Chapter 3

Diurnal ozone cycle in the tropical and subtropical marine boundary layer

Abstract

A conceptual analysis of diurnal ozone (O₃) changes in the marine boundary layer (MBL) is presented. Such changes are most pronounced downwind of O₃ sources in tropical and subtropical latitudes, and during summer at higher latitudes. Previously, it has been assumed that daytime photochemical O₃ loss, and nighttime replenishment through entrainment from the relatively O₃-rich free troposphere, explains the diurnal O₃ cycle. We show, however, that in a net O₃-destruction environment (low NOₓ) this diurnal cycle can be explained by photochemistry and advection, which establish a horizontal O₃ gradient that is typical for the MBL. We support this hypothesis firstly by calculations with a conceptual 1-D advection-diffusion model, and secondly by simulations with an interactive 3-D chemistry-transport model. The results are in good agreement with observations, for example, in the Indian Ocean Experiment (INDOEX).

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3.1 Introduction

Since the recognition of ozone as an important chemical species in the troposphere it has been extensively measured and monitored during campaigns and from ground stations. Some of these campaigns have been performed over the remote oceans, and a number of surface stations are situated in remote areas as well. These campaigns and surface stations were established to improve the knowledge about the “background” troposphere, i.e. the chemistry of unpolluted air. From these campaigns and stations it was discovered that the remote marine troposphere, especially in the tropics, is a significant sink region for many chemical species, including O\textsubscript{3} [e.g. Kley et al., 1996].

It has long been recognized that, depending on the NO\textsubscript{x} concentrations, two distinct O\textsubscript{3} regimes exist (NO\textsubscript{x} = NO + NO\textsubscript{2}). In areas with relatively high NO\textsubscript{x} concentrations (NO\textsubscript{x} exceeding roughly 50-100 pptv) O\textsubscript{3} production dominates destruction during daytime, while in low-NO\textsubscript{x} environments (NO\textsubscript{x} less than roughly 50-100 pptv) net O\textsubscript{3} destruction prevails [Crutzen, 1974]. The chemical lifetime of NO\textsubscript{x} is only a few days, and both O\textsubscript{3} and NO\textsubscript{x} have no oceanic source, so that most of the marine lower troposphere is a net O\textsubscript{3} destruction area. Indications of whether an area is a net O\textsubscript{3} source or a sink can be derived from the diurnal O\textsubscript{3} cycle, because photochemical production and destruction are restricted to daytime. A summary of such effects is given in Table 2. The table also shows the observed amplitude of the diurnal O\textsubscript{3} cycle, whether the amplitude is calculated from the daytime O\textsubscript{3} depletion rate or averaged over a longer period and the maximum observed O\textsubscript{3} concentration.

The amplitudes of the observed diurnal O\textsubscript{3} cycles have values of the order of a few ppbv. All campaigns observed that the maximum in the O\textsubscript{3} concentration over the oceans occurs late at night (just before sunrise) and that the minimum concentrations occur during the late afternoon (just before sunset). The depletion of O\textsubscript{3} under low-NO\textsubscript{x} conditions, mostly due to the photolysis of O\textsubscript{3} and the subsequent reaction of O(1\textsuperscript{D}) with H\textsubscript{2}O, causes the daytime O\textsubscript{3} decrease. After sunset O\textsubscript{3} starts increasing until sunrise. The increase in O\textsubscript{3} has been attributed to entrainment of relatively O\textsubscript{3}-rich air from the free troposphere into the marine boundary layer (MBL). This has been confirmed by photochemical box models, budget studies and 1-D models in which this exchange was included (Table 1).

<table>
<thead>
<tr>
<th>Reference</th>
<th>Model type</th>
<th>Entrainment rate (mm s\textsuperscript{-1})</th>
<th>Amplitude of diurnal O\textsubscript{3} cycle (ppbv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thompson and Lenschow (1984)</td>
<td>1-D</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Paluch et al. (1995)</td>
<td>Box</td>
<td>0.75-2.25</td>
<td></td>
</tr>
<tr>
<td>Noone et al. (1996)</td>
<td>Budget</td>
<td>7</td>
<td>1</td>
</tr>
<tr>
<td>Heikes et al. (1996)</td>
<td>Budget</td>
<td>7</td>
<td>1</td>
</tr>
<tr>
<td>Ayers et al. (1997)</td>
<td>Box</td>
<td>3 (day)</td>
<td>0.5</td>
</tr>
<tr>
<td>Bremaud et al. (1998)</td>
<td>Box</td>
<td>1 (day)</td>
<td>&lt; 0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14 (night)</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 1. Diurnal O\textsubscript{3} cycle computations from several studies and inferred entrainment rates
One problem with these models, however, is that the entrainment is parameterized because the models cannot resolve the entrainment process explicitly. A usual procedure is to use a constant entrainment flux, which is either calculated from flux measurements, or from the entrainment velocity and an $O_3$ concentration increment across the top of the boundary layer:

$$\text{Entrainment flux} = w_e \Delta O_3$$  \hspace{1cm} (3.1) \hspace{1cm}

in which $w_e$ is the entrainment velocity and $\Delta O_3$ is the $O_3$ increment [Lenschow et al., 1982; Thompson and Lenschow, 1984]. In this approach the models are allowed to reach an equilibrium in which the daytime removal equals the nighttime recovery. These two processes then establish the diurnal $O_3$ cycle.

A more extensive expression for the entrainment of $O_3$ into the boundary layer, derived from thermodynamic equations, is given by Bremaud et al. [1997]:

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Table 2: Measurements of the diurnal $O_3$ cycle in marine locations.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Type of measurement</th>
<th>Location</th>
<th>Amplitude of diurnal $O_3$ cycle (ppbv)</th>
<th>Maximum $O_3$ concentration measured (ppbv)</th>
<th>Type of measurement dataa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oltmans (1981)</td>
<td>Surface Stations</td>
<td>Mauna Loa, Samoa</td>
<td>2</td>
<td>25</td>
<td>T</td>
</tr>
<tr>
<td>Liu et al. (1983)</td>
<td>Ship</td>
<td>Eq. Pacific Ocean</td>
<td>1</td>
<td>20</td>
<td>D</td>
</tr>
<tr>
<td>Piotrowicz et al. (1989)</td>
<td>Ship</td>
<td>Eq. Atlantic Ocean</td>
<td>1.5</td>
<td>50</td>
<td>T</td>
</tr>
<tr>
<td>Johnson et al. (1990)</td>
<td>Ship</td>
<td>Eq. Indian Ocean</td>
<td>1</td>
<td>30</td>
<td>T</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Eq. Pacific Ocean</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thompson et al. (1993)</td>
<td>Ship</td>
<td>Eq. Pacific Ocean</td>
<td>0-1.15</td>
<td>22</td>
<td>T</td>
</tr>
<tr>
<td>Anderson et al. (1993)</td>
<td>Aircraft</td>
<td>Eq. Atlantic Ocean</td>
<td>4</td>
<td>50</td>
<td>D</td>
</tr>
<tr>
<td>Oltmans and Levy II (1994)</td>
<td>Surface stations</td>
<td>Bermuda, Barbados</td>
<td>1</td>
<td></td>
<td>T</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Paluch et al. (1994)</td>
<td>Aircraft</td>
<td>Eq. Pacific Ocean</td>
<td>1.5-4</td>
<td>40</td>
<td>D</td>
</tr>
<tr>
<td>Paluch et al. (1995)</td>
<td>Aircraft</td>
<td>Eq. Atlantic Ocean</td>
<td>2.75</td>
<td>20</td>
<td>D</td>
</tr>
<tr>
<td>Ayers et al. (1996),</td>
<td>Surface station</td>
<td>Cape Grim (summer)</td>
<td>1.4</td>
<td>35</td>
<td>T</td>
</tr>
<tr>
<td>Ayers et al. (1992),</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ayers et al. (1997),</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monks et al. (1998)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bremaud et al. (1998)</td>
<td>Surface station</td>
<td>Reunion</td>
<td>2</td>
<td>30</td>
<td>T</td>
</tr>
<tr>
<td>Lal et al. (1998)</td>
<td>Ship</td>
<td>Eq. Indian Ocean</td>
<td>1.5</td>
<td>30b</td>
<td>T</td>
</tr>
<tr>
<td>This study</td>
<td>Surface station</td>
<td>Eq. Indian Ocean</td>
<td>1.5</td>
<td>40</td>
<td>T</td>
</tr>
</tbody>
</table>

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a D is the daytime $O_3$ depletion rate, and T is the average total over a longer period

b Value valid for the oceanic regions. In coastal regions concentrations increased to 70 ppbv
\[ \delta O_3 = \alpha \frac{H_0 - \Delta O_3}{\rho C_p Z_i \Delta \theta} \]

in which \( \delta O_3 \) is the enhancement of \( O_3 \) throughout the entire boundary layer, \( \Delta O_3 \) is the \( O_3 \) increment at the top of the boundary layer, \( \rho \) is the air density, \( C_p \) is the heat capacity of air, \( H_0 \) is the surface sensible heat flux, \( \Delta \theta \) is the strength of the temperature inversion and \( \alpha \) is a constant which expresses the ratio between the entrainment sensible heat flux and the surface sensible heat flux. The term \( \delta O_3 \) can be interpreted as the amount of \( O_3 \) transported into the boundary layer and distributed throughout the column per unit of time. In Table 3 some typical values for the above mentioned variables are summarized.

| \( \Delta O_3 \) | -30 to 40 ppbv |
| \( H_0 \) | 10-100 Wm\(^{-2}\) |
| \( Z_i \) | 500-1500 m |
| \( \Delta \theta \) | 0.5-3 K |

**Table 3.** Typical ranges of values used in equation (3.2). \( \Delta O_3 \) is the \( O_3 \) increment at the top of the boundary layer, \( H_0 \) is the surface sensible heat flux, \( Z_i \) is the boundary layer height and \( \Delta \theta \) is the strength of the temperature inversion.

With \( \rho C_p = 1.3 \times 10^3 \text{ Jm}^{-3}\text{K}^{-1} \) and \( \alpha = 0.2 \), the value of \( \delta O_3 \) can range between \(-6.6\) and \(8.8\) ppbv hour\(^{-1}\) throughout the boundary layer, assuming \( \Delta O_3 \) ranges between \(-30\) to \(40\) ppbv [Kawa and Person, 1989; Paluch et al., 1995; Noone et al., 1996]. The boundary layer air can be replenished by free tropospheric air within a few hours according to this calculation, and \( O_3 \) concentration changes can be either positive or negative. The entrainment flux (\( \delta O_3 \)) determines to a large extent the amplitude of the diurnal \( O_3 \) cycle.

The enhancement fluxes derived from equation (2) are almost two orders of magnitude larger than what can be derived from Table 2. However, the values given in Table 2 are averages over longer periods of time, and the amplitude of the diurnal cycle on a given day can be 3 or 4 times larger than the average amplitude (see for example figures 3a and 3b). A rather high amplitude of 10 ppbv day\(^{-1}\) requires an enhancement flux of about 0.8 ppbv hour\(^{-1}\), which is still an order of magnitude smaller than the values derived above, and an amplitude of 10 ppbv day\(^{-1}\) in the diurnal \( O_3 \) cycle in the MBL has rarely been observed. It can also be seen from equation (2) that the entrainment rate is strongly dependent on the strength of the inversion and the concentration increment over the inversion. It is therefore not very likely that the entrainment flux is constant, especially since numerous campaigns have shown that a wide range of \( \Delta O_3 \) values can occur, sometimes even in the same area [Kawa and Person, 1989; Paluch et al., 1995; Noone et al., 1996]. The uncertainties involved in these calculations show that the “entrainment” approach, as an explanation for the diurnal \( O_3 \) cycle in the MBL, can be questioned.

The “entrainment” approach also provides a conceptual problem. Observations (Table 2) and models (Table 1) show that the daytime net photochemical destruction is counterbalanced by a nighttime increase. In the “entrainment” approach the \( O_3 \)
concentration increase is caused by transport of O$_3$ rich air from the free troposphere. Both observations and model results in Tables 1 and 2 refer to a fixed “Eulerian” frame. If, however, such an airmass were advected horizontally, and no net O$_3$ depletion would occur because of the balance between daytime net photochemical destruction and nighttime replenishment, downwind reduction of O$_3$ concentrations and horizontal O$_3$ gradients could not occur. This disagrees with numerous observations, which clearly indicate that horizontal O$_3$ gradients do exist in the MBL and that very low O$_3$ values occur regularly. The entrainment flux as an explanation of the observed diurnal O$_3$ cycle is therefore questionable.

In this study an alternative explanation for the diurnal O$_3$ cycle under low NO$_x$ conditions will be presented. This approach can explain why O$_3$ gradients and low O$_3$ concentrations exist in some parts of the MBL. In section 2 the model will be described, and in section 3 model results will be compared with observations from an island site in the Indian Ocean. A conceptual model to explain the diurnal O$_3$ cycle will be presented in section 4. The results from a case study are presented in section 5, after which a discussion follows in section 6.

### 3.2 The ECHAM model

The General Circulation Model (GCM) used in this study is the 19 layer European Center Hamburg Model, version 4 (ECHAM4). In this study the T30 version of the model, with a horizontal resolution of about 3.75° x 3.75° and a time resolution of 1800 seconds, is used. The model uses a hybrid _-p coordinate system from the surface to 10 hPa. Average pressure levels relevant for the troposphere and lower stratosphere are 990, 970, 950, 900, 840, 760, 670, 580, 490, 400, 320, 250, 190, 140, 100 and 75 hPa, referring to approximate mid-layer altitudes of 0.03, 0.14, 0.38, 0.78, 1.4, 2.1, 3.1, 4.2, 5.6, 7.0, 8.6, 10.2, 11.9, 13.8, 15.9 and 18.0 km above the surface. Tracer transport is calculated using a semi-Lagrangian advection scheme [Rasch and Williamson, 1990]. Vertical transports are included through parameterizations of vertical diffusion and convection [Roeckner et al., 1996; Tiedtke, 1989]. An elaborate description of ECHAM4 and the simulated climate can be found in Roeckner et al. [1995], Chen and Roeckner [1996], and Haskins et al. [1995]. In this study, ECHAM4 is coupled to a tropospheric chemistry model that considers background CH$_4$-CO-NO$_x$-HO$_x$ chemistry, emissions of NO and CO, dry deposition of O$_3$, NO$_2$, HNO$_3$ and H$_2$O$_2$, and wet deposition of HNO$_3$ and H$_2$O$_2$. Concentration changes due to chemical reactions are calculated explicitly for all species by means of an Eulerian Backward Iterative (EBI) scheme. A detailed description and analysis of the coupled chemistry GCM is given in Roelofs and Lelieveld [1995, 1997].

The model considers a biomass-burning source for NO of 6 Tg N yr$^{-1}$, and for CO of 700 Tg CO yr$^{-1}$, distributed according to Hao and Liu [1994]. NO emissions from soils and from lightning play an important role in the tropical tropospheric O$_3$ budget. These sources in the model are 5.5 Tg N yr$^{-1}$, distributed according to Yienger and Levy [1995], and 5 Tg N yr$^{-1}$ parameterized according to Price and Rind [1992], respectively. Further, the model considers global NO emissions from fossil fuel burning (21 Tg N yr$^{-1}$; Benkovitz et al. [1996]), and CO emissions from fossil fuel burning (450 Tg CO yr$^{-1}$).
vegetation (100 Tg CO yr\(^{-1}\)), formation from natural (280 Tg CO yr\(^{-1}\)) and antropogenic (300 Tg CO yr\(^{-1}\)) higher hydrocarbons, oceans (40 Tg CO yr\(^{-1}\)) and wildfires (30 Tg CO yr\(^{-1}\)). CO emissions are distributed according to Lelieveld and Van Dorland [1995]. The total NO and CO emissions considered in the model are 37.5 Tg NO yr\(^{-1}\) and 1900 Tg CO yr\(^{-1}\), consistent with IPCC [1994]. In view of the relatively long lifetime of CH\(_4\), the CH\(_4\) surface concentrations are prescribed.

The parameterization for dry deposition of O\(_3\), NO\(_x\), and HNO\(_3\) is described in Ganzeveld and Lelieveld [1995, 1998]. It derives aerodynamic and stomatal resistances directly from parameters calculated by ECHAM4. The wet scavenging of HNO\(_3\) and H\(_2\)O\(_2\) is calculated using the large scale and convective cloud and precipitation properties calculated on-line by the climate model as described in Roelofs and Lelieveld [1995, 1997]. Stratospheric O\(_3\) concentrations are prescribed between 1 to 2 model layers above the tropopause up to 10 hPa, the top level of the GCM. Transports of O\(_3\) across the tropopause depend directly on the air motions simulated by the GCM. The simulated tropopause is marked by a potential vorticity of 3.5·10\(^{-6}\) K m\(^2\) kg\(^{-1}\) s\(^{-1}\) poleward of 20\(^\circ\) latitude [Hoerling et al., 1993], and by a -2 K km\(^{-1}\) temperature lapse rate equatorward of 20\(^\circ\) latitude.

The model realistically represents the seasonal variability of the O\(_3\) photochemical production and of O\(_3\) transport from the stratosphere [Roelofs and Lelieveld, 1995, 1997]. Surface O\(_3\) concentrations as measured in remote and relatively clean conditions are also reproduced, but the model appears to underestimate O\(_3\) concentrations in some polluted regions due to the neglect of higher hydrocarbon chemistry [Roelofs et al., 1997].

In this study the ECHAM4 model was relaxed towards ECMWF analysis (nudged) for two periods: 16 March 1995 - 31 April 1995 and 1 February 1998 - 1 April 1998, applying the method described by Jeuken et al. [1996] and De Laat et al. [1999]. For the period 16 March –31 March 1995 output was available every hour (every second model time step).

### Measurements

As part of the Indian Ocean Experiment (INDOEX), an observatory was established at the island of Kaashidhoo on the Maldives. This site is situated at 4.965\(^\circ\)N and 73.466\(^\circ\)E, and continuous measurements of several chemical species (e.g. O\(_3\) and CO), aerosols and radiation are performed since 1998. In this study we will take a closer look at the surface O\(_3\) measurements performed during February-March 1998 when the First Field Phase (FFP) of the INDOEX campaign took place. Figure 1 shows the observed surface O\(_3\) concentrations at Kaashidhoo and O\(_3\) concentrations from the nudged ECHAM model at that site. The observations show that the O\(_3\) concentrations range between roughly 15 and 30 ppbv with a superimposed diurnal cycle. The ECHAM model shows higher O\(_3\) concentrations than observed, with an average difference of about 10 ppbv. De Laat et al. [1999] have discussed a similar offset over the Indian Ocean, based on shipborne O\(_3\) measurements. The discrepancy is likely explained by (1) overestimation of O\(_3\) formation by “artificial” NO\(_x\) transport by instantaneous mixing of emissions in the coarse (3.75\(^\circ\)) grid cells of the model, and (2) underestimation of O\(_3\) destruction through heterogeneous activation of reactive halogens from sea salt in the MBL [Vogt et al., 1996]
Figure 1: Observed and modeled \(\text{O}_3\) concentrations during February and March 1998 at the Kaashidhoo surface observatory (4.965°N and 73.466°E) on the Maldives; \(\text{O}_3\) concentrations in ppbv, time as Julian Days (JD 44.5 = February 13, 12:00 UTC).

Figure 2: As Figure 1 but for the surface wind velocity.
The model reproduces the general tendencies, e.g. maxima in $O_3$ concentration around JD 53, between JD 58 and 70 and around JD 78 and minima around JD 48, 53 and 72. This is not surprising considering the fact that the modeled and observed surface-wind speeds (Figure 2) and wind directions (not shown) agree very well. The discrepancy between the observed temporal $O_3$ change and the modeled $O_3$ one between JD 80 and 88 are likely associated with differences between the observed and modeled wind speed and direction. In the model the winter monsoonal winds consistently originate from the northeast so that the airmasses travel over the southern tip of India and Sri Lanka towards Kaashidhoo. These areas are sources of $O_3$ precursors, thus counteracting the $O_3$ loss in the MBL. Therefore, the $O_3$ concentrations remain more or less constant. The observations, however, show west-northwesterly winds over this period, indicating a different origin of the airmass and thus a different chemical composition.

The diurnal $O_3$ cycles from both the observations and the model are shown in Figures 3a and 3b, where a running mean is calculated for both observations and model. Figures 3a and 3b show that the model produces a very similar diurnal $O_3$ cycle as seen in the observations, in spite of the ~ 10 ppbv offset in $O_3$ levels: a maximum concentration at the end of the night and a minimum concentration in the late afternoon. The model somewhat underestimates the amplitude of the diurnal cycle, although it should be considered that the model output was only available at 0, 6, 12, and 18 UTC, so that it is possible that not all the modeled peaks in $O_3$ are captured. The agreement between model and observations can be seen even better in Figure 4, which shows the daily averaged diurnal cycle from the running mean for both observations and model.

![Figure 4](image_url)

**Figure 4**: The averaged diurnal $O_3$ cycle for the period of 13 February to 1 April 1998, from the observations at the Kaashidhoo observatory and from the ECHAM model. Hours in UTC, local noon is at 07:00 UTC.
Figure 3a: Diurnal $O_3$ cycle as observed at Kaashidhoo and from the ECHAM model for the period 13 February to 7 March (JD 44 - 66) 1998. The figure shows the difference between the actual concentrations and a 24-hour running mean. Concentrations in ppbv.

Figure 3b: As Figure 3a but for 7 March – 1 April (JD 66 - 89) 1998.
Considering that the ECHAM model has a vertical resolution of 19 layers, and the MBL is resolved by only 4 (5) layers (~ 30, 140, 380 and 780 (1480) meter altitude), the model is obviously not capable of resolving a small scale process like the entrainment of free tropospheric air into the MBL. The possibility of the vertical diffusion parameterization being responsible for entraining free tropospheric air, and thus the diurnal cycle of O₃ in the model, can be ruled out. Figure 5 shows the O₃ concentrations at the five lowest ECHAM model levels for the period 17-23 March 1995 at 5.559°N, 61.875°E. This grid point is situated at the central Arabian Sea, and the temporal O₃ changes are typical for the modeled tropical MBL. The O₃ concentrations in the three lowest layers (up to 380 m) are the same and show a very distinct diurnal cycle (local time of sunrise is approximately 03:00 UTC). These 3 layers represent the MBL in the model. If vertical diffusion would be responsible for the downward transport of O₃, it can be expected that during JD 76-78.5 a gradual decrease in O₃ would take place. Vertical mixing would bring air with lower O₃ concentrations into the boundary layer and O₃ would be photodissociated during daytime as well. Since such a gradual decrease is not discernable, the vertical diffusion can be assumed to be small. In fact, a small exchange between the MBL and the free troposphere is quite realistic. Due to the nearly constant surface temperatures over the ocean, the dynamics of the MBL are much the same during night and day (contrary to the continental boundary layer, which shows a distinct diurnal cycle). The height of the MBL changes only very slowly in time, it shows no diurnal cycle and has a well-defined inversion [Garratt, 1992]. If vertical transport can be ruled out as an explanation for the diurnal O₃ cycle in the model, the question remains what is responsible. Below we will show that this is solely caused by horizontal transport.

![Figure 5](image_url)

**Figure 5**: The modeled O₃ concentration for the grid point at 5.559°N, 61.875°E for the period of 17 – 23 March 1995 (JD 76 – 82) at the 5 lowest model levels. Hours in UTC, local noon is at 08:00 UTC.
3.4 1-Dimensional advection-diffusion equation

Consider an airmass being transported over sea in an NO$_x$-poor environment (lagrangian view). In the absence of vertical mixing, O$_3$ would remain constant during the night. During daytime O$_3$ would be depleted due to net photochemical destruction. Such a sequence will show up as step-wise changes in time: an O$_3$ decrease during the day and no change in O$_3$ concentration during the night [e.g. Sander and Crutzen, 1996]. Turbulence in the boundary layer will moderate the step-wise O$_3$ decrease to a more gradual profile. This has been observed regularly in the MBL [Johnson et al., 1990; Lal et al., 1998], and a typical meridional O$_3$ gradient over the Indian Ocean is 1.5 ppbv deg$^{-1}$ [Lal et al., 1998]. Suppose that the airmass is transported with an average wind speed of 4 ms$^{-1}$ (Figure 2). The airmass will travel 170-175 km ($\approx$ 1.5 deg) in 12 hours. With an O$_3$ gradient of 1.5 ppbv deg$^{-1}$ the O$_3$ level must be replenished by 2.25 ppbv during the 12 nighttime hours. Net photochemical destruction during daytime will then again lead to the depletion of O$_3$ so that the amplitude of the diurnal cycle is 1.125 ppbv for this example. According to Table 2, the observed amplitudes of the diurnal O$_3$ cycle agree well with this calculation. For an observer at a fixed point the O$_3$ changes would thus appear as a nighttime increase (transport) and daytime decrease (net photochemical loss).

The gradient causing the nighttime increase is directly related to the daytime depletion in O$_3$. A stronger decrease during the day would also lead to a larger horizontal O$_3$ gradient, and thus a sharper increase during the night. In this approach the daytime decrease will always be counteracted by the same nighttime increase. This hypothesis can be tested numerically by solving the 1-dimensional advection-diffusion equation:

$$\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} - D \frac{\partial^2 c}{\partial x^2} = 0$$                    (3)

In which $c$ is a tracer concentration, $u$ is the average horizontal velocity and $D$ is the diffusion coefficient. This equation describes the horizontal transport of a substance by the wind in the presence of horizontal diffusion. This is a good analogy for the horizontal transport of O$_3$, in which case diffusion is equivalent to boundary layer turbulence. The equation is solved with a Crank-Nicholson numerical scheme [Vreugdenhil, 1992]. The daytime depletion rate (amount of tracer depleted per second) is calculated as a $\cos^2$ function of time, and in such a manner that the total daytime depletion is roughly 3 concentration units. At night no depletion is assumed. The model was run with a time step of 600 seconds and during 2000 time steps. The horizontal grid distance was 2500 m and the number of grid points was 1000. The average horizontal velocity was chosen at 4 ms$^{-1}$ and the tracer concentration at the boundary ($x=0$) was chosen at 20. It appears that the model reaches equilibrium within two days. Figure 6 shows the concentration as a function of the distance for two different values of the diffusion coefficient after equilibrium is reached. For a relatively low diffusion coefficient the profile shows the step-wise changes, while for a higher value of the diffusion coefficient the profile shows a constant gradient. Observations show that O$_3$ gradients are quite smooth [Johnson et al., 1993; Lal et al., 1998], so that a small diffusion coefficient is probably not realistic.
Figure 6: Tracer concentration calculated from the 1-dimensional advection-diffusion equation for two different values of the diffusion parameter.

Figure 7: Concentration (arbitrary units) as a function of time for the solution of the 1-dimensional advection-diffusion equation with \( D = 40,000 \text{ m}^2\text{s}^{-1} \). From top to bottom the concentrations are plotted (solid lines) at distances of 500, 1000 and 1500 km respectively, and the dotted line shows the depletion factor.
Figure 7 shows the temporal concentration changes for $D = 40,000 \text{ m}^2\text{s}^{-1}$ for different fixed points. The lowest concentrations appear during late afternoon after the maximum depletion rate, as expected. The concentration at every grid point shows the same temporal behavior and the amplitude of the diurnal cycle is the same, because, in this example, the depletion rate is only a function of time and not of the concentration of the tracer. Figure 7 thus shows a sharp daytime decrease and a gradual nighttime increase. This feature has often been observed [Oltmans, 1981; Ayers et al., 1997; Lal et al., 1998] and can also be seen in the ECHAM model results (Figure 5).

The amount of photochemically destroyed $O_3$ is, however, dependent on the $O_3$ concentration itself. Numerical experiments in which the depletion rate is assumed to be dependent on the concentration indeed show that the amplitude of the diurnal cycle decreases with decreasing concentration, but the gradual increase in concentration during the night and the rapid daytime decrease remain unchanged. These experiments also lead to the conclusion that in a lagrangian time frame, i.e. travelling with the airmass, the temporal $O_3$ profile shows step-wise decreasing values. This can be seen in Figure 8, which shows the tracer concentration when travelling with the airmass.

![Figure 8](image_url)

**Figure 8:** Concentration of a tracer calculated from the 1-dimensional advection-diffusion equation when travelling with the airmass (Lagrangian experiment).

### 3.5 Results from the ECHAM model

To compare the lagrangian conduct of $O_3$ in the ECHAM model with the 1-D advection-diffusion concept, a trajectory model was used to monitor the $O_3$ during transport. The trajectory model was applied to the 3-D ECHAM wind fields. The wind fields were updated every 6 hours. A fourth-order Runge-Kutta scheme was used to advect a set of points in 3-D space, and the wind velocities were linearly interpolated for the parcel in both space and time. The time step used for the trajectory calculations was
Figure 9a: Horizontal position of three 5-day back-trajectories calculated from the ECHAM model output. Trajectories were started on 25 March 1995 at 12:00 UTC (JD 84.5), at an altitude of 950 hPa, at 60°E, 5°N (trajectory A), 60°E, 10°N (trajectory B) and 50°E, 5°N (trajectory C).

Figure 9b: Vertical displacements of the back-trajectories shown in Figure 9a.
30 minutes. Time and location of the trajectories were subsequently used to retrieve 1-hourly fields along the trajectories. Figure 9a shows the position of three 5-day back-trajectories starting on 25 March 1995 at 12:00 UTC at an altitude of 950 hPa. The trajectories A and B clearly follow the northeasterly flow over the Arabian Sea. Figure 9b shows the vertical displacements. The trajectories A and C remain in the lowest levels of the MBL most of the time, while trajectory C originates from a higher altitude, although still close to the top of the MBL.

Figure 9c: O₃ concentrations and the precipitation rates along back-trajectory A, as calculated with the ECHAM model.

Figure 9c shows O₃ and the precipitation rate along trajectory A. The O₃ concentration shows the step-wise changes as predicted. Calculated NOₓ concentrations varied between 24 and 40 pptv, which is in the net O₃ destruction regime. The small increases in O₃ around JD 82 and JD 84 are related to convective precipitation in the model. The precipitating clouds in the model are associated with mixing of boundary layer air with air from aloft which, in this case, had a higher O₃ concentration. This step-wise O₃ decrease is typical for model output in areas remote from NOₓ sources, so that NOₓ concentrations are well below the net O₃ production limit and the airmasses are subject to net O₃ loss at least a few days. In such cases almost all the O₃ increases along the trajectories are related to convection in the model [Lelieveld and Crutzen, 1994].

Figure 9d shows the concentrations of O₃ and NOₓ along trajectory B. Again, the step-wise changes in O₃ are evident. As can be seen in Figure 9a, this trajectory starts close to the Indian subcontinent where pollutants are emitted. This explains the relatively high NOₓ concentrations at the start of the trajectory. The rates of O₃ changes in this case are different compared to trajectory A. Between JD 79.5 and 81.5 the net O₃ destruction is small. The concentrations of NOₓ are close to the net O₃ production limit so that relatively little O₃ is lost during daytime compared to the total O₃ concentrations.
Figure 9d: O₃ and NOₓ concentrations along back-trajectory B, as calculated with the ECHAM model.

Figure 9e: As Figure 9d but for back-trajectory C.

Between JD 81.5 and 83.5 the daytime O₃ loss increases as NOₓ is depleted to about 16-17 pptv. During this period the O₃ concentration also decreases during the night, caused by the reaction between O₃ and NO₂, heterogeneous removal of N₂O₅ and dry deposition of O₃ and HNO₃. An observer at a fixed point would see a relatively large amplitude in the diurnal O₃ cycle. Note that much of the variability in NOₓ removal and net O₃
destruction is associated with (broken) clouds fields that (enhance) reduce photodissociation frequencies.

Figure 9e shows the NO\textsubscript{x} concentrations along trajectory C. In this case the airmass moved from the Arabian Sea towards and along the African east coast. During the first three days the air is still moving away from the Indian O\textsubscript{3} source region. NO\textsubscript{x} concentrations are low throughout the first three days, and O\textsubscript{3} shows the typical step-wise decrease. After JD 82 the airmass approaches the African coast and mixes with more polluted air. NO\textsubscript{x} concentrations increase rapidly, and O\textsubscript{3} increases due to advection and local photochemical formation.

3.6 Summary and discussion

The model calculations show that the combination of horizontal advection, daytime net photochemical O\textsubscript{3} destruction and horizontal mixing cause a distinct diurnal O\textsubscript{3} cycle in the tropical MBL. The mechanisms can be summarized as follows:

1. If NO\textsubscript{x} concentrations exceed 50-100 pptv, net photochemical O\textsubscript{3} formation takes place, and the diurnal O\textsubscript{3} cycle shows a minimum at the end of the night and a maximum during late afternoon. This agrees, for example, with observations at Cape Grim (Tasmania) by Ayers \textit{et al.} (1997), whose measurements were partially performed in relatively polluted air that was transported towards Cape Grim from the Australian continent.

2. If O\textsubscript{3} and NO\textsubscript{x} concentrations are still relatively high, but NO\textsubscript{x} concentrations attain the net photochemical O\textsubscript{3} production regime, O\textsubscript{3} concentrations show a decrease during daytime, whereas during nighttime additional O\textsubscript{3} depletion can occur due heterogeneous removal of O\textsubscript{3} and NO\textsubscript{2} through N\textsubscript{2}O\textsubscript{5}. This also means that, due to the stronger horizontal O\textsubscript{3} gradient, the amplitude of the observed diurnal O\textsubscript{3} cycle is relatively large. This agrees with observations by Anderson \textit{et al.} [1993] close to the polluted Brazilian coast, who measured amplitudes in the diurnal cycle between 2.75 and 4 ppbv (associated with a net O\textsubscript{3} destruction rate of about 8 ppbv day\textsuperscript{-1}). The measurements were performed in air masses affected by biomass burning emissions of O\textsubscript{3} precursors (O\textsubscript{3} concentrations between 30 and 70 ppbv), thus showing large amplitudes in the diurnal O\textsubscript{3} cycle. The other campaigns listed in Table 2 indicate smaller diurnal O\textsubscript{3} cycles because the measurements were performed remote from pollution sources.

3. If both NO\textsubscript{x} and O\textsubscript{3} concentrations are relatively low, which is the case for much of the MBL, net photochemical O\textsubscript{3} destruction prevails during daytime. The diurnal O\textsubscript{3} cycle is also related to the intensity of sunlight. Oltmans [1981] showed that in Barrow, northern Canada (~ 70ºN), the diurnal O\textsubscript{3} cycle is much smaller than at Samoa (14ºS), associated with the much lower insolation at Barrow. Ayers \textit{et al.} [1997] showed that at Cape Grim (41ºS) the diurnal O\textsubscript{3} cycle in summer is much larger than in winter. Our hypothesis implicates that a possible difference between the summer and wintertime boundary layer entrainment flux of O\textsubscript{3}, as suggested by Ayers \textit{et al.} [1997], is not necessary to explain the observed diurnal O\textsubscript{3} cycles.

Anderson \textit{et al.} [1993] showed that, on average, the nighttime concentrations of O\textsubscript{3} in the boundary layer are higher than the daytime concentrations, and that the differences
are uniformly distributed over the entire boundary layer. This is an important observation because Vilà-Guerau de Arellano and Duynkerke [1999] demonstrated that, if chemical species are entrained from the free troposphere, the concentration differences in time should be higher close to the top of the boundary layer than close to the surface.

To further illustrate the different regimes, Figure 10 shows a global view of the diurnal O$_3$ cycle amplitude at the surface for the latter half of March, derived from the ECHAM model. The amplitude appears to be much larger and much more variable in the continental boundary layer (not shown) than in the MBL. This is related to the larger NO$_x$ concentrations over land, which causes net O$_3$ production during daytime. The amplitude of the diurnal O$_3$ cycle over the ocean does not show such high variability, in line with the findings from the different campaigns listed in Table 2. Furthermore, over the oceans as well as over land the maximum amplitudes occur in areas with the highest insolation. These “bands” stretch zonally between 20ºN and 20ºS. The maximum amplitudes of the diurnal O$_3$ cycle in the MBL appear in areas where the average wind direction is offshore, e.g. the Indian west-coast, the Australian and Indonesian west coasts, the African west-coast and the west-coasts of central and southern America. This is related to the relatively high O$_3$ concentrations in net O$_3$ destruction environments. Figure 11 shows that the largest gradients in O$_3$ concentration gradients are found in a longitudinal band between the Equator and 15ºN, which is also the area where the largest diurnal O$_3$ cycle amplitudes occur. In the ITCZ over the Indian and Pacific Oceans, where O$_3$ concentrations reach minimum values, the diurnal O$_3$ cycle shows the smallest amplitude. Over the tropical Atlantic Ocean the O$_3$ concentrations do not reach values as low as those over the Indian and Pacific Oceans. Figure 12 shows the local time of the maximum in the diurnal O$_3$ cycle for the same period, as simulated by the ECHAM model. The marine regions show a maximum around sunrise, typical for net O$_3$ destruction regimes, and the local time of the maximum is very uniformly distributed. Over landmasses the maximum occurs during the day and over a wider range of local times, although always during daytime, which is typical for net O$_3$ production regimes.

This conceptual mechanism has several other implications. It explains the diurnal cycle for species, which have a relatively long lifetime (more than a few days) and which do not have an oceanic source. However, it does not describe the diurnal cycle of species with an oceanic source and/or very short lifetimes. This mechanism also implies that the often observed very low O$_3$ concentrations (< 5 ppbv) over marine regions, especially over the Pacific Ocean [Routhier et al., 1980; Johnson et al., 1990; Thompson et al., 1993; Kley et al., 1996], can be the result of airmasses having traveled and aged without interaction with more polluted airmasses from either the continents or from the free troposphere.

Although we propose that the entrainment process is not the main mechanism responsible for the observed diurnal cycle in O$_3$, entrainment of free tropospheric air into the boundary layer will have additional effects. The exact contribution of entrainment is, however, strongly dependent on the local conditions, for example the strength of the inversion and the O$_3$ concentrations in the free troposphere. Some observations of entrainment velocities in stratocumulus show an increase [de Roode and Duynkerke, 1997]. Other observations, however, do not show such an increase at all [Kawa and Pearson, 1989]. In general, the range of observed entrainment velocities is large and the methodologies used are associated with uncertainties. It also needs to be mentioned that
**Figure 10:** The average amplitude of the diurnal O$_3$ cycle at the surface over the globe, calculated by the ECHAM model for the period of 17–31 March 1995.

**Figure 11:** The average O$_3$ concentration at the surface over the globe from the ECHAM model, averaged for the period of 17-31 March 1995. For convenience the O$_3$ concentrations over landmasses have not been included.

**Figure 12:** The local time at which the maximum amplitude in the diurnal cycle in O$_3$ appeared in the ECHAM model between 45ºN and 45ºS, averaged for the period of 17-31 March 1995.
entrainment in stratocumulus can lead to the breakup of the cloud layer [Duynkerke, 1993], after which entrainment velocities decrease.

3.7 Conclusions

It is shown that horizontal transport and photochemical processes explain the typical diurnal O\textsubscript{3} cycle in the MBL (nighttime maximum and daytime minimum). In this mechanism the daytime decrease and nighttime increase are closely related. Daytime net photochemical O\textsubscript{3} destruction in combination with horizontal advection and diffusion (due to turbulence) creates a gradual decrease (gradient) in O\textsubscript{3} from the source regions. Such a gradual decrease has been observed regularly, for example, over the Pacific and Indian Oceans [Johnson et al., 1993; Lal et al., 1998]. This gradient causes the nighttime increase because air with higher O\textsubscript{3} concentrations is advected to regions with lower O\textsubscript{3} concentrations. In this approach the daytime decrease will always be counteracted by the nighttime increase. The daytime depletion rate is thus a measure for the amplitude of the diurnal O\textsubscript{3} cycle. Although the horizontal advection of airmasses with higher O\textsubscript{3} concentrations continues during daytime, net photochemical O\textsubscript{3} destruction dominates the daytime O\textsubscript{3} tendency. As the daytime depletion is controlled by insolation, the amplitude of the diurnal O\textsubscript{3} cycle is very similar in most tropical marine regions. This is confirmed by the available observations (Table 2). This mechanism also implies that the amplitude of the diurnal O\textsubscript{3} cycle is larger close to NO\textsubscript{x} emission regions because the O\textsubscript{3} concentrations are higher and net photochemical loss takes place at a higher rate, which is also in agreement with observations [Anderson et al., 1993].

Finally we note that for MBL simulations of O\textsubscript{3} with a box model it is not relevant whether the mechanism that causes the diurnal O\textsubscript{3} cycle is entrainment of free tropospheric air (often assumed previously) or horizontal advection in conditions with photochemical O\textsubscript{3} loss (posed here). Both approaches have the same result: O\textsubscript{3} is transported from an area with higher O\textsubscript{3} concentrations Conclusion from studies in which box models have been used to explain the chemistry in the MBL are therefore not less valid, however, the physical mechanism behind the O\textsubscript{3} influx is different.

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