximal PAN interference would be ~ 3 ppt. In addition, the zero-air measurement (see section 2.3) revealed no indication for a spurious NO_2 signal induced by irradiation of photolysis cell surfaces as described in *Kley and McFarland* [1980]. The light stream in the photolysis cell was focused in a long narrow cylinder thereby minimizing irradiation of the chamber walls that may cause secondary reactions.

The uncertainty of the Leighton ratio can be estimated using Gaussian error propagation [cf. *Hauglustaine et al.*, 1996; *Mannschreck et al.*, 2004]. An uncertainty of 20% was assigned to the rate constant k_3 [see *Atkinson et al.*, 2004]. Since we did not measure $j(NO_2)$, we applied an empirical parameterization (derived from in-situ measurements in the Amazon) from *Trebs et al.* [2009] to estimate $j(NO_2)$ from the measured solar global irradiance. This method has a 2σ uncertainty of about 25%. An error of 5 % was assigned to the ozone mixing ratio. The uncertainty of the NO and NO_2 measurements was estimated from the statistical error and the systematic error [cf. *Yang et al.*, 2004]. The statistical error comprises the detection limit (75 ppt for NO and 135 ppt for NO_2) and the analyzer precision, 2σ) of 4 % (see section 2.3). The systematic error from calibrations and potential artifacts and uncertainties that could not be determined directly from our measurements (see above) was estimated to 20 %. The uncertainty increases with decreasing signal to noise ratio and was < 30 % ([NO] > 0.8 ppb, $[NO_2]$ > 1.4 ppb), 30 - 95 % ([NO] = 0.1 - 0.8 ppb, $[NO_2]$ = 0.2 – 1.4 ppb) and > 95 % ([NO] < 0.1 ppb, $[NO_2]$ < 0.2 ppb). Hence, the estimated uncertainty of Φ (see section 3.4.2) is clearly dominated by the errors of the NO_x measurements, in particular when mixing ratios approach the LOD. The uncertainty of estimated XO_2 mixing ratios was also estimated using Gaussian error propagation. Considering that mainly HO_2, CH_3O_2 and $C_2H_5O_2$ contribute to XO_2, an average uncertainty of 20 % was assigned to the rate constant k_{eff} [see *Atkinson et al.*, 2004; 2006].

3. Results and Discussion

Our dataset includes five days of remote measurements when relatively clean air masses were sampled with only occasional anthropogenic influence, distinguishing three different cases (Figure 1). These are (i.) 10-11 July (3.0324°S, 61.3445°W, *"Lago Manacapuru"*, distance to Manaus ~147 km, color-code blue), (ii.) 18-19 July (3.0948°S, 60.4102°W, distance to Manaus ~43 km, color-code orange) and (iii.) 25 July (3.0316°S, 60.4736°W, distance to Manaus ~50 km, color-code turquoise). In addition, we observed two distinct cases when air masses were substantially influenced by anthropogenic pollution from the city of Manaus. These are (i.) 20 July (3.0922°S, 60.1968°W, distance to Manaus ~19 km, color-code violet) and (ii.) 26-27 July (3.0185°S, 60.1725°W, distance to Manaus ~19 km, color-code magenta).

3.1 Meteorological conditions

The convective boundary layer (CBL) above the Amazonian rain forest typically reaches its maximum height of 1000 to 1500 m at around 17:00 LT [*Fisch et al.*, 2004; *Martin et al.*, 1988]. Radiative cooling starts after 17:00 LT and the thermodynamically stable stratified nocturnal boundary layer develops to a final height of 100 to 300 m. Meteorological conditions at the boat platform were mainly determined by background synoptic winds (northeasterly trade winds) and the formation of thermally driven diurnal mesoscale circulations. Wind roses averaged for all boat locations at the southern bank of the rivers (Figure 1) reveal prevailing winds from east-northeast during the night and morning (Figure 2a), while during the afternoon and evening winds from south-southeast were dominating (Figure 2b). Both regimes are characterized by relatively high wind speeds (2 to 5 m s^{-1}). The transition between the two regimes typically occurred around 15:00 LT and 00:00 LT. A similar pattern had been observed previously by *de*

Oliveira and Fitzjarrald [1993] from measurements in an area north of the Rio Negro, about 60 km north of Manaus. They hypothesized that this circulation pattern can be attributed to a river breeze caused by the thermal contrast between the Rio Negro and the land surface. They found that the river breeze is asymmetric (i.e., not exactly perpendicular to the river) due to the influence of the easterly trade winds.

This wind pattern was most distinct on 18/19 July. The HYSPLIT model [*Draxler and Hess*, 1998; meteorological REANALYSIS data set] provided supporting information on the dispersion of air masses originating from Manaus. Wind vectors expressed as one-hour forward trajectories starting at 3.0948°S, 60.4102°W on 18 July at 18:00 LT at different heights within the CBL (Figure 3) reveal a southeasterly wind direction in the lower part of the boundary layer (< 300 m), which agrees with our observations (Figure 4a). This was also experimentally confirmed by results of radio soundings at the K34 tower (not shown). The wind direction turned towards northeast with increasing height, indicating that the southeastern flow close to the ground was generated by processes within the CBL (e.g., decoupling, local pressure gradients). On 18/19 July the wind direction measured on the boat platform also compares quite well with the wind direction measured at the K34 tower about 58 km north-northeast of the boat position (see Figure 4a). This confirms the existence of a mesoscale circulation system. *Betts et al.* [2008] pointed out that the generation of such mesoscale systems is not only caused by river breezes (depending on the shape of the rivers and their position towards the background synoptic flow), but may also be facilitated by other surface heterogeneities (topography, differences in roughness length between water and land, different vegetation types, soil water availability). Results from the HYSPLIT model for days outside our measurement period indicate that this wind system is not always prevailing around the Manaus region, but was obviously the predominant pattern during the particular days when our measurements took place.

We observed one significant exception from the typical wind pattern, which occured on 26 and 27 July, the only instance when the boat was located at the northern bank of the Rio Negro close to Manaus (Figure 1). A diel oscillation of the local wind perpendicular to the river was observed. The wind blew from the rain forest (north) to the Rio Negro river during nighttime and from the river (south) to the rainforest during daytime (Figure 4a), which we attribute to a symmetrical river breeze.

Typical daytime wind speeds measured on the boat were 2 to 5 m s^{-1}, and during nighttime the wind speed dropped to values between 0.5 and 2 m s^{-1} (Figure 4a). The relative humidity (RH) typically ranged from 60% during daytime up to 90-100% during nighttime (Figure 4b). Daytime and nighttime temperatures ranged between 29-32°C and 23-26°C, respectively. The global irradiance featured a typical diel course with maximal values of 900-1000 W m^{-2} during clear sky periods (Figure 4c). On most days, cloudy skies prevailed during the afternoon hours when rain showers and, occasionally, thunderstorms occurred.

3.2 Trace gas mixing ratios and aerosol concentrations

3.2.1 Ozone (O_3)

The O_3 mixing ratios reveal a typical diel cycle with significantly higher values during daytime (Figure 4c). For the remote cases on 10, 18 and 19 July a near twofold increase of the O_3 mixing ratios during the late afternoon indicates the influence of anthropogenic pollution (see below). Excluding these events, the measured daytime O_3 mixing ratios for the remote cases (10-11, 18-19 and 25 July) were on average 21 ± 2 ppb. For comparison, *Kuhn et al.* [2010] measured background O_3 mixing ratios of 18 to 24 ppb downwind of Manaus during the CLAIRE-

2001 airborne measurements. Wet season median daytime O_3 values measured by *Rummel et al.* [2007] over a remote rainforest canopy were around 13 ppb, which is substantially lower than our values.

Observed daytime O_3 mixing ratios for the polluted cases (20, 26-27 July) were on average 31 ± 14 ppb with maximal values of 60 ppb on 26 July at a distance of 19 km downwind of Manaus. *Kuhn et al.* [2010] observed maximal O_3 mixing ratios of 65 ppb at 100 km distance from Manaus in photochemically aged air masses at altitudes of several hundred meters above ground.

Furthermore, we observed major differences in nighttime O_3 mixing ratios depending on whether or not the air had a riverine or a tropical forest footprint (Figure 1 and Figure 4a,c). Nighttime O_3 mixing ratios were often considerably higher (~10 ppb) than measured above a tropical rain forest (< 5 ppb, [see e.g., *Rummel et al.*, 2007]). This can be explained by (i.) the less stable nocturnal thermal stratification over (still warm) water surfaces than over land, facilitating intermittent downward transport of O_3 from aloft and (ii.) depending on the residence time of the air masses over the river also by a smaller efficiency of O_3 uptake by a water surface than by vegetation [*Ganzeveld et al.*, 2009; *Wesely et al.*, 1981]. One exception was found during nighttime on 26/27 July (symmetric river breeze, see section 3.1), when air masses with O_3 well below 5 ppb were advected directly from the rain forest. Ozone dry deposition and removal through reaction with soil-biogenic NO emissions accumulated in the forest trunk space [*Rummel*, 2005] resulted in much lower nighttime O_3 levels than observed at the other locations.

3.2.2 Nitric oxide (NO) and nitrogen dioxide (NO_2)

The mixing ratios of NO for the remote cases on 10-11, 18-19 and 25 July were mostly lower than 500 ppt and sometimes fell below the detection limit of 75 ppt (Figure 4d). These values compare well with NO mixing ratios measured by *Bakwin et al.* [1990] and *Rummel* [2005] during the Amazonian wet season within and above the rain forest canopy. The major NO source under these remote conditions is biogenic emission from forest soils, potentially enhancing the NO_x mixing ratios of sub-canopy air masses being sampled at our measurement location on the river as a result of advection. Since the O_3 mixing ratios within and below the forest canopy are typically much lower than above the forest [see *Rummel et al.*, 2007], such events are mostly accompanied by a drop in the O_3 mixing ratio. Fresh pollution from biomass burning was sometimes transported to the boat (e.g., 10 July after 6:00 LT, see Figure 4d). On 19 and 20 July the wind direction changed abruptly from south-southeast to east-northeast around midnight (see above), resulting in a NO mixing ratio increase to 0.6-1.0 ppb accompanied by a drop of the O_3 mixing ratio. The measured NO mixing ratios for the polluted cases (20, 26-27 July), were largely influenced by fresh pollution originating from anthropogenic activities close to Manaus. During these events NO mixing ratios reached values of up to 4-10 ppb before midday (Figure 4d).

For the remote cases, the NO_2 mixing ratios were typically close to the detection limit of 135 ppt, e.g., on 10 July around midday or on 25 July during nighttime (Figure 4d). Very low NO_2 mixing ratios (< 300 ppt) were also observed on 18 July from 00:00 to 15:00 LT at a distance of ~43 km from Manaus on the Rio Negro. After that, the typical change of the wind direction from east-northeast to south-southeast (Figure 2, 5a) resulted in an NO_2 increase to about 3 ppb while NO mixing ratios remained low, suggesting the arrival of an aged pollution plume (indicated also by an increase of O_3, see above) that lasted until the early morning of the next day. A similar event occurred on 19 July with even higher NO_2 mixing ratios.

However, close to Manaus, on 26-27 July, NO_2 mixing ratios were typically highest before midday reaching a maximum of 18 ppb in the morning of 26 July. Comparably high NO_2 mixing ratios of about 16 ppb were also observed during the airborne measurements (410 m a.g.l.) on 15

July during the same time at nearly the same distance west of Manaus, and were attributed to the plume originating from power plants in the southern part of the city [*Kuhn et al.*, 2010].

3.2.3 VOCs

VOC mixing ratios and MVK/MACR ratios are presented for a remote (background) case (10 July, distance to Manaus ~147 km) and for a polluted case close to Manaus (26 July, distance to Manaus ~19 km) (see Figure 5a,b). As described in detail by *Kuhn et al.* [2007, 2010] for tower-based and airborne measurements during LBA-CLAIRE-2001, isoprene was the dominant compound observed, followed by the monoterpene α-pinene, both being emitted in a light-dependent manner [see *Kuhn et al.*, 2004]. While for the remote case a typical diel pattern for biogenic isoprene with daytime maxima of about 3 ppb was observed (Figure 5a), the polluted case revealed somewhat lower mixing ratios during daytime (< 2 ppb, Figure 5b), which was at least partly caused by lower radiation (Figure 4c). The contribution of anthropogenic isoprene emissions related to industrial activities and in particular to vehicle exhaust [*Borbon et al.*, 2001; *Duane et al.*, 2002; *Reimann et al.*, 2000] might be a reasonable explanation for the higher variability for the polluted case, particularly during nighttime. The diel cycle of α-pinene resembles that of isoprene with maximal daytime mixing ratios of 0.2 ppb (not shown).

The isoprene degradation reactions yield the unsaturated C4 carbonyls MACR and MVK plus formaldehyde (CH_2O). High concentrations of these carbonyls as well as formaldehyde have been found previously in the tropical atmosphere [*Kesselmeier et al.*, 2002]. They constituted a significant fraction of VOC in the remote background case as well as in the polluted case close to Manaus during LBA-CLAIRE-2001 [*Kuhn et al.*, 2010]. The observed MVK/MACR values close to (and exceeding) a value of two resemble those measured throughout the CBL during LBA-CLAIRE-2001 [*Kuhn et al.*, 2010], and are indicative of OH-dominated isoprene degradation [see *Kuhn et al.*, 2007, 2010], where OH adds to one of the double bonds of isoprene, forming alkyl radicals that in turn add O_2 to form peroxy radicals (RO_2).

3.2.4 Aerosol scattering coefficient

For the remote cases, the lowest values of the aerosol scattering coefficient (σ_s) ranged from 3 to 10 Mm^{-1} during daytime (Figure 4e). These values are comparable to the background airborne measurements in the boundary layer made during LBA-CLAIRE-2001 by *Kuhn et al.* [2010], as well as to those measured by *Guyon et al.* [2003] in southern Amazonia during the wet season. Nighttime σ_s values were typically several times higher, which was most likely also related to the change of the wind direction in the late afternoon (particularly evident on 18/19 July) and the influence of a pollution plume, as already found for O_3 and NO_2. Maximal σ_s values were 50-60 Mm^{-1} for the polluted cases.

As shown in the previous sections, the remote cases were occasionally influenced by anthropogenic pollution during the afternoon. For further analysis, we classify our data in remote and polluted cases according to the prevailing σ_s, which constitutes a quantity that is relatively independent of the trace gas mixing ratios. *Guyon et al.* [2003] found that σ_s values representative for pristine background conditions are typically below 11 Mm^{-1}. In our case, this corresponds to NO_x mixing ratios below ~ 0.6 ppb. Henceforth, we refer to remote cases (mainly clean air masses with very minor influence of anthropogenic pollution) with $\sigma_s < 11$ Mm^{-1} and $NO_x < 0.6$ ppb and to polluted cases with $\sigma_s > 11$ Mm^{-1} and $NO_x > 0.6$ ppb.

3.3 Impact of the Manaus plume

The impact of the Manaus plume on Amazonian remote background conditions can be studied very well on 10, 18 and 19 July. During all three days we measured a near twofold increase of the O_3 mixing ratio in the late afternoon (see section 3.2.1), which was due to the typical change of the wind direction from east-northeast to south-southeast. On 10 July (distance to Manaus ~147 km) after 15:40 LT the O_3 mixing ratio increased sharply from 19 ppb to 32 ppb within a few minutes (Figure 4c). Besides the potential impact of anthropogenic pollution, a sudden drop in global irradiance indicates an increase in cloud cover associated with a thunderstorm, which occurred near the boat location. According to *Betts et al.* [2002], this O_3 increase may suggest the occurrence of a strong convective downdraft, which brought O_3 rich air from the lower troposphere down to the surface. However, results from the HYSPLIT model indicate that the boat was located north of the Manaus plume in the morning, but that due to a change of the wind direction to south-southeast near the surface the plume swung northwards in the afternoon and reached the boat location at around 16:00 LT (not shown).

We demonstrate this pattern in further detail for 18 and 19 July (distance to Manaus ~43 km), when comparable increases of the O_3 mixing ratio were observed. Figure 6 shows results of air mass dispersion calculations with the HYSPLIT model for 18 July. The main flow was from northeast before midday and the plume did not reach the boat (Figure 6a). Measured trace gas mixing ratios and aerosol concentrations around midday were close to Amazonian background conditions ([NO] ~ 50 ppt (< LOD), $[NO_2] = 200$ ppt, $[O_3] = 16$ ppb, $\sigma_s = 6\ Mm^{-1}$) (Figure 4). The change of the wind direction to south-southeast near the surface in the late afternoon (measured on the boat and calculated from HYPSLIT, see Figure 2 and 4) is evident in Figure 6b, causing a northward swing of the plume that now reached the boat. Accordingly, trace gas mixing ratios and aerosol concentrations increased substantially ([NO] = 300 ppt, $[NO_2] = 3$ ppb, $[O_3] = 35$ ppb, $\sigma_s = 30\ Mm^{-1}$).

Since no airborne measurements west of Manaus were made on 18 July, we further validate these findings using results from Flight #18: 10:00-14:00 LT and Flight #19: 15:45-18:00 LT on 19 July [see *Kuhn et al.*, 2010]. This can be justified by the fact that (i.) the diel cycle of the wind direction is nearly identical for 18 and 19 July (Figure 4a), (ii.) the diel variation of O_3 mixing ratios shows a comparable pattern for 18 and 19 July (Figure 4c) and (iii.) in agreement with our wind measurements at the boat and at the K34 tower site (see above, Figure 4a) the HYSPLIT dispersion calculations reveal a comparable result for 18 and 19 July. After takeoff from Manaus airport, Flights #18 and #19 were set up as a Lagrangian experiment with a series of stacked horizontal profiles [*Kuhn et al.*, 2010]. We use results measured at various altitudes for a longitude of ~ 60.41°W directly over the boat. On 19 July between 11:08 LT and 11:40 LT, the O_3 mixing ratios were 26 ppb, 28 ppb, 29 ppb, 23 ppb and 33 ppb at heights of 3 m (boat), 30 m, 220 m, 544 m and 860 m a.g.l., respectively. These vertical mixing ratio differences suggest that convective transport away from the surface enables precursor compounds to achieve their full ozone generating potential [cf. *Kuhn et al.*, 2010].

Figure 7 presents crosswind transects in the urban outflow for O_3 and aerosol number (CN) concentrations at 220 m a.g.l.. Just before midday (11:25-11:34 LT, Flight#18) on 19 July the boat was located at the northern edge of the plume (3.0948°S, 60.4102°W) (Figure 7). Compared to 18 July, when no anthropogenic influence was present just before midday, O_3 mixing ratios measured on the boat were slightly elevated (26 ppb) at 11:31 LT (the time the airplane flew over) on 19 July. In the afternoon the O_3 mixing ratio on the boat was 30 ppb when the airplane flew over again at 16:45, while a mixing ratio of 34 ppb was measured at a height of 220 m a.g.l. (Figure 7). The center of the plume before midday ($[O_3]$ = 44 ppb) was at around 3.18°S (south of the Rio Negro); while during the afternoon (16:40-16:48 LT, Flight#19) the center ($[O_3]$ = 50 ppb) was at around 3.0°S (northern bank of the Rio Negro). This is also visible in the corresponding CN concentrations. Hence, Figure 6 strongly suggests that the plume indeed swung northwards as already indicated by results from the HYSPLIT model due to the southeasterly flow component (Figure 3 and 6). Apparently, the center of the plume swept over the boat platform around 14:00 LT when O_3 mixing ratios on the boat exceeded 40 ppb. Hence, we sampled air masses that were significantly affected by anthropogenic pollution from Manaus during the afternoon. The arrival of the plume at the boat platform on 18/19 July is also evident from NO_2 mixing ratios and σ_s values that increased substantially during the late afternoon and typically remained high during the whole night. On 20 July, elevated mixing ratios measured on the boat in the proximity of Manaus (~19 km distance) suggest that the air masses sampled were influenced by the Manaus plume, which is supported by the results from the airborne measurements in the afternoon.

3.4 Photo-stationary state (PSS)

Since data measured during the afternoon often had to be rejected due to cloudy conditions (section 2.5, Figure 4c), only a limited number of data points was available for the PSS analysis. The application of the rejection criteria generally resulted in the rejection of measured NO_2 mixing ratios lower than NO_2 mixing ratios predicted by the PSS approach ($\Phi < 1$). Such cases might be attributed to local fresh NO emissions [cf. *Rohrer et al.*, 1998], e.g., from the generator, but also to sunrise and sunset periods. Only 42 % of the original daytime data could be used for the calculation of Φ. As shown in Figure 4e, the calculated Φ values (eq. 1) exceed unity in most cases. Just after sunrise (high solar zenith angle) Φ frequently reveals a tendency towards unity, which most likely is caused by the absence of peroxy radicals during this period. This is expected because during these times the emission of hydrocarbons from vegetation [e.g., *Kesselmeier and Staudt*, 1999] (see Figure 5) as well as photochemistry forming OH and peroxy radicals is still low [see *Griffin et al.*, 2007], and no significant additional oxidation pathway for NO is present. The deviation of Φ from unity sometimes follows the diel course of $j(NO_2)$ (Figure 4f), indicating the relation to photochemically derived radicals, which is consistent with findings by, e.g., *Griffin et al.* [2007] and *Rohrer et al.* [1998].

We found the largest deviations from PSS ($\Phi > 2.5$) for the clean remote cases ($\sigma_s < 11$ Mm^{-1} and $NO_x < 0.6$ ppb). This was mainly caused by the coincidence of NO mixing ratios below 200 ppt and low O_3 mixing ratios (13-17 ppb). For comparison, above a very remote Taiga woodland, *Bakwin et al.* [1994] found Φ values > 5, with prevailing NO_x levels < 100 ppt and O_3 < 30 ppb. *Hauglustaine et al.* [1996] and *Ridley et al.* [1992] investigated PSS at the Mauna Loa Observatory in Hawaii and despite remarkably low NO_x levels (< 100 ppt), Φ values were less than 3. The significantly lower O_3 mixing ratios observed for our remote cases compared to the O_3 mixing ratios measured at Mauna Loa, coinciding with low NO mixing ratios, explain that our Φ values sometimes exceeded a value of 3. *Hosaynali Beygi et al.* [2011] found Φ values >> 10 under pristine background conditions (NO_x = 5-25 ppt) in the Southern Atlantic boundary layer at O_3 levels of about 20 ppb.

Previously reported near-ground Φ values at locations influenced by urban or suburban air masses were 1 – 3 [e.g., *Carpenter et al.*, 1998; *Griffin et al.*, 2007; *Matsumoto et al.*, 2006; *Parrish et al.*, 1986; *Rohrer et al.*, 1998; *Volz-Thomas et al.*, 2003]. These Φ values compare well with cases that were influenced by anthropogenic pollution in our study.

3.4.1 Influence of environmental factors and anthropogenic pollution on PSS

Generally, the photochemical equilibrium is not reached and Φ values deviate from unity when the timescales of turbulent transport are comparable or shorter than τ_{PSS}, e.g., when there are nearby soil biogenic NO emissions and/or dry deposition of NO_2 and O_3. Turbulent timescales above a flat surface are often faster than the establishment of PSS (1-10 seconds, [cf. *Trebs et al.*, 2006]), indicating that the photochemical equilibrium ("steady state") may not be reached. Moreover, advection of O_3-depleted and NO_x-enriched air masses from the rain forest, reflecting an efficient dry deposition and reaction of O_3 with biogenic soil NO emissions in the trunk space, may have a significant influence on Φ values. However, these influences can be largely neglected if the footprint of the measurements consists of a fetch of open water, lacking substantial sources or sinks (deposition) of NO_x and O_3 (see section 3.2.1).

Maximal Φ values were calculated for the clean remote cases ($\sigma_s < 11$ Mm^{-1}, $NO_x < 0.6$ ppb, mostly on 10, 18/19, 24/25 July), comprising about 45 % of all calculated Φ values. They ranged from 2.5 to 16, and the upper values were often derived from either NO or NO_2 mixing ratios below the LOD (white circles, Figure 4e). About 55% of the Φ values are assigned to polluted cases and were mostly below 2.

Periods in the afternoon when a change of the wind direction occurred (see section 3.1) often coincided with periods of increased cloudiness due to convection (Figure 4a,c). Since the rejection criteria had to be applied during these periods (see above), an analysis of the influence of the Manaus plume arrival during 18/19 July (see section 3.3) on the diel evolution of Φ values was not possible. These periods also do not meet the "steady state" criterion due to strong mixing ratio fluctuations (see e.g., 18 July, Figure 4c).

However, we found that the Φ values were dependent on the position of the boat relative to the Manaus plume, and consequently also on the distance of the measurement location to Manaus. From 18 to 20 July we observed a gradual decline of calculated midday Φ values (Figure 4e). As previously shown, on 18 July no anthropogenic influence was present during midday, while on 19 July the boat was located at the edge of the plume and on 20 July the boat moved closer to Manaus and the sampled air masses were strongly affected by the plume. The Φ values were closest to unity when polluted air was sampled, particularly on 20 and 26/27 July, when the distance of the boat was only 19 km from Manaus.

3.4.2 Discussion of uncertainties and dependence on NO_x

Figure 8 combines the results from all locations. The 2σ uncertainty of Φ (black line, see section 2.6) increases with decreasing NO_x. All Φ values above the 2σ uncertainty present significant deviations from PSS. The values below the black line may be the result of measurement imprecision or represent true deviations from PSS. More than half of the estimated Φ values deviate significantly from PSS. This deviation is most pronounced at NO_x mixing ratios below 1 ppb, whereas Φ approaches unity with increasing NO_x mixing ratios, which is the behavior also found in previous studies [e.g., *Griffin et al.*, 2007; *Volz-Thomas et al.*, 2003]. This trend is corroborated by the increase of Φ during midday (higher $j(NO_2)$ values), which is related to radical formation, as previously discussed. The Φ values close to unity at low NO_x mixing ratios are mainly confined to periods with lower $j(NO_2)$ and low VOC mixing ratios (see Figure 5) just after sunrise and before sunset. On the other hand, higher NO_x levels favor the rapid establishment of the PSS, as the sink for XO_2 increases when higher NO mixing ratios are present [cf. *Volz-Thomas et al.*, 2003]. Furthermore, under high-NO_x conditions the reaction of NO_2 with OH, forming HNO_3, leads to a competition with the oxidation of CO and hydrocarbons by OH, limiting the production of significant levels of peroxy radicals [e.g., *Mannschreck et al.*, 2004; *Volz-Thomas et al.*, 2003]. In our study, the ratio Φ reaches unity within its uncertainty range at NO_x mixing ratios of about 3 ppb. This value is comparable to studies at other locations and implies that no significant net production of ozone takes place at NO_x mixing ratios >> 3 ppb (corresponding to NO mixing ratios >> 1.4 ppb). For example, *Griffin et al.* [2007] also found Φ ~ 1 at NO_x mixing ratios > 3 ppb and *Volz-Thomas et al.* [2003] found Φ ~ 1 at NO mixing ratios > 1 ppb.

3.5 XO_2 mixing ratios

The formation and cycling of radicals in tropical environments like the Amazon Basin is still subject of ongoing discussion. The high isoprene mixing ratios over tropical forest clearly have a considerably smaller effect on OH (depletion) than previously thought. Recent estimates and measurements within the CBL indicate that prevailing OH concentrations are an order of magnitude higher (about 6×10^6 molecules cm^{-3} or 0.25 ppt, respectively) than currently predicted by state-of-the-art atmospheric chemistry models [see *Kuhn et al.*, 2007; *Ganzeveld et al.*, 2008; *Lelieveld et al.,* 2008*; Martinez et al.*, 2010; *Kubistin et al.*, 2010]. The presence of OH radicals controls the formation of XO_2 in the atmosphere through the oxidation of CO and hydrocarbons.

3.5.1 Estimation of XO_2 from PSS

In this study, we provide estimates of XO_2 in the region west of Manaus according to eq. (3) (see Figure 4f). It should be noted that some XO_2 mixing ratios were derived from either NO or NO_2 mixing ratios below the LOD (white circles, Figure 4f). Median midday/afternoon (PSS derived) XO_2 mixing ratios (eq. 3) for the remote cases ($\sigma_s < 11\ Mm^{-1}$ and $NO_x < 0.6$ ppb) range from 90 to 120 ppt, while for the polluted cases ($\sigma_s > 11\ Mm^{-1}$ and $NO_x > 0.6$ ppb) our estimates range from 15 to 60 ppt. The uncertainty of the peroxy radical mixing ratios is a function of Φ (see eq. 3) and significantly exceeds 100 %, which is mainly caused by the imprecision of the NO_x measurements at low mixing ratios (see section 2.6). This constitutes a major disadvantage of the PSS method to estimate XO_2. Furthermore, PSS is known to generally overestimate XO_2 mixing ratios by a factor of two or higher, which is most likely attributable to yet unidentified or unaccounted-for NO_2 formation pathways [*Cantrell et al.*, 1997; *Volz-Thomas et al.*, 2003; *Hosaynali Beygi et al.*, 2011].

3.5.2 Estimation of XO_2 using a chemistry box model

We have additionally used the atmospheric chemistry box model CAABA/MECCA-3.0 (**C**hemistry **A**s **A** **B**oxmodel **A**pplication-**M**odule **E**fficiently **C**alculating the **C**hemistry of the **A**tmosphere) [*Sander et al.*, 2011], which contains the Mainz Isoprene Mechanism 2 (MIM2) [*Taraborrelli et al.*, 2009] to predict XO_2 mixing ratios. The model runs were constrained by fixing the measured species (NO, NO_2, O_3, H_2O, C_5H_8, MVK, MACR) to their observed values (scenario 1). *Peeters and Müller* [2010] and *Peeters et al.* [2009] proposed that unimolecular reactions of certain RO_2 radicals lead to additional OH formation. Since MECCA-3.0 does not include these new reactions yet, it currently significantly underpredicts OH and consequently also HO_2 within the CBL in the Amazon [see *Kubistin et al.*, 2010]. As a consequence, we performed additional model runs based on the first scenario but also fixing OH [*Kuhn et al.*, 2007; *Martinez et al.*, 2010], HCHO [*Kesselmeier et al.,* 2002] and H_2O_2 [*Quesada et al.* 2001] to measured values (scenario 2). For all cases the model was run until a steady state value of HO_2 was reached. The results presented in Table 1 indicate that the predicted XO_2 mixing ratios are mostly within the range of those estimated by the PSS method. For scenario 2, the XO_2 predicted by the model would be two times lower if the OH mixing ratio fixed in the model input is reduced by a factor of two. The modeled XO_2 is sometimes higher than the PSS estimates in the afternoon, which might be caused by the missing RO_2 sink attributed to the not yet included OH formation mechanism proposed by *Peeters and Müller* [2010] and *Peeters et al.* [2009] in MIM2. In the early afternoon of 26 July (polluted case), the XO_2 mixing ratios estimated from PSS significantly exceed the model results.

3.5.3 Comparison to previous results from tropical environments

Mixing ratios of HO_2 only (providing a lower limit on the XO_2 mixing ratios), measured in the CBL over pristine rainforest in Suriname during the GABRIEL campaign, showed maxima of about 70 ppt around noontime [*Martinez et al.*, 2010]. Within the surface layer west of Manaus the HO_2 mixing ratio calculated with a single column chemistry-climate model (SCM) [*Ganzeveld et al.*, 2002], also being applied in another study of the Manaus city plume [*Kuhn et al.*, 2010], reached 50 ppt, with the CH_3O_2 mixing ratio as small as 3 ppt during midday. The XO_2 mixing ratios measured in a comparably remote tropical environment in the rainforest of Borneo ranged from 20 to 40 ppt around midday [*Pugh et al.*, 2010].

4. Conclusions

We have measured mixing ratios of the trace gases NO, NO_2,O_3, and VOCs as well as the aerosol scattering coefficient, σ_s, in a previously unexplored environment using a boat platform cruising on rivers west of Manaus (Amazon Basin) on 10-11, 18-20, 25-27 July 2001. To our knowledge, these are the first trace gas measurements made on rivers in the Amazon Basin, which are a unique location for studying atmospheric processes within the tropical boundary layer. The temporal and spatial dispersion of the Manaus plume had a significant influence on the measured mixing ratios at the different boat locations. The measured trace gas mixing ratios and calculated Φ values reflect the interaction between river breezes and/or mesoscale circulations, and the impact of synoptic winds transporting pollution from Manaus to pristine areas of the Amazonian rain forest. In particular, during our measurement period the wind mainly blew from east-northeast during the night and in the morning (influence of easterly trade winds), while wind directions from south-southeast dominated during the afternoon and evening. The remote cases with very minor anthropogenic influence were characterized by σ_s values below 11 Mm^{-1} and NO_x below 0.6 ppb, coinciding with midday O_3 mixing ratios often lower than 20 ppb. For these cases, significant deviations from the photo-stationary state in the NO-NO_2-O_3 triad were observed. The combination of low NO (< 200 ppt) with low O_3 (< 20 ppb) in the absence of anthropogenic pollution caused the Leighton ratio, Φ, sometimes to be higher than 3. The change of the wind direction to south-southeast in the afternoon facilitated a northward swing of the Manaus plume, which then often reached the boat. These polluted air masses were characterized by σ_s values of about 30 Mm^{-1}, NO_x mixing ratios between 2 and 4 ppb and by O_3 mixing ratios of up to 35 ppb. For these polluted cases the calculated Φ values were close to unity. Results from the PSS method and the box model CAABA/MECCA-3.0 suggest that the XO_2 mixing ratios are at least a factor of two higher in remote areas west of Manaus compared to locations influenced by the Manaus urban plume. This implies that anthropogenic pollution from Manaus significantly alters the chemical composition of the otherwise pristine Amazonian background air near the surface. This may in turn have a significant influence on surface-atmosphere exchange processes of reactive species. The limited knowledge of HO_2 and RO_2 mixing ratios in tropical regions like the Amazon Basin emphasizes the need for in-situ measurements in the near future to improve our understanding of O_3 production pathways and the cycling of reactive nitrogen as well as of OH and XO_2 in clean and polluted air masses.

We anticipate that due to the rapidly growing population of Manaus to meanwhile more than 1.7 million human inhabitants, and consequently rising pollution levels, the impact on atmospheric chemistry in the region west of Manaus is growing. It is recommended to establish long-term monitoring stations downwind of Manaus and to apply mesoscale models to investigate the influence of the Rio Negro river breeze on the dispersion of the Manaus urban plume.

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Figure Captions

Figure 1. GIS map showing the study area and boat positions on 10-11, 18-20, 25-27 July (LBA-CLAIRE-2001 boat experiment). The position of the boat on the different days is represented by colored circles.

Figure 2. Wind roses for (a) 00:00 to 14:50 LT and (b) 15:00 to 23:50 LT including 10-min averaged wind data from all locations shown in Figure 1 except 26/27 July (for explanation see text) during the LBA-CLAIRE-2001 boat experiment. The time periods chosen for the wind roses are in accordance with *de Oliveira and Fitzjarrald* [1993].

Figure 3. Wind vectors (expressed as one-hour forward trajectories) calculated for five different heights within the CBL using the HYSPLIT model based on the meteorological REANALYSIS dataset. The start time at the boat position on 18 July (3.0948°S, 60.4102°W) was 18:00 LT.

Figure 4. Measured and calculated time series (10-min averages) of (a) wind speed (ff) and wind direction (DIR, for 18/19 July also shown for the K34 tower site about 58 km NNE of the boat), (b) relative humidity (RH) and air temperature (T), (c) global irradiance (G) and O_3 mixing ratios, (d) NO and NO_2 mixing ratio, (e) aerosol scattering coefficient (σ_s) and the Leighton ratio, (Φ), and (f) $j(NO_2)$ and the inferred XO_2 mixing ratio during 10-11, 18-20 and 25-27 July 2001 for the LBA-CLAIRE-2001 boat experiment. Error bars for trace gas measurements indicate standard deviations. Measured data points below the LOD and Φ values and XO_2 mixing ratios calculated from NO or NO_2 mixing ratios below the LOD are represented by light or white circles. Gaps are caused by data rejection due to local contamination by moving boats or the diesel generator and the application of the "steady state" criterion. The color code at the top refers to the locations of the boat platform shown in Figure 1.

Figure 5. Measured isoprene mixing ratios and MVK/MACR ratios on (a) 10 July (remote case) and (b) 26 July (polluted case) during the LBA-CLAIRE-2001 boat experiment.

Figure 6. Simplified GIS map showing the study area during the LBA-CLAIRE-2001 boat experiment (orange circle shows the boat location on 18/19 July) including the results of a HYSPLIT dispersion model run (0-1000 m level) based on the meteorological REANALYSIS dataset. The start time in Manaus City (3.11°S, 60.03°W) was 17 July, 08:00 LT. The duration of the run was 36 hours. Shown are average air mass dispersions for (a) 18 July, 08:00-11:00 LT indicated by the grey contours and (b) for 18 July, 17:00 to 20:00 LT indicated by the red contours. The flight tracks of (a) Flight #18: 10:00-14:00 LT and (b) Flight #19: 15:45-18:00 LT on 19 July are also shown.

Figure 7. Measured O_3 mixing ratios and aerosol number (CN) concentrations (σ_s data were not always available) from crosswind transects in the urban outflow during Flight #18 and Flight #19 (10:00-14:00 LT and 15:45-18:00 LT on 19 July). Transects are shown for a longitude of ~ 60.41°W (~ 43 km downwind of Manaus) directly over the boat platform at 220 m (a.g.l.). CN data were cut off at 10,000 cm^{-3} [cf. *Kuhn et al.*, 2010]. Corresponding O_3 mixing ratios measured at the boat platform when the airplane flew over (at 11:31 and 16:45 LT) are also shown.

Figure 8. Leighton ratio, Φ, versus measured NO_x mixing ratios (geometric averages) from 10-11, 18-20 and 25-27 July 2001 (N = 242) color-coded with $j(NO_2)$ during the LBA-CLAIRE-2001 boat experiment. The black line indicates the calculated 2σ uncertainty of Φ. Values above the black line significantly deviate from PSS. The Φ values calculated from NO or NO_2 mixing ratios below the LOD are indicated by white circles.

Tables

Table 1. Comparison of XO_2 mixing ratios modeled with CAABA/MECCA-3.0 to those derived from PSS (eq. 3) for 10 July (remote case) and 26 July (polluted case). The input values used for the model (NO, NO_2, O_3, H_2O, photolysis frequencies*) were averaged for the respective VOC sampling period. Mixing ratios of long-lived trace gases were kept constant (10 July: [CO] = 80 ppb, [CH_4] = 1820 ppb, 26 July: [CO] = 175 ppb, [CH_4] = 1875 ppb).

VOC sample (local time)	XO_2 (scenario 1**) (ppt)	XO_2 (scenario 2**) (ppt)	mean XO_2 (PSS) (ppt)
10 July 8:41-9:31	30	22	30
10 July 11:31-12:27	83	115	97
10 July 14:21-15:11	115	247	144
26 July 13:25-14:15	20	11	34
26 July 14:25-15:15	48	30	107
26 July 16:25-17:15	38	112	81

*Photolysis frequencies, such as $j(O(^1D))$, were calculated using the radiative transfer model TUV v4.1. The ozone column was determined from GOME satellite data. The calculated photolysis frequencies were corrected for cloud and aerosol effects by scaling to $j(NO_2)$ [cf. *Kubistin et al.*, 2010].

** For explanation of scenarios see text.

Figures

Figure 1.

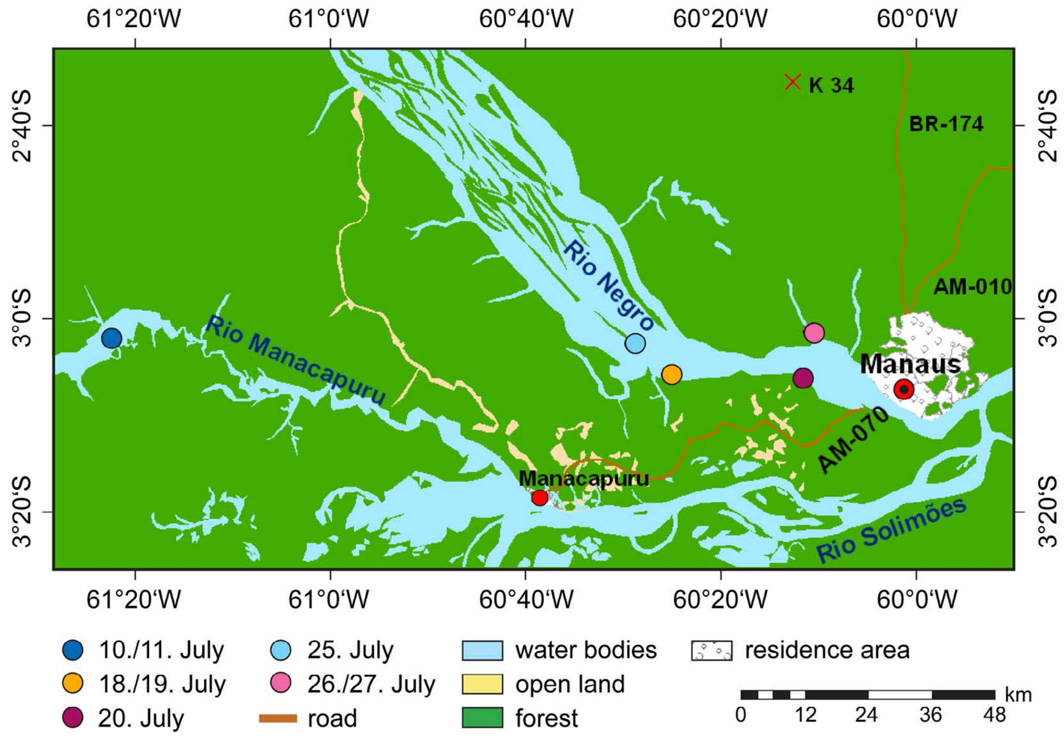


Figure 2.

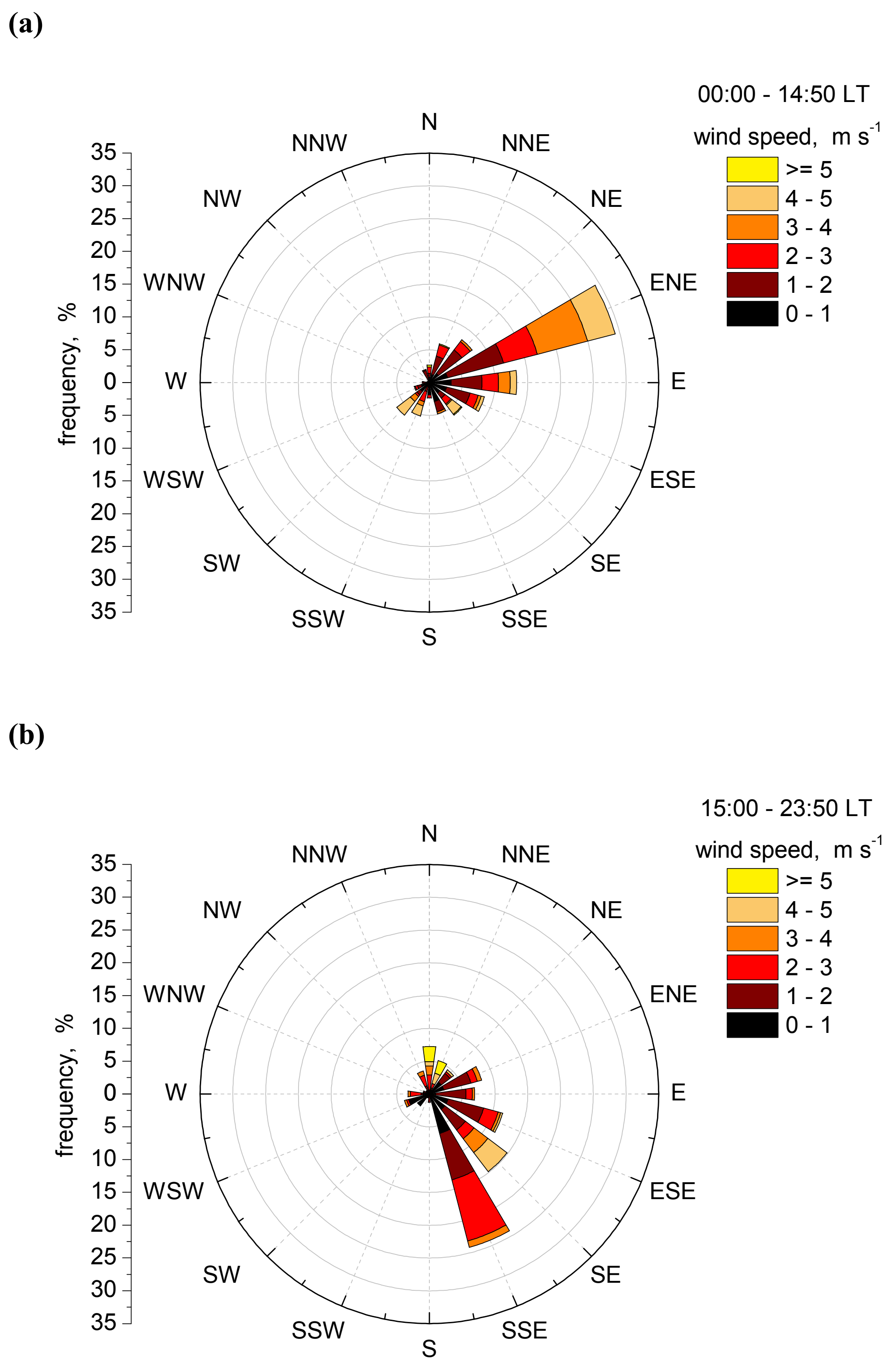
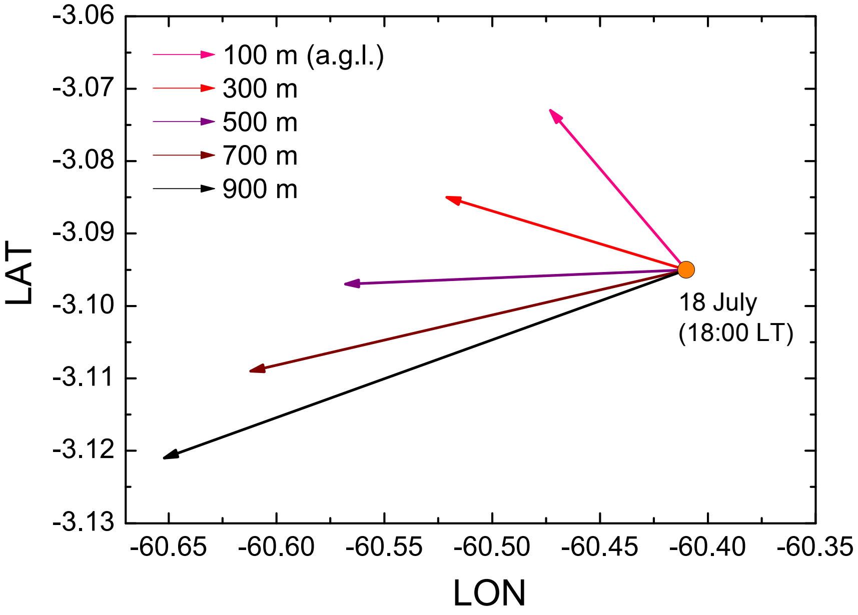

(a)
00:00 - 14:50 LT
wind speed, $m\ s^{-1}$
>= 5
4 - 5
3 - 4
2 - 3
1 - 2
0 - 1
frequency, %
35
30
25
20
15
10
5
0
N
NNE
NE
ENE
E
ESE
SE
SSE
S
SSW
SW
WSW
W
WNW
NW
NNW
(b)
15:00 - 23:50 LT
wind speed, $m\ s^{-1}$
>= 5
4 - 5
3 - 4
2 - 3
1 - 2
0 - 1
frequency, %

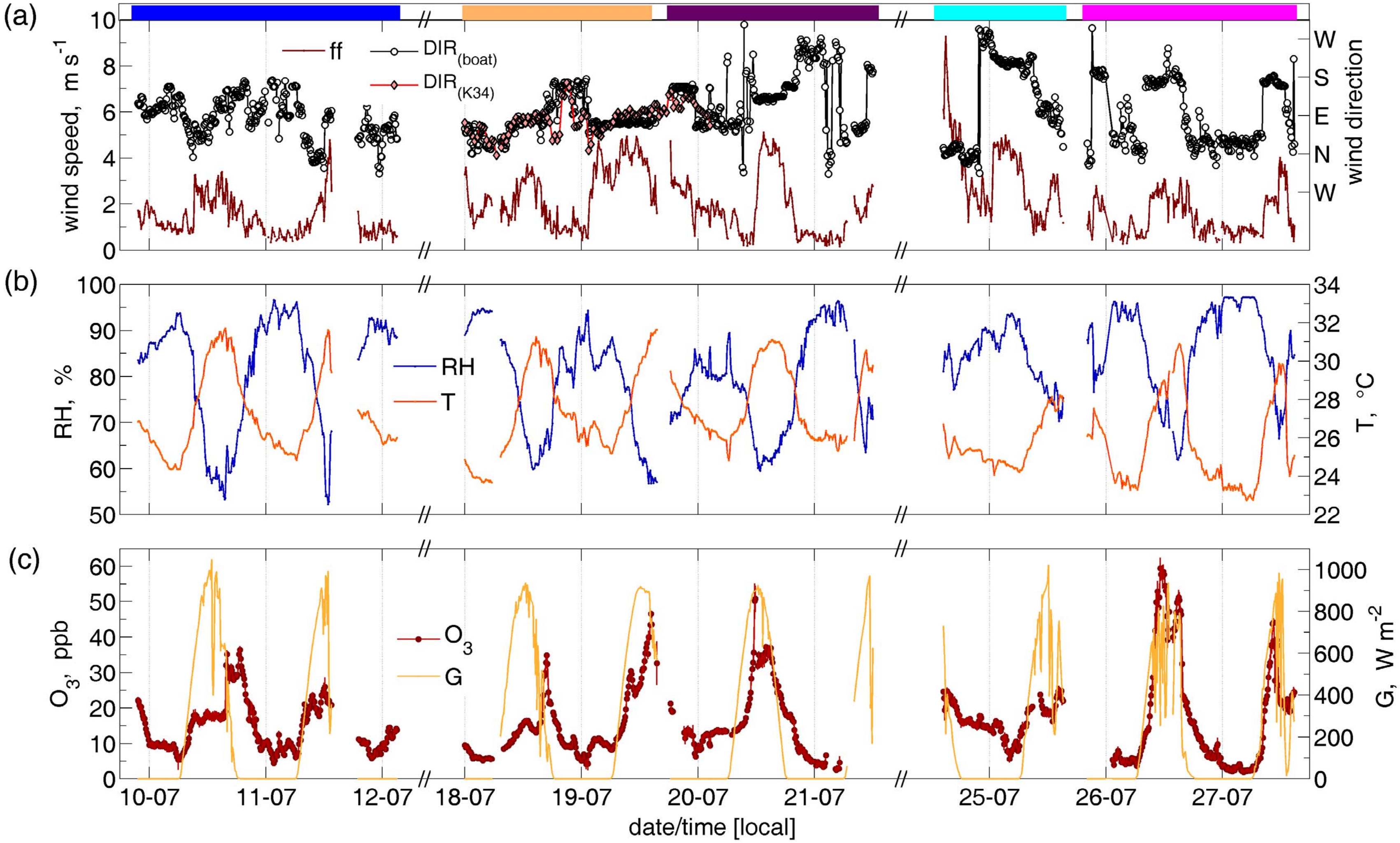
Figure 3.



100 m (a.g.l.)
300 m
500 m
700 m
900 m
18 July
(18:00 LT)
LAT
-3.06
-3.07
-3.08
-3.09
-3.10
-3.11
-3.12
-3.13
LON
-60.65
-60.60
-60.55
-60.50
-60.45
-60.40
-60.35

984

Figure 4a-c.



985

986

Figure 4-f.

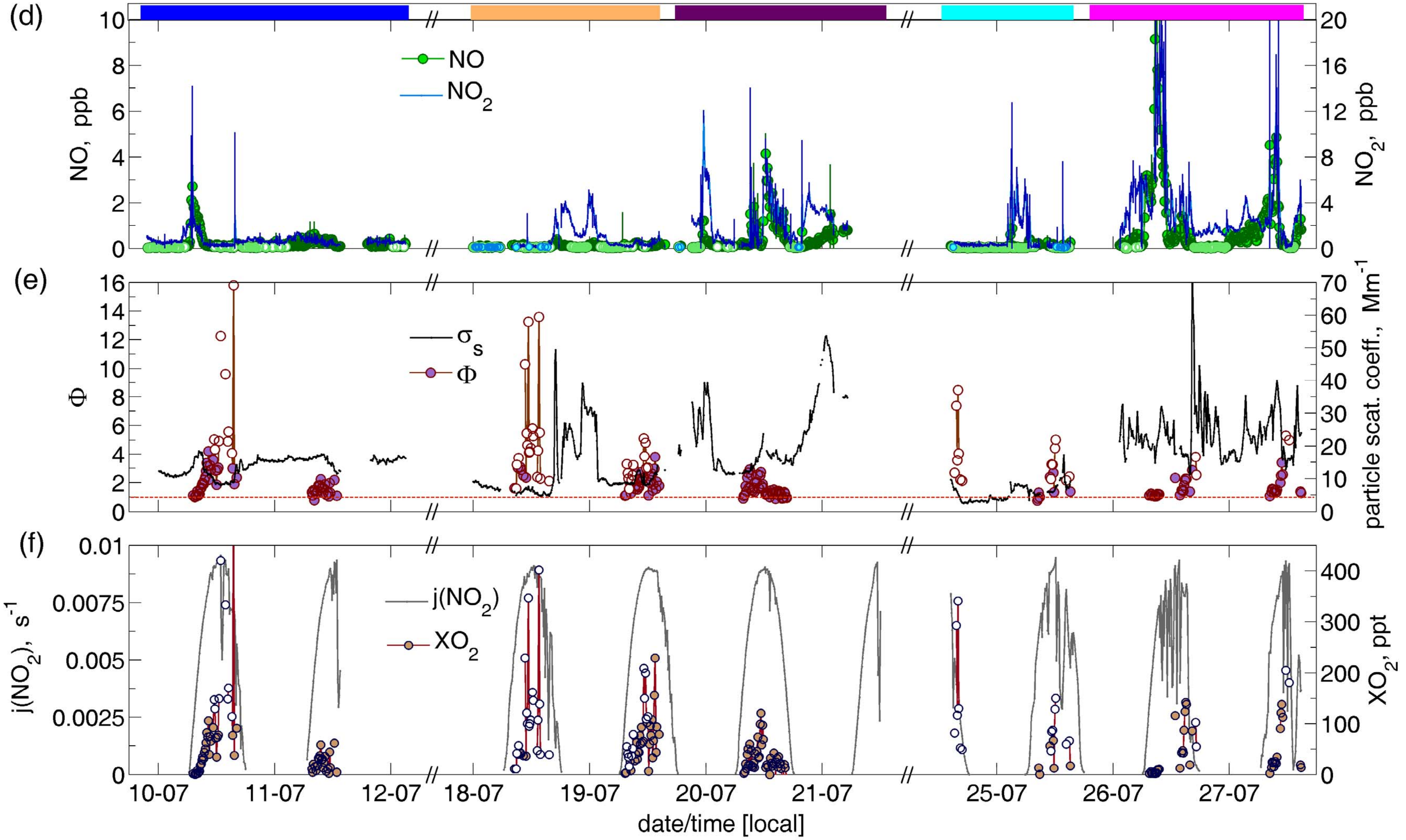
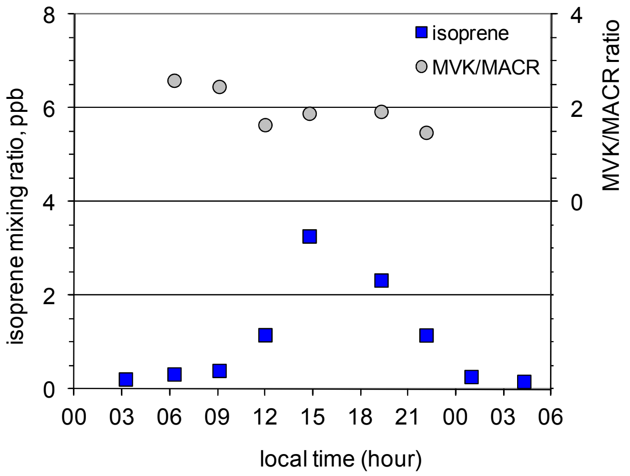

(d)
NO
NO$_2$
NO, ppb
NO$_2$, ppb
0
2
4
6
8
10
0
4
8
12
16
20
(e)
σ_s
Φ
Φ
particle scat. coeff., Mm^{-1}
0
2
4
6
8
10
12
14
16
0
10
20
30
40
50
60
70
(f)
j(NO$_2$)
XO$_2$
j(NO$_2$), s^{-1}
XO$_2$, ppt
0
0.0025
0.005
0.0075
0.01
0
100
200
300
400
10-07
11-07
12-07
18-07
19-07
20-07
21-07
25-07
26-07
27-07
date/time [local]

Figure 5.

(a)


isoprene
MVK/MACR
isoprene mixing ratio, ppb
MVK/MACR ratio
8
6
4
2
0
4
2
0
00
03
06
09
12
15
18
21
00
03
06
local time (hour)

(b)

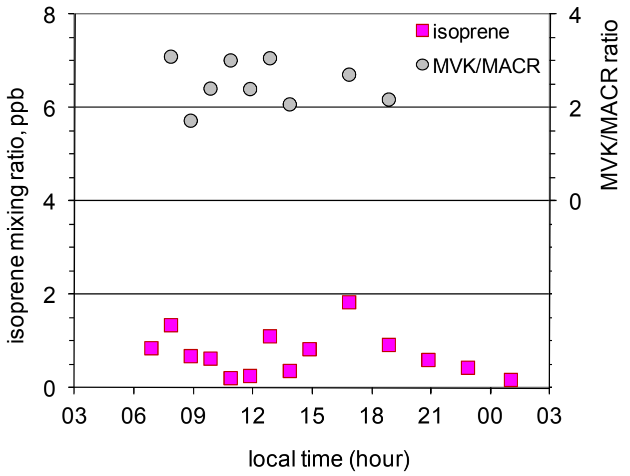
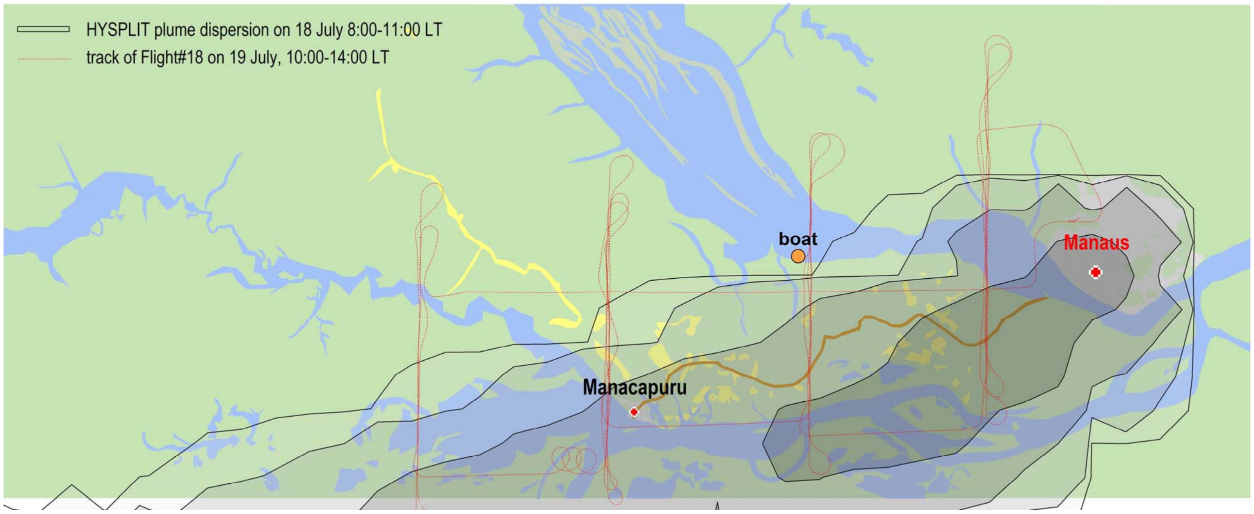

isoprene
MVK/MACR
isoprene mixing ratio, ppb
MVK/MACR ratio
8
6
4
2
0
4
2
0
03
06
09
12
15
18
21
00
03
local time (hour)

Figure 6.

(a)


HYSPLIT plume dispersion on 18 July 8:00-11:00 LT
track of Flight#18 on 19 July, 10:00-14:00 LT
boat
Manaus
Manacapuru

(b)

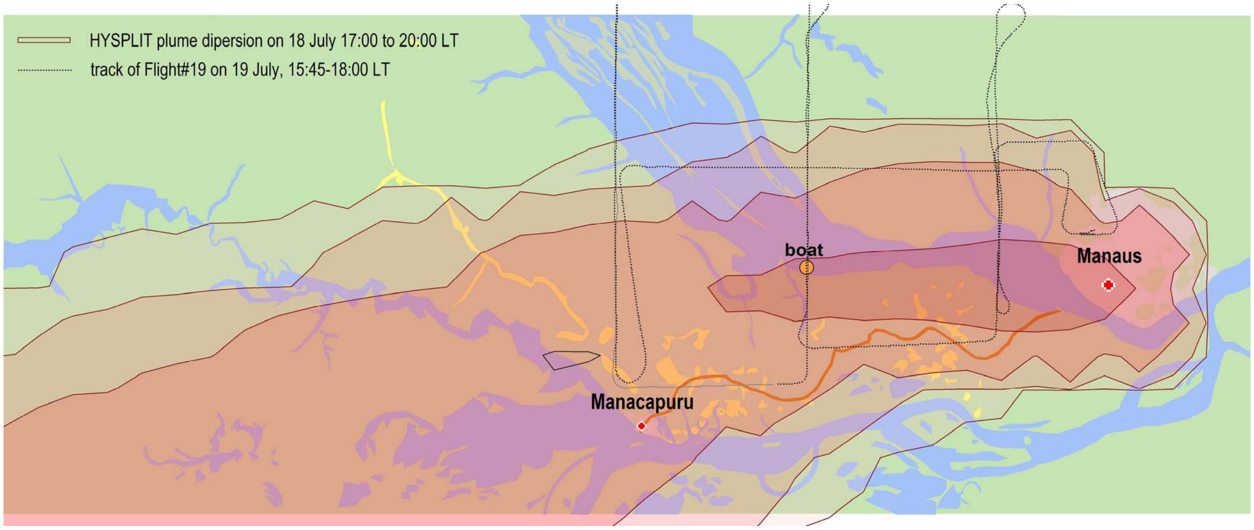
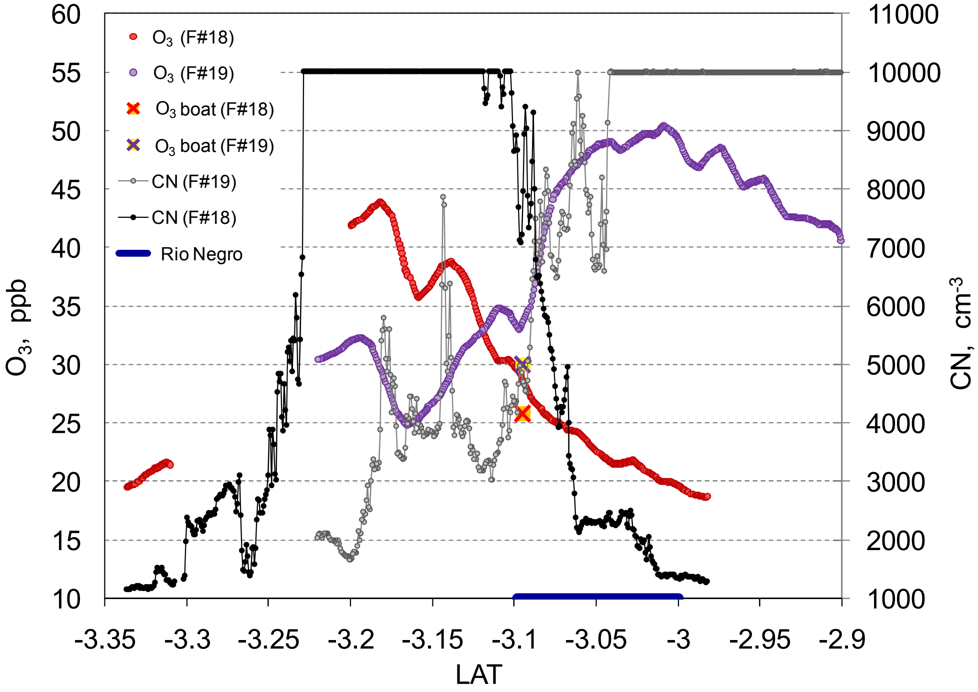
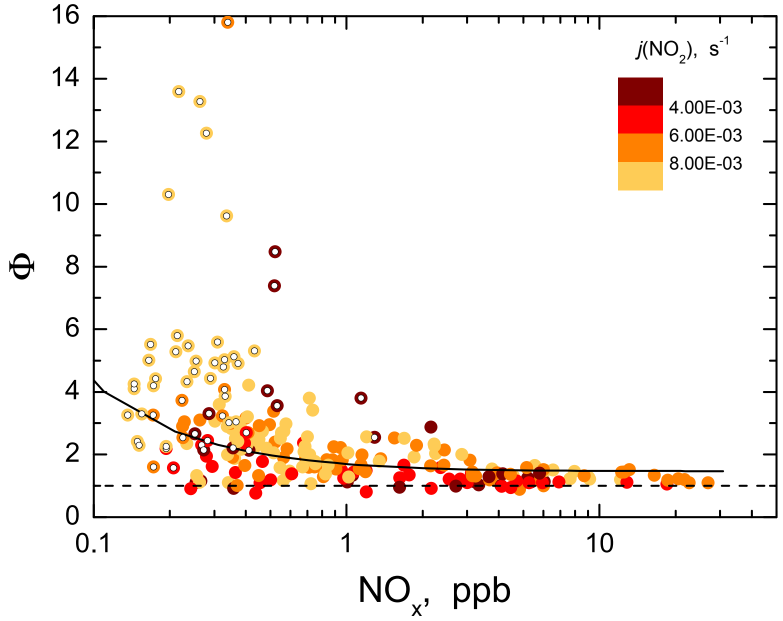

HYSPLIT plume dipersion on 18 July 17:00 to 20:00 LT
track of Flight#19 on 19 July, 15:45-18:00 LT
boat
Manaus
Manacapuru

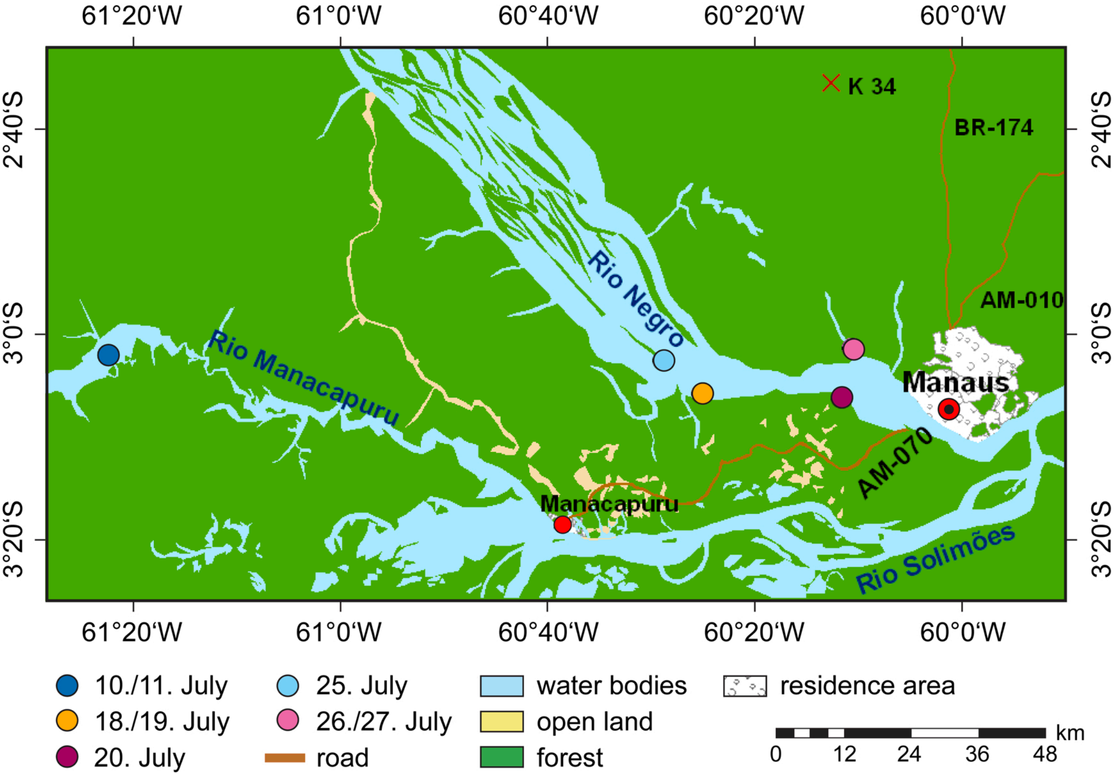
Figure 7.

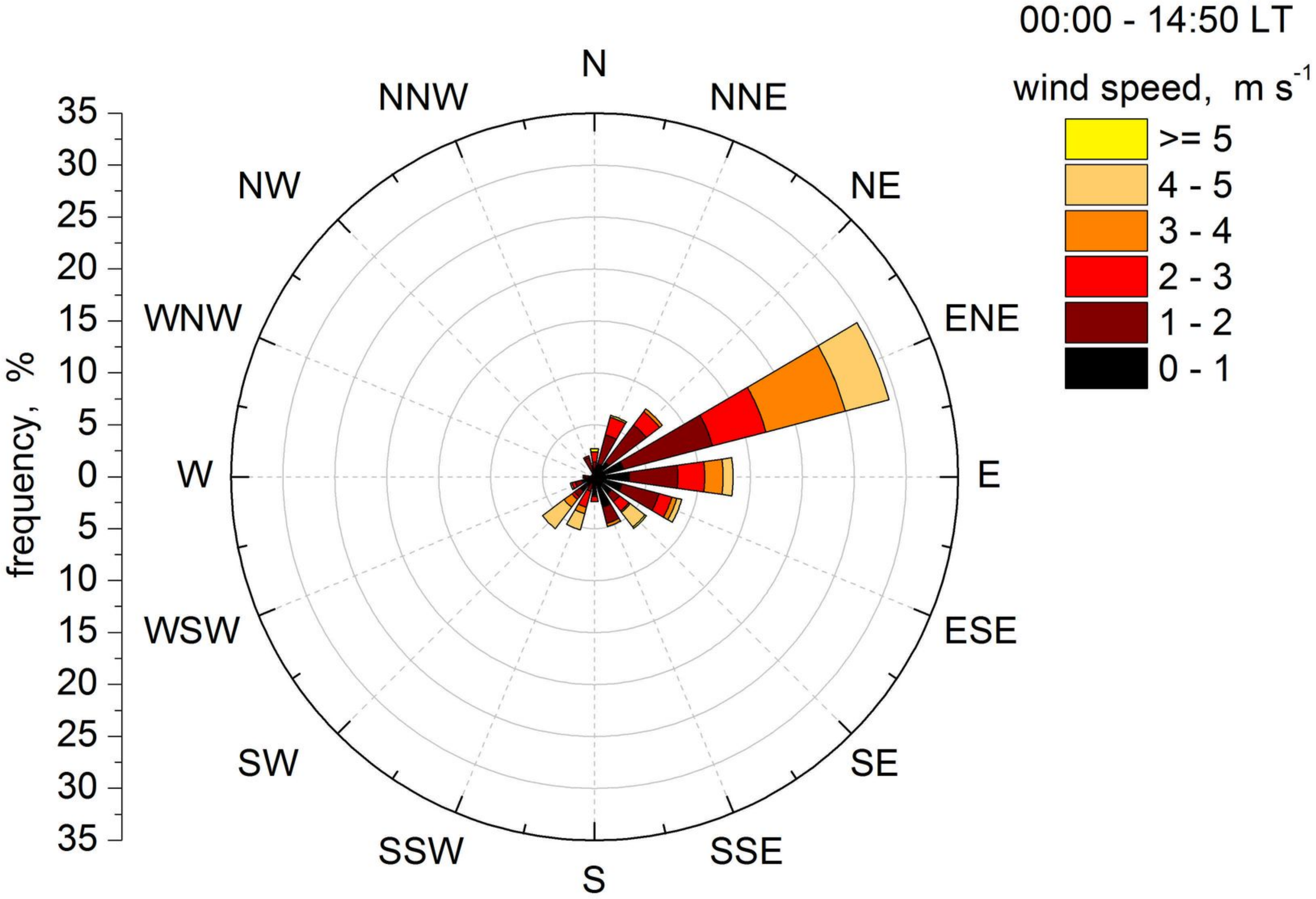


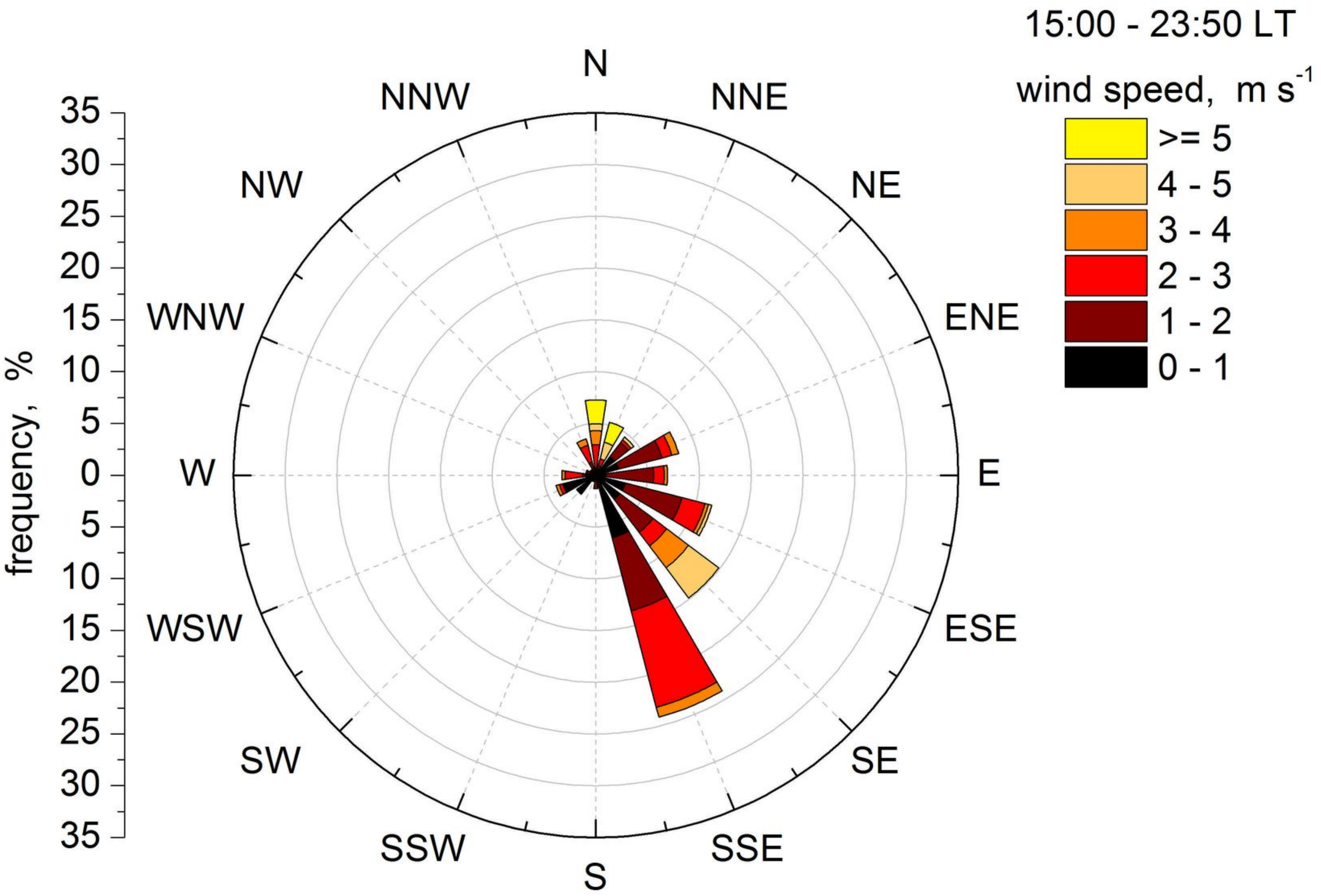
O_3 (F#18)
O_3 (F#19)
O_3 boat (F#18)
O_3 boat (F#19)
CN (F#19)
CN (F#18)
Rio Negro
O_3, ppb
CN, cm^{-3}
LAT
60
55
50
45
40
35
30
25
20
15
10
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
-3.35
-3.3
-3.25
-3.2
-3.15
-3.1
-3.05
-3
-2.95
-2.9

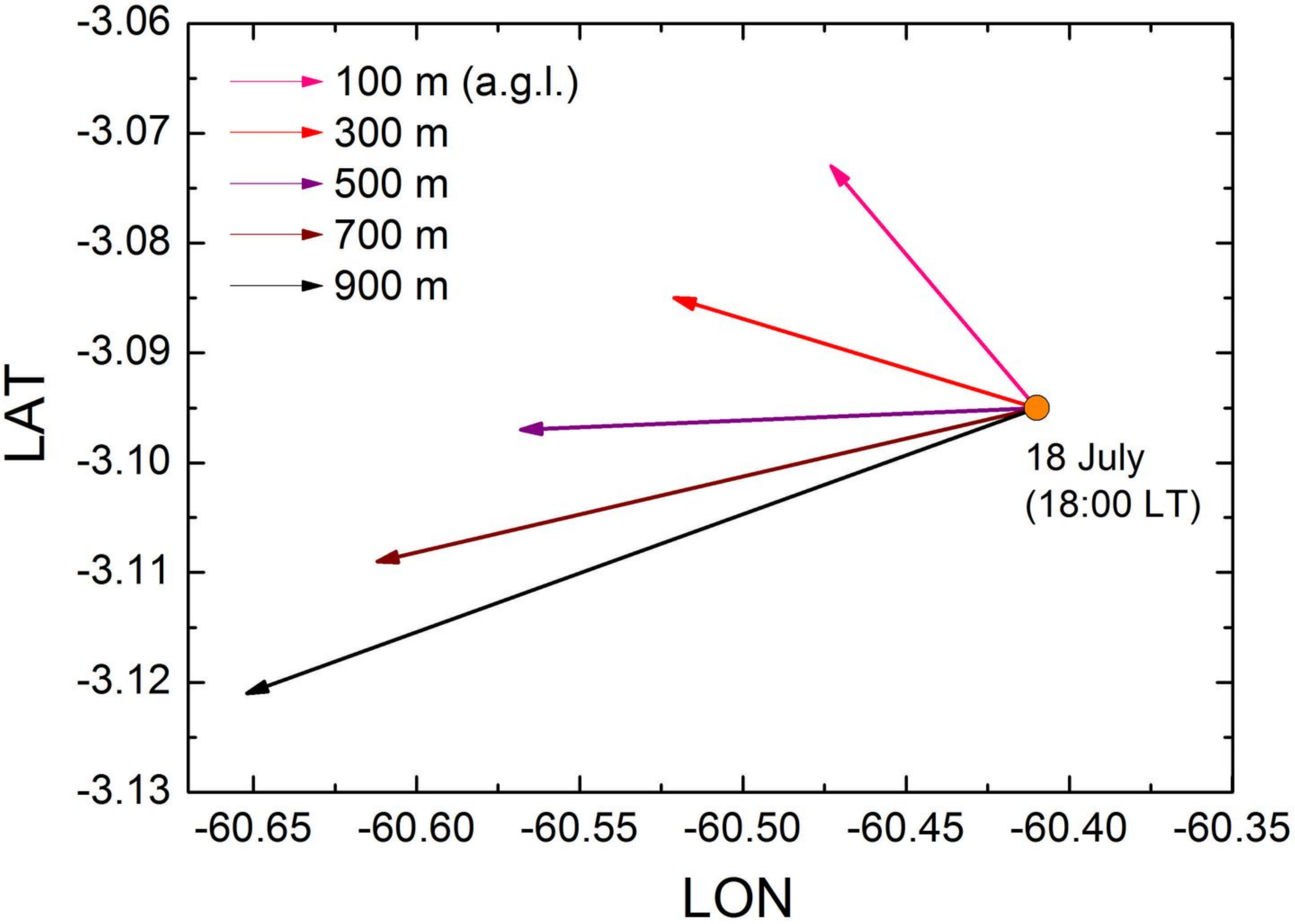
Figure 8.

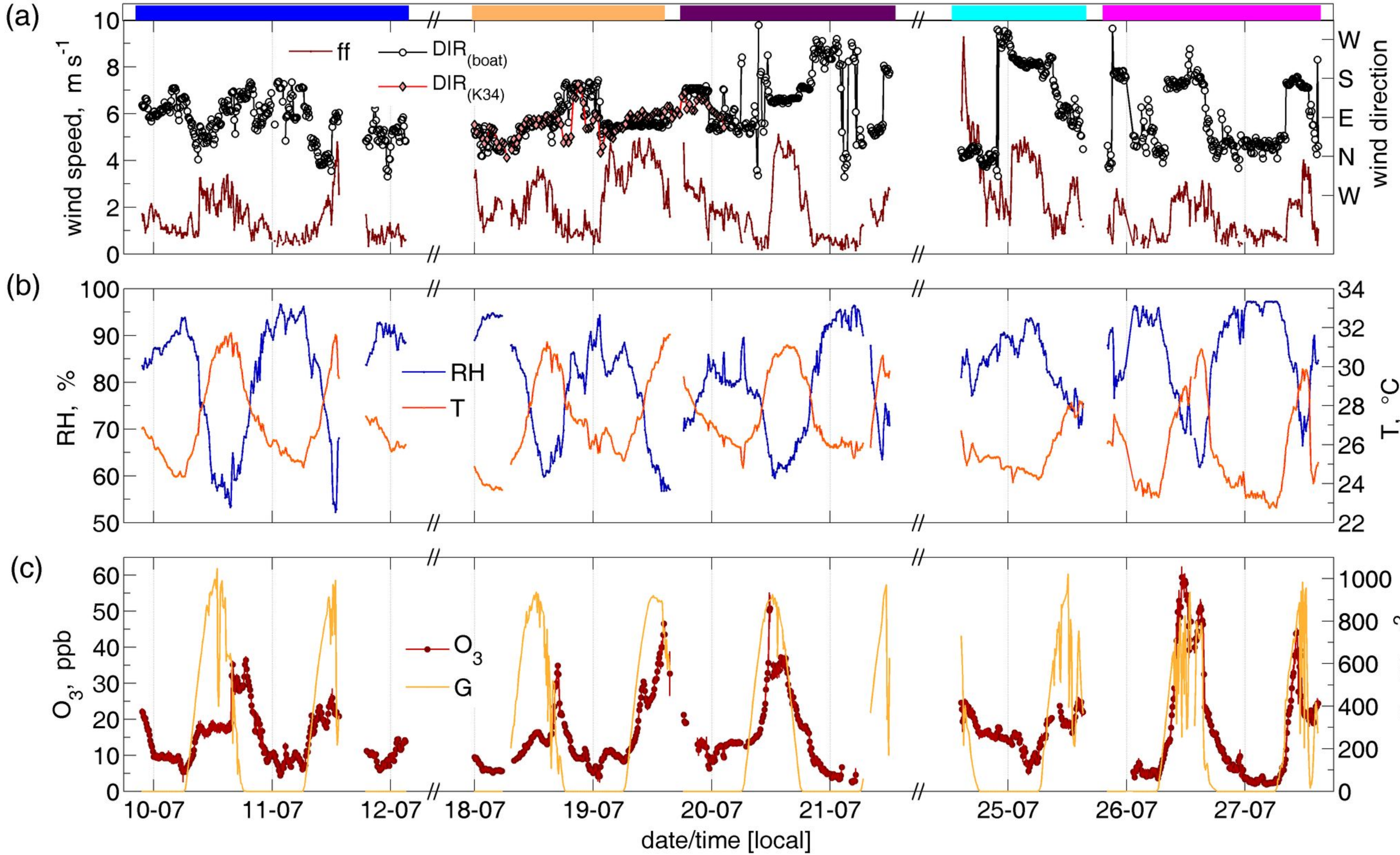


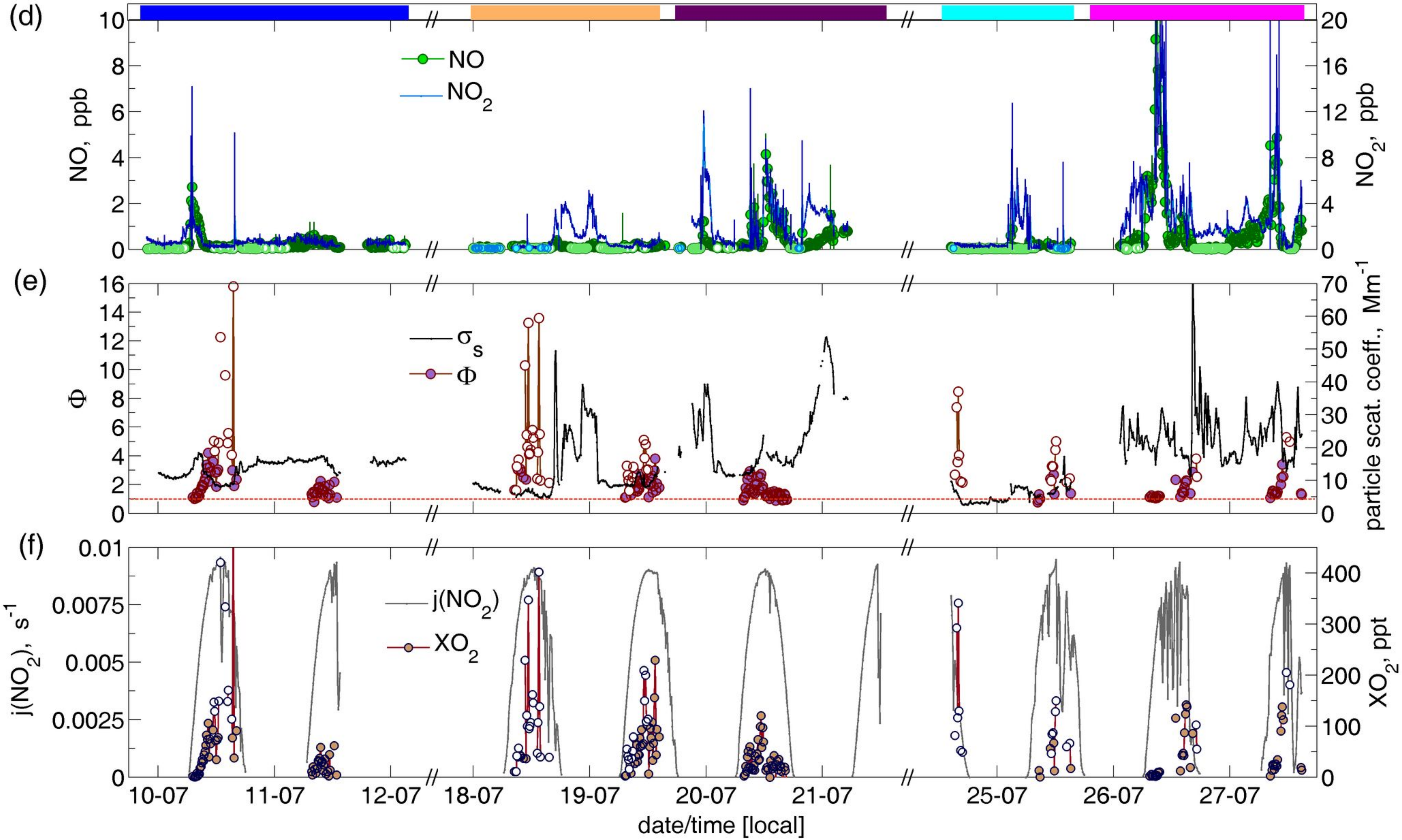

61°20'W
61°0'W
60°40'W
60°20'W
60°0'W
2°40'S
3°0'S
3°20'S
K 34
BR-174
AM-010
Rio Negro
Rio Manacapuru
Manaus
AM-070
Manacapuru
Rio Solimões
10./11. July
18./19. July
20. July
25. July
26./27. July
road
water bodies
open land
forest
residence area
km
0
12
24
36
48

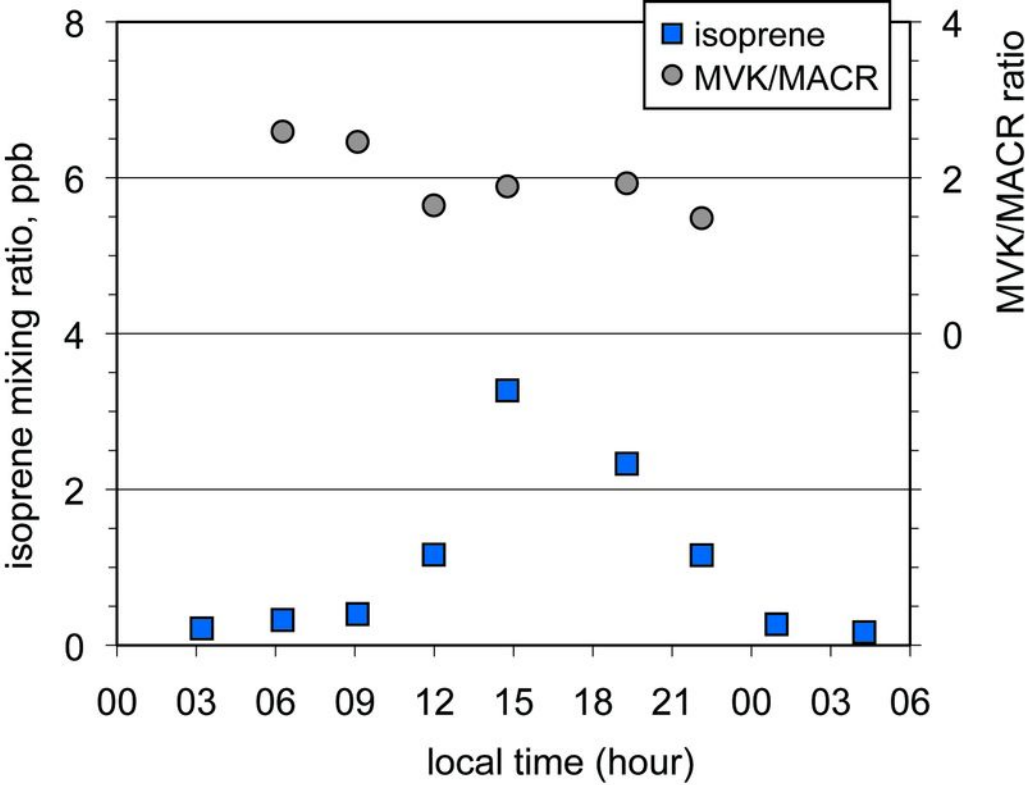

00:00 - 14:50 LT
wind speed, m s-1
>= 5
4 - 5
3 - 4
2 - 3
1 - 2
0 - 1
frequency, %
35
30
25
20
15
10
5
0
5
10
15
20
25
30
35
N
NNE
NE
ENE
E
ESE
SE
SSE
S
SSW
SW
WSW
W
WNW
NW
NNW

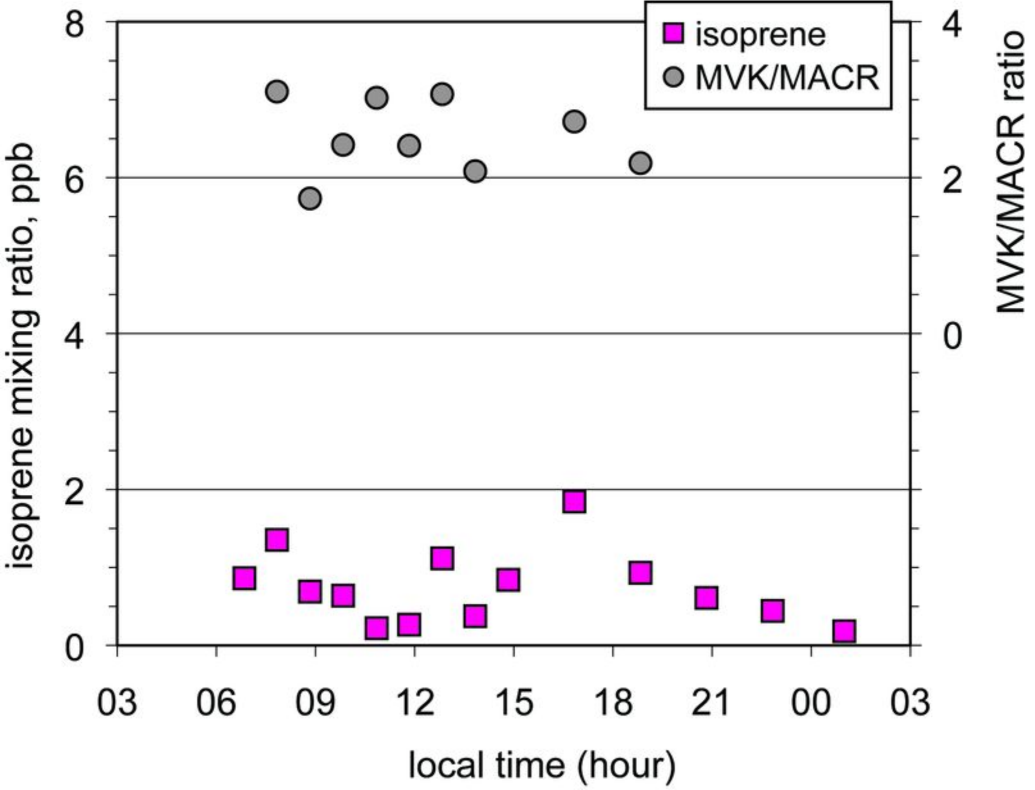

15:00 - 23:50 LT
wind speed, m s^{-1}
>= 5
4 - 5
3 - 4
2 - 3
1 - 2
0 - 1
frequency, %
35
30
25
20
15
10
5
0
5
10
15
20
25
30
35
N
NNE
NE
ENE
E
ESE
SE
SSE
S
SSW
SW
WSW
W
WNW
NW
NNW


100 m (a.g.l.)
300 m
500 m
700 m
900 m
18 July
(18:00 LT)
LAT
-3.06
-3.07
-3.08
-3.09
-3.10
-3.11
-3.12
-3.13
LON
-60.65
-60.60
-60.55
-60.50
-60.45
-60.40
-60.35


(a)
wind speed, m s^{-1}
0
2
4
6
8
10
ff
DIR$_{(boat)}$
DIR$_{(K34)}$
wind direction
W
S
E
N
W
(b)
RH, %
50
60
70
80
90
100
RH
T
T, °C
22
24
26
28
30
32
34
(c)
O$_3$, ppb
0
10
20
30
40
50
60
O$_3$
G
G, W m^{-2}
0
200
400
600
800
1000
10-07
11-07
12-07
18-07
19-07
20-07
21-07
25-07
26-07
27-07
date/time [local]

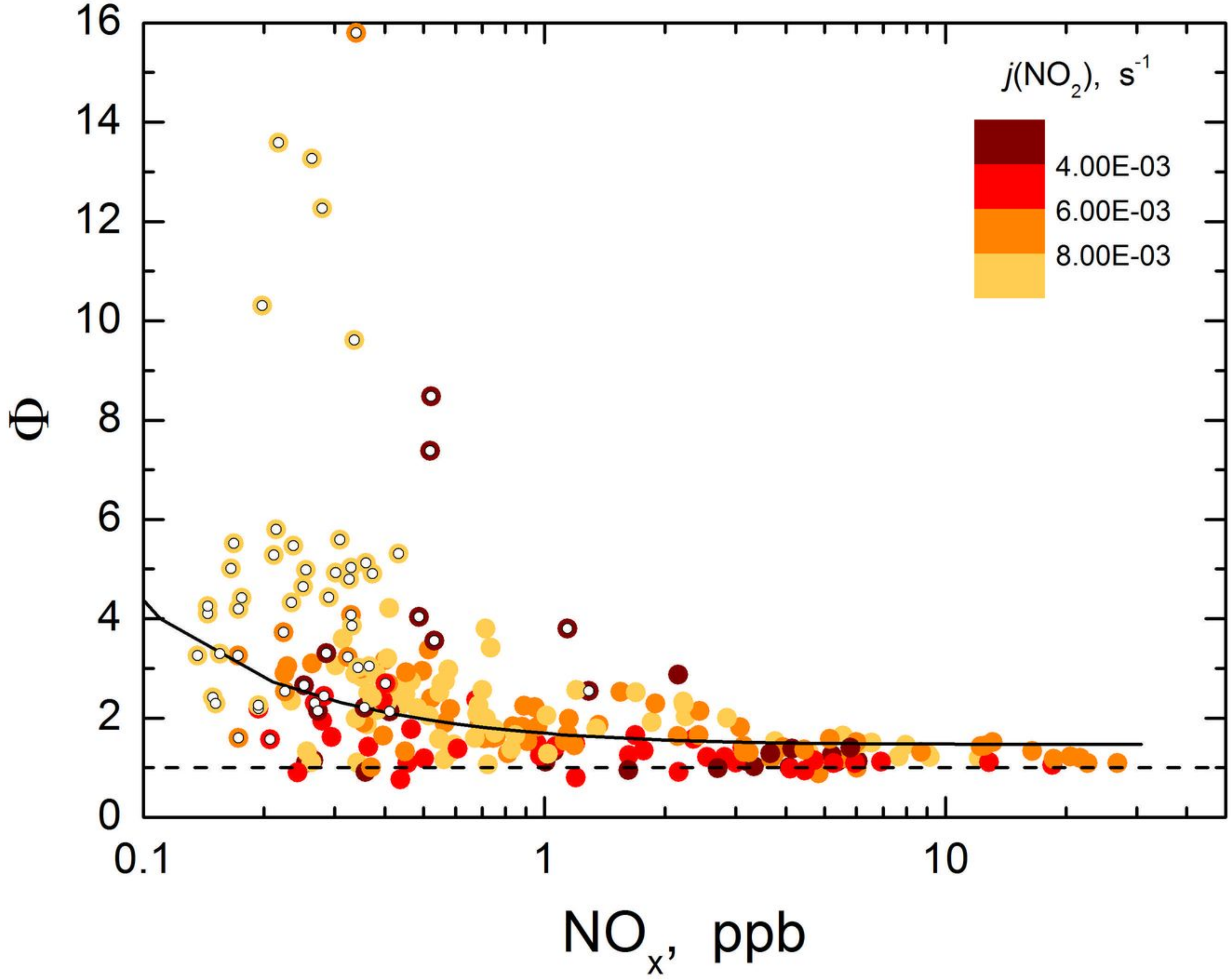

(d)
NO
NO$_2$
NO, ppb
NO$_2$, ppb
0
2
4
6
8
10
0
4
8
12
16
20
(e)
σ_s
Φ
Φ
particle scat. coeff., Mm^{-1}
0
2
4
6
8
10
12
14
16
0
10
20
30
40
50
60
70
(f)
j(NO$_2$)
XO$_2$
j(NO$_2$), s^{-1}
XO$_2$, ppt
0
0.0025
0.005
0.0075
0.01
0
100
200
300
400
10-07
11-07
12-07
18-07
19-07
20-07
21-07
25-07
26-07
27-07
date/time [local]


isoprene
MVK/MACR
isoprene mixing ratio, ppb
MVK/MACR ratio
8
6
4
2
0
4
2
0
00
03
06
09
12
15
18
21
00
03
06
local time (hour)


isoprene
MVK/MACR
isoprene mixing ratio, ppb
MVK/MACR ratio
8
6
4
2
0
4
2
0
03
06
09
12
15
18
21
00
03
local time (hour)


HYSPLIT plume dispersion on 18 July 8:00-11:00 LT
track of Flight#18 on 19 July, 10:00-14:00 LT
boat
Manaus
Manacapuru


HYSPLIT plume dipersion on 18 July 17:00 to 20:00 LT
track of Flight#19 on 19 July, 15:45-18:00 LT
boat
Manaus
Manacapuru


16
14
12
10
8
6
4
2
0
Φ
0.1
1
10
NO_x, ppb
$j(NO_2)$, s^{-1}
4.00E-03
6.00E-03
8.00E-03