\mathbb{N}_{x}^{0} above a tropical rainforest: an analysis with a global and box model

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Abstract. A cross-platform field campaign, OP3, was conducted in the state of Sabah in Malaysian Borneo between April and July of 2008. Among the suite of observations recorded, the campaign included measurements of NO_x and O₃-crucial outputs of any model chemistry mechanism. We describe the measurements of these species made from both the ground site and aircraft. We use the output from the global model p-TOMCAT to illustrate the ability of a global model chemical mechanism to capture the chemistry at the rainforest site. The basic model performance is good for NO_x and poor for ozone. We use a box model containing the same chemical mechanism to explore the weaknesses in the global model. Without some parameterization of the nighttime boundary layer-free troposphere mixing (i.e. the use of a dilution parameter), a time dependent box model will not reproduce the observations. We conclude with a discussion of box model budget calculations of individual chemical reaction fluxes in comparison with deposition and mixing.

1 Introduction

A four month field campaign, part of the NERC-funded 'Oxidant and Particle Photochemical Processes' (OP3)¹, was conducted in the Malaysian state of Sabah, on the island of Borneo, between April and July of 2008 (Hewitt et al., 2010). There were two intensive periods of observation: the first between 8 April and 3 May, and the second between 25 June and 23 July. A key goal of the project is to assess our understanding of photochemical processes above a rainforest and their impacts on various scales; to this end, the campaign utilized simultaneous ground, airborne, and satellite measure-

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¹More information on OP3 can be found online at: http://www.es.lancs.ac.uk/op3/ ments². A further aim is to understand the scale relationships of these measurements as they are used by and contribute to mesoscale, regional, and global models.

Atmospheric oxidation above a tropical rainforest is complex (e.g. Kuhn et al., 2007; Ganzeveld et al., 2008; Lelieveld et al., 2008), and it is therefore beyond current computational resources to represent it explicitly in a global model. Furthermore, the horizontal resolution of the current generation of global models is 2-5° (approximately equivalent to 220 and 550 km at the equator) (Stevenson et al., 2006), which limits their ability to model processes that occur at the subgrid scale, such as emission variability. At the same time, these models attempt to simulate the production and destruction of ozone, which is dependent on local chemical conditions (Crutzen, 1973; Sillman et al., 1990; Jenkin and Clemitshaw, 2000). Ozone is important for radiation (Gauss et al., 2006), and at high concentrations is detrimental to both human (Wilkins et al., 2001; Jerrett et al., 2009) and crop health (van Dingenen et al., 2009). Our understanding of the future impacts of ozone very often relies on the output of global models (Forster et al., 1996; Fuglestvedt et al., 1999; Stevenson et al., 2006) and it is therefore essential to understand how global chemical mechanisms perform in relation to the local measurements which help to constrain them.

Production of tropospheric ozone is a non-linear function of its precursor concentrations (Liu et al., 1987; Jenkin and Clemitshaw, 2000), and depends largely on local concentrations of volatile organic compounds (VOC), the hydroxyl radical (OH), and the oxides of nitrogen (NO + NO₂ = NO_x) (e.g. Sillman, 1995). NO and NO₂ act as catalysts in many oxidation cycles in the atmosphere due to their rapid interconversion; the availability of NO_x largely determines whether ozone production or destruction dominates in a specific region of the tropical boundary layer (Liu et al., 1987; Trainer et al., 1991), and the impact of NO_x on ozone pro-

²For a full list of instrumentation see Hewitt et al. (2010).

duction in the observation region has been previously described (Hewitt et al., 2009). Photolysis of NO_2 is the largest known production mechanism for ozone in the troposphere, while loss occurs through photochemical reaction with other trace gases and deposition to surfaces such as the ocean or vegetation. Ozone can also be entrained into the troposphere from the ozone-rich stratosphere (Holton et al., 1995). The lifetime of tropospheric ozone can range from a few days to over a month, depending on location in the atmosphere (e.g Stevenson et al., 2006; Wild, 2007), and as such transport from the free troposphere may influence local boundary layer measurements of ozone.

The odd oxygen ($O_x = O_3 + NO_2$) budget can be described by:

$$\frac{d[\mathbf{O}_{\mathbf{x}}]}{dt} = k_{prod}[\mathbf{O}_{\mathbf{x}}] - k_{loss}[\mathbf{O}_{\mathbf{x}}] + k_{mixing}\delta[\mathbf{O}_{\mathbf{x}}] - k_{dep}[\mathbf{O}_{\mathbf{x}}](1)$$

where the each term represents chemical production, chemical loss, transport, and deposition, respectively; for the mixing term, $\delta[O_x]$ represents the gradient. For our purposes, chemical production of odd oxygen is represented by the oxidation f NO to NO₂ by peroxy radicals:

$$k_{prod}[O_{x}] = k_{a}[NO][HO_{2}] + k_{b}[NO][RO_{2}]$$
⁽²⁾

where RO_2 is a generic hydrocarbon peroxy radical. O_x loss can be schematically represented as:

$$k_{loss}[O_x] = k_c[O_3][HO_2] + k_d[O(^1D)][H_2O] + k_e[O_3][alk.](3)$$

where alk. represents a generic alkene. An additional term to the chemical loss can be oxidation of NO_2 to other nitrogen species, such as nitric acid.

Nitrogen oxides are emitted both by natural processes and human activities. Of the natural sources, emission from soils (Yienger and Levy II, 1995; Delon et al., 2008) and formation during lightning storms (Franzblau and Popp, 1989; Schumann and Huntrieser, 2007) are the major contributors. Fossil fuel combustion, biomass burning and aircraft emissions are the major anthropogenic sources (Kasibhatla, 1993; Levy II et al., 1999; Toenges-Schuller et al., 2006). Although fluxes from tropical areas are not yet well constrained, the work of Bakwin et al. (1990) suggested significant emissions from tropical forested areas. Jaeglé et al. (2004) reported that soil emissions could be as large as biomass burning emissions in Africa. In these remote tropical areas the potential for NO_x species to influence local chemistry is significant due to low background NO_x and high concentrations of both the hydroxyl radical and biogenic VOC (Steinkamp et al., 2009). An increase in the frequency and spatial distribution of tropical NO_x measurements will help quantify local tropical fluxes and sources. But global models will largely play the role of quantifying the impact of these fluxes on a regional and global scale. For this reason, it is important to understand how global models relate to local measurements.

The NO budget can be described in a similar fashion to ozone in Equation 1, with the ratio between NO and NO_2 can be expressed as:

$$\frac{[\text{NO}]}{[\text{NO}_2]} = \frac{j_{\text{NO}_2}}{k_f[\text{O}_3] + k_g[\text{HO}_2] + k_h[\text{RO}_2]}$$
(4)

Here, we present measurements of NO, NO₂, and O₃ taken over two four-week periods in a remote rainforest location from ground and aircraft platforms. We use a global model chemical mechanism implemented in both a global model and a box model to explore the budget of NO_x and ozone at the rainforest site. In section 2 we present a summary of the measurement techniques and the data. Section 3 examines our ability to reproduce the measurements in two different chemical modelling frameworks. In section 3.1, we use the global model p-TOMCAT at two different resolutions. In section 3.2, we introduce a box model with the same chemical mechanism as p-TOMCAT and examine the budget of ozone and NO_x. Finally, section 4 summarizes the study and the results.

2 Measurements

2.1 Methods

Nitrogen oxides and ozone measurements were taken at the Bukit Atur Global Atmospheric Watch (GAW) station (04°58'53", 117°50'37", and elevation 426 m). NO measurements were made by chemiluminescence using an Ecophysics CLD 780 TR nitric oxide analyzer, with an Ecophysics PLC 762 NO₂ photolytic converter connected to allow conversion of NO₂ to NO. NO and NO₂ concentrations were measured from an inlet situated at 5 m above ground level through quarter-inch PFA tubing. Measurements were run on continuous sampling except during calibrations and when running NO_x-free air. The analyzer was calibrated using an Eco Physics PAG003 pure air generator, an Environs calibration gas blender S6100 and a cylinder of 450 ppbv NO in nitrogen. The photolytic converter efficiency is also determined as part of the calibration. NOx-free air was run through the system on several occasions to allow more accurate determination of the systematic artefact and detection limit.

Each measurement cycle lasted for 1 minute and consisted of 12 seconds of NO measurement, 12 seconds of NO₂ measurement and 24 seconds of interference determination. The remaining 12 seconds allowed for switching between the different modes and purging of the reaction cell. The 1σ limit of detection for 10 minute frequency data was approximately 2.8 pptv for NO and 7 pptv for NO₂.

Ozone concentrations were measured using a Thermo Environmental Instruments (TEI) 49i UV absorption ozone analyzer. The data was internally averaged to one minute frequency and the detection limit was 0.6 ppbv.



Fig. 1. Time series of measured NO, NO_2 , and O_3 at the Bukit Atur GAW ground site, plotted versus local time (GMT+8).



Fig. 2. Left: Median diurnal cycle of ground-based measured NO (dark red), NO₂ (dark green), and O₃ (dark blue) in April. The corresponding 25-75 quartile interval is shown with each measurement: NO in pink, NO₂ in light green, and O₃ in light blue. Right: median diurnal measurements in July, shown only for the days when corresponding flight data is available between 6:00 and 18:00 h; diurnal profiles are the same color. Average flight data for morning and afternoon profiles above the site are shown as whiskered points and are separated by height. NO boundary layer measurements are show in red (boundary layer) and yellow (free troposphere). NO₂ is shown in light green (boundary layer) and brown (free troposphere). O₃ is shown in light blue (boundary layer) and purple (free troposphere).

sive measurement periods of OP3. In June and July 2008, the campaign was complemented by airborne measurements. On board the Facility for Airborne Atmospheric Measurements (FAAM) BAe 146 aircraft, NO and NO₂ were measured using the the University of East Anglia (UEA) NOxy instrument, which employed the same technique as the ground based instrument described above. Interference determinations were carried out at the beginning of level runs during the flights and calibrations took place during transit to and from the airport. Detection limits of the UEA NOxy are on the order of 3 pptv for NO and 15 pptv for NO₂ for 10s data, with estimated accuracies of 10% for NO at 1 ppbv and 10% for NO₂ at 1 ppbv. The instrument is described in detail by Brough et al. (2003). Ozone was measured on board the aircraft using a TEI 49C UV absorption analyser.

Isoprene fluxes, used in our box modelling experiments, were measured using a PTR-MS instrument at the Bukit Atur site. Its response was optimized so as to achieve the best compromise between the optimal detection limit for VOCs and the minimization of the impact of high relative humidity. The operational details of the instrument have been presented elsewhere (e.g Lindinger et al., 1998; de Gouw et al., 2003; Blake et al., 2009) whereas the experimental setup and methodology for OP3 will be described in a forthcoming paper (Langford, et al., Fluxes of volatile organic compounds from a south-east Asian tropical rainforest, 2009. This special issue, in prep.). High frequency temperature data were obtained from a 20-Hz sonic anemometer (Windmaster Pro, Gill Instruments Ltd.), which was collocated with the sampling inlet for PTR-MS.

2.2 Discussion

Time series of NO, NO₂, and O₃ data are shown in Fig. 1. Although the frequency of data collection is 1 minute (section 2.1), it is shown here with a running average of 10 minutes for smoothing purposes. NO levels were typically below 0.1 ppbv, although there were regular spikes above this level which reached up to 0.4 ppbv. NO₂ levels were higher, generally below 0.4 ppbv but reaching 0.8 ppbv. Ozone concentrations ranged from near zero up to 30 ppbv, but were only consistently above 20 ppbv on three days (11-13th April).

Fig. 2 shows the median diurnal profiles for the entire April measurement period for all three species³. The 25-75 quartile limit is shown in shaded regions around each of the profiles. The ozone diurnal cycle shows a minimum of approximately 6 ppbv around 7:00 h followed by a rise through the morning. Ozone concentrations of approximately 11 ppbv remain until the evening, when concentrations slowly fall to their minimum in the morning. NO₂ concentrations

exhibit the most amplified diurnal cycle, which peaks at midnight around 240 pptv and reaches a low of 80 pptv in midafternoon. The loss of NO_2 between midnight and midday occurs less rapidly than the buildup between late afternoon and evening. An NO peak of around 70 pptv is observed at 8:00 h and quickly recovers to a fairly constant level between 30 and 40 pptv. This persists until 18:00 h when a further drop to 20 pptv occurs. Non-zero NO concentrations between 15-20 pptv persist throughout the night.

In July, an aircraft joined the campaign in order to make dedicated measurements above the site and over the surrounding areas. On the right side of Fig. 2, the diurnal cycles of NO, NO₂, and O₃ from the ground site at the Bukit Atur GAW tower are shown for this second observation period. These diurnal cycles are sampled only for the four days for which equivalent aircraft data is also available. The average measurements made in profile flight patterns directly over the site are plotted as whiskered points and show values for both boundary layer and free troposphere.

The values of ozone aloft show little difference, and therefore vertical structure, when compared to values of the ground-based measurements. A diurnal structure in the ground based O_3 observations in July is not clear, with the values around 9 ppbv. Morning aircraft measurements are slightly higher (10-12 ppbv) than the ground based. Aircraft measurements of ozone levels rise slightly to approximately 13 ppbv in the late afternoon, though boundary layer and free troposphere values remain indistinguishable (within uncertainty) from each other.

Boundary layer NO_2 matches the ground based measurements closely, which remain in the range of 100-200 pptv for most of the day. NO_2 measurements show a similar structure (rise until midnight and subsequent decrease afterwards) to the first campaign, but because only four days are sampled here the full diurnal cycle is not shown. NO_2 measurements of around 20 pptv in the free troposphere are much lower than those in the boundary layer and at the surface, demonstrating that NO_2 has a strong vertical structure. NO displays a similar pattern to NO_2 with boundary layer values of 80-200 pptv, that resembles ground-based measurements well, and free tropospheric values that are much lower (less than 10 pptv). The diurnal cycle of NO also bears significant resemblance to that of the first campaign, (i. e. a rise in early morning followed by a slow tapering into the afternoon).

For comparison, the NO concentrations at the ground site in both measurement periods are in between measurements made in the Amazon Rainforest of 20 pptv (Lelieveld et al., 2008) and 100 pptv (Karl et al., 2009). Ozone, on the other hand, is lower at the Borneo site than in reported values for the Amazon for both the boundary layer (19 ppbv) and the free troposphere (37 ppbv) (Lelieveld et al., 2008).

 $^{^{3}}$ A version of this Figure appeared in Hewitt et al. (2010). The Figure that appears here has higher temporal resolution (10 minute data) than the previous version (1 hour data).

3 Model simulations

In this section, we describe two sets of model simulations. In section 3.1, a global model is used to simulate the diurnal cycle of the three measured species NO, NO_2 , and ozone. In section 3.2, we use a box model to explore the chemical and physical budget terms and examine how they influence the mechanism's performance in replicating observations.

3.1 Global model

3.1.1 Model description

We use the Cambridge global chemistry transport model (CTM) p-TOMCAT to simulate the diurnal cycles of NO, NO₂, and O₃ observed during the April measurement period. The Cambridge p-TOMCAT global CTM is described in more detail in Cook et al. (2007) and Hamilton et al. (2008). The model was used for this study in both a high horizontal resolution mode ($0.56^{\circ} \times 0.56^{\circ}$, approximately 62 km in the tropics) and a low resolution mode $(2.8^{\circ} \times 2.8^{\circ}, \text{ approx-}$ imately 310 km in the tropics). Both have 31 levels in the vertical, from the surface to 10 hPa. Over Borneo the thickness of the surface layer is about 60 m with the next layer about 130 m. Both are driven by 6 hourly operational analyses of wind, temperature, and humidity from the European Centre for Medium-range Weather Forecasting (ECMWF). The boundary layer height is diagnosed from input ECMWF operational analyses using the non-local scheme of Holtslag and Boville (1993).

The model mechanism is the same as described by Arnold et al. (2005), with the addition of the Mainz isoprene mechanism (Pöschl et al., 2000) which is implemented as described by Young et al. (2009) (for the UM_CAM model). It is a medium-size chemistry for a global model, simulating the oxidation of methane, ethane, propane, and isoprene, with 81 tracers and ~200 reactions. Time dependent chemical concentrations are calculated with the ASAD package (Carver et al., 1997). Photolysis rates for 37 species are determined using offline look-up tables gnerated by the Cambridge 2D model (Law and Pyle, 1993) using the multiple scattering scheme of Hough (1988). These offline rates are based on climatological cloud cover and a fixed aerosol profile.

Emissions of NO_x , CO, ethane, propane and isoprene are included and are based on Gauss et al. (2003). The lightning emissions are scaled to produce 5 Tg N yr⁻¹ using the parameterization of Price and Rind (1992) according to Stockwell et al. (1999). A seasonal variation is applied to the biomass burning emissions using the distribution of Hao and Liu (1994). Isoprene emissions are taken from the Global Emissions Inventory Activity (GEIA) of Guenther et al. (1995) and have a diurnal cycle applied in the model. Dry deposition velocities are calculated according to the method of Giannakopoulos (1998) using prescribed land type-specific data based on data from Ganzeveld and Lelieveld (1995) and Zhang et al. (2003).

3.1.2 Global model results

Monthly mean diurnal variations of surface NO, NO₂, and ozone in the boundary layer are shown for both model resolutions in Fig. 3. Both resolutions show a fit for NO which matches the data well; the model reaches a maximum of 65 pptv in the morning around 8:00 h, when the measurement data also peaks (at 60 pptv). At low resolution, there is a dip in midday values to 40 pptv, which was not recorded in the measurements. NO drops to zero around 18:00 h in p-TOMCAT, coinciding with the point when measurement values also drop. As described above, residual NO concentrations of approximately 20 pptv are present throughout the night, and these values are not captured by the global model at either resolution.

The fit to measurements for NO_2 is reasonable for both global models, though the range of the diurnal cycle is 10% too high at 222 pptv, compared with 203 pptv in the measured data. The low resolution version of the model shows constant NO₂ concentrations at night, while the high resolution version of the model shows an increase in NO2 until dawn. At higher altitudes in the model (not shown), NO₂ concentrations are lower (less than 50 pptv) than in the boundary layer levels, which is consistent with the observed vertical profile (section 2.2). We argue below that the measurements reflect a large component of free tropospheric character due to mixing during the second half of the night (24:00 to 6:00 h). It seems possible that mixing between boundary layer and free tropospheric air in the global model is not sufficient to capture the nighttime decrease in NO₂ shown in the measurements. In addition, the diurnal pattern in both resolutions of the model is slightly too narrow, with a more precipitous decrease in concentrations in the morning and a stronger rise in the evening. In contrast, the measurements show a smoother rise and fall throughout the day and night. Both models capture the rise between 14:00 and 18:00 well.

Finally, the modelled ozone is a factor of 4 too high in the global model. Concentrations in the low resolution model are as high as 26.8 ppbv. The higher resolution model performs slightly better with values of approximately 20 ppbv. In contrast, measured mixing ratios are between 6 and 13 ppbv. Despite this, the diurnal cycle of the model seems to capture the observed data, which are relatively constant, well. The higher resolution version has a more realistic representation of deposition, which is an important loss process for ozone. Variation in the land surface type, which helps control the deposition rate, can be captured better in the high resolution model, which has a much higher resolution land sea mask, and also shows a much stronger land-sea gradient in ozone concentrations than the low resolution version of the model (Fig. 10, section 5, Hewitt et al. (2010)).



Fig. 3. Global model comparison to diurnal cycle of NO, NO₂, and O_3 from the median diurnal cycle in the measurements (black, with 25-75 quartile in grey). The global model is shown in red (low resolution) and green (high resolution) for the lowest model level.

3.2 Box Model

Using these global model results as a starting point, we next employ a box model fitted with the same chemical mechanism to explore the budgets of ozone and NO_x .

3.2.1 Model description

Dry deposition in the box model uses the same tabulated values as the global model, but only six species are deposited: NO, NO_2 , O_3 , peroxy acetyl nitrate (PAN), peroxy-

Table 1. Dry deposition velocities $[\text{cm s}^{-1}]$ for species in the box model, which are the same as rainforest values for the global p-TOMCAT model.

| Species | V _d Day | V _d Night |
|---------|--------------------|----------------------|
| O_3 | 0.85 | 0.30 |
| NO | 0.14 | 0.01 |
| NO_2 | 0.83 | 0.04 |
| PAN | 0.63 | 0.14 |
| MPAN | 0.63 | 0.14 |
| ISON | 1.00 | 0.06 |

methacrylic nitric anhydride (MPAN), and a lumped nitrate species representing the products from isoprene oxidation ((ISON, see Pöschl et al., 2000)). Nitric acid is not deposited. Table 1 shows the deposition velocities for day and night. These closely match the deposition velocities for the forested land type in the p-TOMCAT model. The photolysis follows the scheme of the Master Chemical Mechanism (MCM, Saunders et al., 2003).

Only NO and isoprene are emitted into the box. Isoprene emissions into the model are taken from ground based flux measurements (see Figure 9a in Hewitt et al. (2010)), which are described in section 2.1. In order to maintain consistency between both models, we do not include monoterpene emissions or chemistry, though monoterpene emission measurements were made (Hewitt et al., 2010). Initial reaction of a monoterpene species with OH, O₃, and NO_v could contribute to the budgets at the site. Occasionally, isoprene flux measurements were not available due to power outages; in these instances, we used linear interpolation to fill in the gaps. We used NO emissions of 6×10^9 molec cm² s⁻¹, in between the values of Pugh et al. (2010) and Bakwin et al. (1990). This emission rate was held constant since, in the absence of NO flux measurements at the site, we were not able to constrain NO emissions to a diurnal pattern. NO flux measurements were made nearby underneath the canopy layer (J. Dorsey, et al., Observations of soil NO_x emission from a Southeast Asian rainforest: a technique to assess biological controls, 2009. This special issue, in prep.). In contrast, the Bukit Atur GAW station is in a clearing, and therefore canopy flux measurements are not representative of this site; there can be a strong difference between below- and abovecanopy fluxes of NO_x (e.g. Duyzer et al., 2004). For these reasons, we assume that NO is emitted constantly into the model; this is also consistent with the emissions used in the global model.

The box model boundary layer height is fixed to a set value during the day (6:00 to 18:00 h) and fixed to a different value at night. The boundary layer height is effectively a mixing depth, and therefore controls the range over which emissions are mixed into the model, and the rate of sinks via depo-

Table 2. Initial concentrations of six species used in the box model.

| Species | Concentration |
|--------------|---------------|
| CO | 130 ppbv |
| H_2O_2 | 3 ppbv |
| C_2H_6 | 500 pptv |
| C_3H_8 | 50 pptv |
| HCHO | 1 ppbv |
| CH_3COCH_3 | 50 pptv |
| CH_4 | 1700 pptv |
| H_2 | 500 pptv |
| | |

sition. Based on the backscatter measurements of Pearson et al. (2010), we set the boundary layer height during the day to 600 m, and the boundary layer height at night to 200 m.

Temperature data were taken from measurements made alongside the isoprene flux measurements (described in section 2.1) used as 30-min averages, and pressure was set to 950 mb in the box, appropriate to the conditions of the rainforest site (this value was also used for the back trajectories described in section 2.3 of Hewitt et al., 2010). Initial concentrations of chemical species in the box model are set to the values shown in Table 2, and were based on approximate concentrations measured during the campaign from the on site gas chromatographs (see Hewitt et al., 2010). NO, NO₂, and O₃ are initialized to their midnight values from the diurnal cycle in the measurements. All other species are initialized to zero.

For the our model-measurement comparisons, both the model and the data are sampled for 15 days to account for day to day variability in isoprene flux measurements.

This 'constrained' version of the box model was formulated after a number of sensitivity studies were carried out in a 'fixed' box model. These experiments and the model set-up of the 'fixed' model are described in the Supplementary Materials. We found that the 'fixed' model exhibited very low sensitivity to chemical parameters, and higher sensitivity to physical ones. The parameter that made the single largest difference was the introduction of a dilution parameter, which is described below.

3.2.2 Dilution

To capture the behaviour of NO_x at night, a dilution parameter was introduced to simulate mixing with the free troposphere resulting from a collapse of the boundary layer at night. This dilution parameter removes 2% of chemical tracers at each 10 minute timestep between 24:00 h and 6:00 h by relaxing each species to a concentration of zero, similar to the work of Biesenthal et al. (1998). The value of 2% was determined through a series of sensitivity tests performed with a 'fixed' model (see Supplementary Material), in which we



Fig. 4. Box model comparison with (red) and without (blue) venting against diurnal cycle of NO, NO_2 , and O_3 from the median diurnal cycle in the measurements (black, with 25-75 quartile in grey).

allowed a number of parameters to be 'fixed', including the boundary layer height. Using this alternative configuration of the box model, we performed a cost function analysis of physical parameters. A 2% dilution per timestep is approximately equivalent to a 50% reduction in concentration during the period of dilution (6 hours), or a 95% reduction over a 24 hour period. Doppler lidar measurements of the backscatter from aerosol (Pearson et al., 2010) provide strong evidence for dilution of aerosol in the boundary layer during this period. The ground measurements were made in an area of complex topography, with the lidar measurements made in a valley at an elevation of 198 m (Pearson et al., 2010) compared with 426 m for the Bukit Atur site where the NO_x and ozone measurements were conducted. The median boundary layer height dropped to approximately 200 m according to the lidar measurements, suggesting that on some nights the Bukit Atur site may have effectively been in the free troposphere. The dilution parameter is a simple way to simulate the mixing between the boundary layer box and the free troposphere by parameterizing dilution of species which are concentrated in the boundary layer. As is evident in Fig. 4, the box model was not able to capture the diurnal structure of NO_2 before the introduction of the dilution parameter.

The dilution parameter simulates exchange with free tropospheric air at night and assumes that this incoming air has lower concentrations of NO and NO₂. O₃, however, displays little to no vertical structure in the measurements (see Figure 2). For this reason, ozone is not diluted. Not diluting O_3 is the numerical equivalent of removing O_3 and introducing an equal amount during the same amount of time, such that a collapse of the boundary layer and mixing with the free tropospheric air may well bring in 'new' ozone, but the concentrations will be similar to the boundary layer air it is replacing. This methodology is reinforced by the difference between the species in their distribution of sources and sinks; NOx has a source which is largely surface dominated at a remote rainforest location (higher in the troposphere, lightning can contribute as well), whereas ozone has a significant surface sink due to deposition.

Fig. 4 shows that NO measurements and model simulations are in fairly good agreement following the addition of the dilution parameter. The buildup of NO₂ until midnight and subsequent reduction in concentrations is well captured. At sunrise, when the boundary layer begins to grow, a steep drop in NO₂ concentrations appears around 6:00 h in the box model due to the onset of photolysis. The largest divergence between modelled and measured values occurs in the afternoon, between 12:00 and 16:00 h. Base case modelled and measured ozone display similar diurnal cycles. Both show minima between 7:00 h and 8:00 h and maxima in the late afternoon, though the measurements have more structure in the afternoon than the modelled ozone.

3.2.3 Budget Calculations

In order to investigate the relative contributions of chemistry, mixing, and deposition, we implemented some budget diagnostics into the box model. Tables 3 and 4 shows the integrated fluxes through a number of key chemical reactions as well as the contribution from emission, deposition, and mixing of NO_2 and NO.

For O_x , we find that the the reaction between HO_2 and NO constitutes approximately half of total production. The isoprene peroxy radical, represented in the MIM as the lumped species ISO₂, has the next largest flux of ~3 ppbv day⁻¹, followed by nearly equal contributions from the methyl peroxy

radical and the acetyl radical. The only remaining significant contribution is the reaction between NO and MACRO₂, a four-carbon radical species used in the degradation of isoprene in the MIM, at ~750 pptv day⁻¹. Recycling of NO₂ from NO_y is negligible. Total net production (P-L) of O_x is -44 pptv day⁻¹, i. e. a net loss.

In terms of O_x loss, we find that chemical loss is dominated by the reaction of $O(^{1}D)$ with water vapour and direct reaction with alkenes (in our model, this is isoprene and the lumped four carbon species MACR), both of which contribute nearly equally. Loss of NO_2 to NO_v and O_3+HO_2 contribute smaller amounts to chemical loss. Mixing is calculated by taking the difference before and after the dilution parameter is applied, which occurs after the chemistry time step, and contributions ~ 325 pptv day⁻¹. The dilution parameter is only in effect at night for 6 hours, which means that the relative impact of mixing during these 6 hours is rather higher (equivalent to 1.3 ppbv day $^{-1}$). After this normalization is taken into account, we find that mixing plays the second largest instantaneous role of any loss process. The impact of O_3 deposition is by far the largest contribution to total loss, with a total daily flux of almost 8 ppbv day^{-1} ; we also found that deposition was the strongest sensitivity of a number of chemical parameters in the fixed box model (see Supplementary Materials). The evidence from the global models also suggests that deposition plays a role in the overestimation of ozone, as the high resolution version of the model (with a more accurate land-sea mask) produces less ozone than the low resolution version of the model.

NO production is dominated by photolysis, which contributes over 95% to total production. Emission contributes 743.2 pptv day⁻¹. Chemical loss of NO is largest for reaction with O_3 and HO₂ followed by ISO₂, the acetyl radical, methyl peroxy, and MACRO₂. Deposition and mixing are very small contributors to the NO budget.

Figure 5 shows timeseries of production, loss, mixing, deposition, emission, and net production for the O_x and NO budgets. For the production of O_x , the fluxes of NO+HO₂ and NO+ISO₂ are shown in blue dashed lines. We find that for both, the reaction fluxes taper off in the evening, when isoprene emission has waned and concentrations are falling due to reaction with OH. Loss of O_x is dominated by deposition, with a contribution from $O(^1D)$ +H₂O affecting the diurnal pattern in the middle of the day, when photolysis is important. In contrast, the direct loss of ozone via reaction with alkenes is larger in the late afternoon and throughout the night. NO₂ mixing is only important at night, when the dilution parameter is being used.

Figure 5 also shows the timeseries of relevant fluxes for NO. NO production is almost entirely dominated by photolyis of NO₂, with a small contribution from emission. Loss of NO is dominated by its reaction with RO₂ (mainly HO₂ and ISO2), with a significant portion also coming from reaction with ozone. NO is in steady state for the entire 24 hour period, while there is a net production of O_x during most of

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| Production | Flux | Loss | Flux |
|-----------------------------|---------|----------------------------|---------|
| $NO + HO_2$ | 4685.1 | $O(^{1}D) + H_{2}O$ | 837.4 |
| $NO + CH_3O_2$ | 907.6 | $O_3 + HO_2$ | 195.9 |
| $NO + CH_3C(O)O_2$ | 1031.9 | $O_3 + OH$ | 11.9 |
| $NO + ISO_2$ | 3077.5 | O_3 + alkene | 858.6 |
| $NO + MACRO_2$ | 743.6 | NO ₂ mixing | 325.5 |
| NO + other RO_2 | 0.2 | O ₃ deposition | 7996.2 |
| $CH_3C(O)O_2 + HO_2$ | 49.4 | NO ₂ deposition | 60.4 |
| Nitrate recycling of NO_2 | 10.7 | Loss to NO_y | 264.5 |
| Total | 10506.3 | Total | 10550.5 |

Table 3. Budget statistics for integrated O_x in [pptv day⁻¹].

Table 4. Budget statistics for integrated NO in [pptv day $^{-1}$].

| Production | Flux | Loss | Flux |
|-------------------|---------|---------------------|---------|
| $NO_2 + h\nu$ | 15633.9 | $NO + O_3$ | 5837.8 |
| Other chem. prod. | 15.0 | $NO + HO_2$ | 4685.5 |
| NO emission | 743.2 | $NO + CH_3O_2$ | 908.5 |
| | | $NO + CH_3C(O)O_2$ | 1031.9 |
| | | $NO + ISO_2$ | 3077.5 |
| | | $NO + MACRO_2$ | 743.6 |
| | | NO + other RO_2 | 0.2 |
| | | NO mixing | 6.7 |
| | | NO deposition | 5.1 |
| | | Other chem. loss | 17.9 |
| Total | 16392.0 | Total | 16314.7 |

the day and net O_{x} destruction (dominated by deposition) at night.

4 Conclusions

The observed diurnal cycle of NO at the Bukit Atur GAW site showed concentrations between 40 and 60 pptv throughout most of the day, with lower (15-20 pptv) concentrations at night. NO₂ displayed a distinct rise and fall during nighttime, with a peak at midnight. NO₂ concentrations ranged between 100 and 300 pptv. Ozone showed a diurnal pattern with a maximum in the afternoon and a minimum in the early morning. Ozone concentrations were between 6 and 13 ppbv.

The global model displayed reasonable comparison with the diurnal patterns of NO and NO₂, but not with O₃. We used a box model to investigate the relative importance of various terms in the budgets of NO, NO₂, and ozone. Using a fixed version of the model (Supplementary Materials), we determined that physical processes played a significant role in determining the concentrations of these species at the rainforest site. We implemented a dilution parameter in order to capture the diurnal structure of the measurements and the free tropospheric character of the air during the second half of the night. There are a number of uncertainties that may influence our results, however, such as the potential importance of OH recycling during isoprene oxidation, the inclusion of monoterpene chemistry, and the impact of hetereogeneous chemistry on NO_x .

Changes in tropical processes, including land use, biogenic VOC emissions, and soil NO_x emissions are important drivers of global change. To assess these changes, we generally have to run global models at moderate resolutions. In contrast, validation of the global models requires comparison with data representative of much smaller spatial scales. For OP3, we found that O_x was net produced during the day, lost at night, and that NO was in steady state throughout the entire diurnal cycle. Deposition was by far the largest loss term for ozone, a process that is limited in its representation with a global model at low resolution. Thus the overestimation of ozone by the global model could either be caused by a too-low deposition flux, or by too-high isoprene emissions, which would increase the flux through the NO+ISO2 reac-



Fig. 5. Time series of production and loss of O_x (left) and NO (right) throughout the day. For both, production is shown in blue, loss is shown in red, and net production is shown in black, and fluxes which make large contributions to the total budget are shown in dashed lines, each of which is indicated in the legend.

tion.

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