Analysis of the CEPEX ozone data using a 3D chemistry–meteorology model

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SUMMARY

The ozone (O$_3$) data collected during the Central Equatorial Pacific Experiment (CEPEX) are analysed with the aid of the 3D global photochemistry model MATCH-MPIC (Model of Atmospheric Transport and Chemistry—Max-Planck-Institute for Chemistry version). This study focuses on using MATCH-MPIC to address three specific questions: (1) are the individual CEPEX O$_3$ soundings, in particular the extremely low O$_3$ levels occasionally observed in the upper troposphere (UT), reproducible by a state-of-the-art global photochemical model driven with analysed meteorological data from the same time period as the measurements (March 1993); (2) are the CEPEX O$_3$ data likely to be representative of the mean state of the regional atmosphere, or do they instead indicate the degree of variability in this region of the atmosphere; and (3) what causes the UT O$_3$ minima? It is found that MATCH-MPIC is not able to reproduce the soundings obtained during CEPEX on an individual basis; however, the model does reproduce some of the key features present in the observations, such as UT minima and mid-tropospheric maxima similar to those observed during CEPEX. The UT O$_3$ minima computed by the model are mainly due to convective pumping of low-O$_3$ marine boundary-layer air, as is demonstrated by comparison with the results of a run in which convective transport of O$_3$ is suppressed. The UT O$_3$ minima simulated by MATCH-MPIC (with O$_3$ between 5 and 10 nmol mol$^{-1}$) are less intense than those observed (with O$_3 < 5$ nmol mol$^{-1}$), even at relatively high model spatial and temporal resolution, and with a convection scheme that would be expected to readily produce UT O$_3$ minima via intense pumping of low-O$_3$ marine boundary-layer air directly into the UT convective outflow regions. This may indicate that additional photochemical loss processes are involved, either in situ in the UT or, in particular, near the surface in the convective inflow regions, where the model tends to overestimate the observed O$_3$ levels. In addition, although a significant temporal variability for O$_3$ in this region is computed, it is still less than indicated by the observations in the UT. This high degree of variability implies that individual O$_3$ soundings will often differ considerably from the mean over a longer period. For instance, 20–50% less O$_3$ in the UT during the CEPEX period is computed with MATCH-MPIC than the average for March. Thus, the CEPEX expedition was perhaps fortunate in encountering extreme conditions which produced extensive UT O$_3$ minima, which have helped to demonstrate one end of the large degree of variability of O$_3$ in the tropical troposphere.

KEYWORDS: Convection Equatorial Pacific Global modelling Ozone Tropics

1. INTRODUCTION

Ozone (O$_3$) in the tropical upper troposphere (UT) has a tremendous degree of variability (Crutzen and Lawrence 1997), ranging from near-zero levels (Kley et al. 1996, 1997) to several hundred nmol mol$^{-1}$ (Suhre et al. 1997). Because O$_3$ is an absorber of both solar and infrared radiation, this variability could have significant implications for radiative transfer in the tropics. This paper focuses on using a three-dimensional (3D) global tropospheric photochemistry model MATCH-MPIC (Model of Atmospheric Transport and Chemistry—Max-Planck-Institute for Chemistry version) to analyse data which represent one of these extremes, collected during the Central Equatorial Pacific Experiment (CEPEX).

CEPEX (Ramanathan et al. 1993) was conducted in March–April 1993; it was primarily focused on understanding the role of deep convection in regulating sea surface temperatures in the warm-pool region of the Pacific Ocean. The intense and frequent deep convection which is prevalent in this region could be expected to affect trace-gas distributions, for instance resulting in low ozone mixing ratios in the UT via rapid vertical transport of low-ozone air from the marine boundary layer (MBL). Within CEPEX,
O₃ measurements were made via balloon sondes launched during a cruise of the RV *Vickers* from Honiara (Solomon Islands) to Christmas Island (Fig. 1); in addition, several sondes were launched over a six-day period from Christmas Island. A listing of the CEPEX O₃ sonde launch points and times is given in Table 1. These measurements are reported in detail by Kley *et al.* (1996, 1997). The O₃ sonde measurements were made using electrochemical concentration cell detectors, with an instrumental uncertainty of about 0.1 mPa O₃ (Smit *et al.* 1994), which converts to about 1–2 nmol mol⁻¹ near the surface, and about 5 nmol mol⁻¹ in the UT. Kley *et al.* (1997) make use of these measurements, along with water vapour measurements also made via the balloon sondes, to conclude that: (a) active convection resulted in a moistened troposphere, with relative humidities (RHs) greater than 75% for most of the column between the surface and 14 km; (b) O₃ maxima and RH minima at about 700 hPa indicate significant transport of subtropical air into the tropics; and (c) low O₃ values in the UT can be used as a tracer of recent convective activity.

One of the most interesting results from the CEPEX observations was a phenomenon which has only rarely been witnessed: the minimum ozone mixing ratios in the UT were often startlingly low—in many instances well below 5 nmol mol⁻¹ (the instrumental uncertainty). Although previous observations had indicated generally low ozone in this region, and even instances of sharply reduced ozone had been observed (Chameides *et al.* 1987) documented one event of 8 nmol mol⁻¹ O₃ in the UT during CITE (Chemical Instrumentation Test and Evaluation) 1), to the extent of our knowledge no other observations of such extremely low ozone mixing ratios in the tropical UT existed before CEPEX. Since that time a few instances of near-zero O₃ in the UT over Europe have been reported by Reichardt *et al.* (1996) and Davies *et al.* (1998). The latter of those two studies used back trajectories to trace the origin of the low-ozone air parcel back to the equatorial Pacific some ten days earlier, indicating that the formation of low-O₃ air masses over the Pacific may have an influence on well-removed regions. Previous analyses of the CEPEX data (Kley *et al.* 1996, 1997; Lawrence 1996) concluded that these minima are caused mainly by convective transport of low-O₃ boundary-layer air directly to the UT, though this in itself may not have been sufficient, and additional loss processes may have contributed to the extreme nature of the observed minima.
TABLE 1. LISTING OF CEPEX O$_3$ SONDE LAUNCH DATES DURING MARCH 1993 AND LOCATIONS

<table>
<thead>
<tr>
<th>Sonde number</th>
<th>Day (GMT)</th>
<th>Latitude (degrees)</th>
<th>Longitude (degrees)</th>
<th>Sonde number</th>
<th>Day</th>
<th>Time (GMT)</th>
<th>Latitude (degrees)</th>
<th>Longitude (degrees)</th>
</tr>
</thead>
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<tr>
<td>RV Vickers cruise</td>
<td>1</td>
<td>13:12</td>
<td>-9.4</td>
<td>160.0</td>
<td>18</td>
<td>16</td>
<td>20:43</td>
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<td></td>
<td>2</td>
<td>11:01</td>
<td>-4.9</td>
<td>162.6</td>
<td>19</td>
<td>17</td>
<td>07:04</td>
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<td></td>
<td>3</td>
<td>22:59</td>
<td>-2.1</td>
<td>169.6</td>
<td>20</td>
<td>17</td>
<td>21:27</td>
<td>-1.1</td>
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<tr>
<td></td>
<td>4</td>
<td>09:25</td>
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<td>171.0</td>
<td>21</td>
<td>18</td>
<td>06:58</td>
<td>0.3</td>
</tr>
<tr>
<td>Christmas Island</td>
<td>5</td>
<td>13:09</td>
<td>-2.0</td>
<td>173.5</td>
<td>22</td>
<td>20</td>
<td>08:08</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>05:03</td>
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<td>178.8</td>
<td>23</td>
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<tr>
<td></td>
<td>7</td>
<td>09:33</td>
<td>-2.0</td>
<td>179.5</td>
<td>24</td>
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<td>01:00</td>
<td>2.0</td>
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<tr>
<td></td>
<td>8</td>
<td>01:30</td>
<td>-2.0</td>
<td>182.0</td>
<td>25</td>
<td>22</td>
<td>21:38</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>08:11</td>
<td>-2.0</td>
<td>183.1</td>
<td>26</td>
<td>23</td>
<td>04:08</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>23:29</td>
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<td>185.2</td>
<td>27</td>
<td>24</td>
<td>00:00</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>08:07</td>
<td>-2.0</td>
<td>186.4</td>
<td>28</td>
<td>24</td>
<td>08:19</td>
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<td>188.6</td>
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<td>24</td>
<td>22:12</td>
<td>2.0</td>
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<td>13</td>
<td>07:54</td>
<td>-2.0</td>
<td>190.3</td>
<td>30</td>
<td>25</td>
<td>07:58</td>
<td>2.0</td>
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<td></td>
<td>14</td>
<td>22:21</td>
<td>-2.0</td>
<td>192.9</td>
<td>32</td>
<td>26</td>
<td>04:44</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Latitudes are positive north and longitudes are east from the null meridian. Note that sondes 5, 7, 17, and 31 did not give viable ozone data.

In this analysis we focus on three primary questions: (1) are the CEPEX data, in particular the UT low-O$_3$ events, reproducible by a state-of-the-art global tropospheric chemistry-transport model; (2) are the CEPEX data likely to be representative of the mean state of the regional atmosphere, or are they instead more likely indicative of the extreme variability in O$_3$ in this region of the atmosphere; and (3) what causes the UT O$_3$ minima? This study can be seen as a follow-up to the earlier CEPEX data analyses of Kley et al. (1996, 1997) and Lawrence (1996). The model used for this analysis is first described, then the three questions posed above are addressed individually, followed by a conclusions section.

2. DESCRIPTION OF MATCH-MPIC

MATCH has been under development for the last several years. The meteorology component is described by Rasch et al. (1997), and is evaluated using tracer studies by Mahowald (1996) and Mahowald et al. (1997a, b). The version used here, MATCH-MPIC version 1.2 (hereafter referred to as MATCH-MPIC), includes a tropospheric photochemistry component developed by Lawrence (1996) and Lawrence et al. (1999). This section gives a brief overview of the salient features of the model.

MATCH is a global off-line tracer model. The simulations here are driven by meteorological data from the National Centers for Environmental Prediction/National Center for Atmospheric Research (NCEP/NCAR) reanalysis project (Kalnay et al., 1996), on a T63 grid (about 1.9° × 1.9° in the horizontal). There are 28 vertical sigma levels between the surface and about 2 hPa, with a layer thickness of 1–2 km in the free troposphere, decreasing closer to the surface, with the surface layer being about 90 m thick. The use of the NCEP reanalysis data to drive the model allows us to employ fields (e.g., horizontal winds and temperature) which are based on meteorological observations for the period of interest. For this study we start the model simulations using data from September 1992, with initial trace-gas distributions based on the September mean from a previous model version (Lawrence 1996), and allow a six-month spin-up period before analysing the data for March 1993 (corresponding to CEPEX). A 30-minute time step is used in the runs, and the O$_3$ data in the CEPEX region were archived every three hours.
Three transport processes are included in this version of MATCH: advection, vertical diffusion, and convection. Advection is computed using the semi-Lagrangian transport scheme (Rasch and Williamson 1990). For vertical diffusion, MATCH employs the non-local boundary-layer scheme of Holtslag and Boville (1993). The convection parametrization employed in this version of MATCH is the same as that used in the NCEP model (Pan and Wu 1995). In addition, the meteorology in MATCH includes a parametrization for determining cloud fraction (Slingo 1987), and a bulk microphysics parametrization (Rasch and Kristjansson 1998) which provides cloud water/ice contents and large-scale (non-convective) precipitation and evaporation rates. Note that the gravitational settling transport of soluble trace gases as recently discussed by Lawrence and Crutzen (1998) was not included in these simulations (which used an earlier version of MATCH); since they found that the impact on O₃ due to this process was small (<10% in the tropical Pacific region), this should only have a minor impact on the simulated O₃ distributions on which we focus in this study. The transport properties of MATCH were tested by Mahowald et al. (1997a) using radon simulations. It was found that MATCH driven by the NCEP data gives radon levels which fall within about one standard deviation of the observations at most surface sites, and are generally closer to the observations than radon from MATCH simulations driven by data from the European Centre for Medium-Range Weather Forecasts (ECMWF). However, in comparison with limited observations of the radon vertical profile, it appears that the Pan–Wu convection scheme (used with the NCEP data) results in a somewhat too strong ‘c-shaped’ profile (see below), which is not found for other convection parametrizations such as the Tiedtke scheme used with the ECMWF data.

Since the simulation of convective transport is critical to this study, this parametrization is described here in somewhat more detail. The Pan–Wu scheme provides convective mass fluxes (updraughts and downdraughts) for trace-gas redistribution, as well as convective precipitation formation and evaporation rates. The parametrization is essentially a simplified Arakawa–Schubert scheme (Arakawa and Schubert 1974); the cloud base is at the vertical level where moist static energy is maximal, while the cloud top is determined by buoyancy. The implementation of the Pan–Wu scheme in MATCH (Mahowald 1996) allows entrainment of air into the updraughts only at the cloud base, and detrainment only at the convective cloud top. For downdraughts, on the other hand, entrainment is in the mid troposphere (MT), and detrainment occurs only below the cloud base. During transport along the convective column, air masses are not allowed to mix with intermediate layers (which normally occurs to an extent via entrainment and detrainment). The design of this scheme will therefore maximize the transport of boundary-layer air directly to the UT (and mid-tropospheric air directly to the boundary layer). This tends to enhance the production of extrema in the UT relative to the middle troposphere, such as the overly-strong ‘c-shaped’ profile for radon mentioned above, as well as UT O₃ minima which originated as low-O₃ air masses in the MBL. However, it will be seen later that even this extreme approach to parametrizing convective transport does not allow us to reproduce the extremely low upper tropospheric O₃ mixing ratios observed during CEPEX.

The MATCH-MPIC tropospheric photochemistry module includes explicit source terms for the major known NOₓ and CO emissions (e.g. industry, biomass burning, lightning, etc.); CH₄ is prescribed at the surface based on observations (Fung et al. 1991), and O₃ and NOₓ are prescribed in the stratosphere based on satellite observations (Keating et al. 1987) and observed ratios between NOₓ and O₃ (Murphy et al. 1993), respectively. The dry deposition sink is based on monthly gridded deposition velocities (from Ganzeveld and Lelieveld (1995)) for the most important trace gases (O₃, HNO₃,
and NO$_3$). Wet scavenging is applied based on the cloud-water and precipitation-rate parameters from the convection and microphysics parametrizations, with Henry’s Law constants re-evaluated for each grid point at each time step. Reaction rates between the simulated trace gases are re-evaluated at each time step (using look-up tables). The photolysis rates are also recomputed each time step, based on on-line actinic flux computations for eight wavelengths (taking into account the presence of simulated clouds and the modelled ozone vertical distribution), multiplied by broad-band approximations for the quantum yield and cross-section for each photolysed gas (using the method of Landgraf and Crutzen (1998)). Finally the chemical transformation processes are handled by an efficient and accurate integration scheme which employs either steady-state or backward- or forward-Euler approximations, depending on the characteristic lifetime of the species being integrated. Further details are given by Lawrence (1996) and Lawrence et al. (1999).

The output from the MATCH-MPIC tropospheric chemistry model has been thoroughly evaluated compared with globally-distributed observations in Lawrence (1996) and Lawrence et al. (1999). Table 2 gives the correlations and linear regressions for comparisons of the O$_3$ and NO data from the model run used in this study versus various sets of observations. Simulated O$_3$ tends to be similar to the observations for nearly all regions, while NO (the critical parameter in photochemical O$_3$ production) tends to be underestimated. However, of particular interest to this study is the comparison with data for nearby regions, e.g. PEM (Pacific Exploratory Mission)-West, and it appears that for these regions the MATCH-MPIC simulations are behaving reasonably enough to provide appropriate boundary conditions for transport into the CEPEX region.

3. **Can the CEPEX O$_3$ data be reproduced with a 3D chemistry-transport model?**

(a) **Comparison of individual O$_3$ profiles**

The O$_3$ soundings obtained during CEPEX are plotted individually in Fig. 2, along with the simulated O$_3$ mixing ratios for the closest corresponding grid points and output times in the MATCH-MPIC run. In most of the observed profiles, O$_3$ mixing ratios were low in the MBL, reached a maximum in the lower troposphere (LT) or MT, and fell off again to a minimum in the UT (before rapidly increasing above the tropopause). The observed profiles also generally have a fine-structured ‘layered’ appearance. These basic characteristics are similar to previous observations in the tropical Pacific (e.g. Routhier et al. 1980; Chameides et al. 1987). However, the minimum UT ozone mixing ratios seen in the CEPEX data are considerably lower than previously observed, often falling well below 5 nmol mol$^{-1}$. 

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**Table 2. Correlation coefficients ($r$) and linear regressions for comparisons of MATCH-MPIC data with observations**

<table>
<thead>
<tr>
<th>Trace gas</th>
<th>$r$</th>
<th>$r^2$</th>
<th>$m$</th>
<th>$b^*$</th>
<th>Dataset</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_3$</td>
<td>0.83</td>
<td>0.69</td>
<td>1.11</td>
<td>-7.8</td>
<td>Global balloon soundings</td>
<td>Lawrence et al. (1999)</td>
</tr>
<tr>
<td>NO</td>
<td>0.70</td>
<td>0.49</td>
<td>0.55</td>
<td>5.0</td>
<td>Global aircraft observations</td>
<td>Lawrence et al. (1999)</td>
</tr>
<tr>
<td>O$_3$</td>
<td>0.78</td>
<td>0.61</td>
<td>0.79</td>
<td>6.74</td>
<td>PEM-West A+B, TRACE-A</td>
<td>Lawrence (1996)</td>
</tr>
<tr>
<td>NO</td>
<td>0.79</td>
<td>0.62</td>
<td>0.96</td>
<td>-2.23</td>
<td>PEM-West A+B, TRACE-A</td>
<td>Lawrence (1996)</td>
</tr>
</tbody>
</table>

The linear regression coefficients are for the line $y = mx + b$.

$^*$ $b$ is in nmol mol$^{-1}$ for O$_3$, and in pmol mol$^{-1}$ for NO.

$^+$ Transport and Atmospheric Chemistry near the Equator—Atlantic.
Figure 2. Ozone soundings obtained during CEPEX (solid lines), and MATCH-MPIC simulated ozone profiles for the corresponding model grid points and times (dashed lines with triangles). The profile plots are labelled by sounding numbers, launch times, and locations. The horizontal bars indicate the maximum and minimum mixing ratios in the MATCH-MPIC simulation within six hours before or after the sonde launch time, and within all the horizontally adjacent model grid cells.
The question we are interested in addressing here is how well a state-of-the-art global 3D photochemical model—in particular one which is run with meteorology from the appropriate period and at high resolution for such a model—can reproduce the instantaneous CEPEX \( \text{O}_3 \) observations. The answer, comparing the profiles in Fig. 2, is mixed. MATCH-MPIC clearly does not reproduce the individual observations on a one-by-one basis. Significant advances in modelling are needed before this will become possible. However, if the question is considered in a broader sense, then the model is indeed able to capture some of the key features of the observations, while missing other important features.

The primary feature which is reproduced by MATCH-MPIC is the general shape of the profiles: low MBL \( \text{O}_3 \) mixing ratios, typically increasing to a maximum in the LT or MT, then falling off again to a minimum in the UT. Further features which are
Figure 3. Conceptual schematic of the Walker/Hadley cell circulation in the equatorial Pacific troposphere during the CEPEX period. The flow lines are drawn based on the mean National Centers for Environmental Prediction reanalysis winds for March 1993.

captured are the strong variability in both space and time, and the sharp tropopause. These features are due to the photochemical and meteorological nature of the region. A schematic of the basic circulation pattern in the equatorial Pacific during the CEPEX period is shown in Fig. 3. This is part of the Walker/Hadley circulation cell, in this case characteristic of the El Niño/Southern Oscillation (Bjerknes 1969) which was active during this time period (Trenberth and Guillemot 1996); under more ‘normal’ conditions the upwelling branch depicted here at 180–150°W is located much farther west.

In this circulation, air in the MBL travels over long distances after leaving the Asian and South American continents before reaching the central Pacific. This allows $O_3$ to be photochemically depleted, primarily via the reactions

$$O_3 + h\nu \rightarrow O(^1D) + O_2$$

$$O(^1D) + H_2O \rightarrow 2OH$$

where $h\nu$ is solar radiation at wavelengths less than about 325 nm. In addition, $O_3$ loss occurs via reactions of HO$_2$ and OH with $O_3$ (deposition of $O_3$ onto the ocean surface, with deposition velocities of about 0.02–0.04 cm s$^{-1}$ in this region, plays a much smaller role). The bright and moist conditions of the equatorial MBL make photochemical ozone destruction particularly efficient, resulting in an overall photochemical lifetime of about 5 days. In the free troposphere this loss is not as strong (due to lower water vapour levels), and $O_3$ can build up to higher levels due to in situ production and transport from other regions. In the UT, however, outflow from convective towers becomes important. The air in this outflow mainly originates in the MBL, and thus tends to reduce the UT $O_3$ mixing ratios to levels below those found in the MT. Convective activity is typically strongest in the western Pacific (due to the high sea surface temperatures in the ‘warm-pool’ region), leading to generally lower UT $O_3$ levels there.

Perhaps the most important feature in the observations which is not captured by the model is the extreme nature of the UT $O_3$ minima, which are much more severe in the observations (often <5 nmol mol$^{-1}$) than in the simulation (occasionally <10 nmol mol$^{-1}$). In addition, the model clearly fails to reproduce the vertical fine structure present in the observations, due to its discretization of the free troposphere into model layers of 1–2 km thickness. Though the model data show a strong temporal and spatial variability, they do not appear to be as strong as indicated by the observations.
Furthermore, the variations produced by the model (i.e. maxima and minima) do not always coincide in time and space with the observed extrema. These differences are discussed further in the following subsections, in which the data are broken down into two parts, the open-ocean data, and the Christmas Island data.

(b) Open ocean O$_3$ data

For this section, the data in Fig. 2 are broken down into three separate subdomains: western CEPEX (160°E–177°E, soundings 1–6), central CEPEX (177°E–171°W, soundings 8–14), and eastern CEPEX (171°W–158°W, soundings 15–21). The mean observed and modelled O$_3$ profile for each region is shown in Fig. 4. An important feature to notice in this figure is that both the observations and the model show an O$_3$ minimum in the UT in the mean profile for all three regions. Thus, it appears that the occurrence of UT O$_3$ minima is not an isolated phenomenon, but a basic part of the general character of equatorial Pacific O$_3$ profiles. MATCH-MPIC predicts the altitude of the minimum O$_3$ mixing ratios correctly (about 15 km), but, as noted previously, does not reproduce the extreme nature of the observed minima. The model also underestimates the magnitude of the observed MT maxima, and predicts their location (about 12 km) to be much higher than observed (5–7 km). This may be an indication that transport from the subtropics, which Kley et al. (1997) associate with the MT O$_3$ maxima, is occurring at too high an altitude in the NCEP data. Another factor which may contribute is that detrainment from convection is limited to occurring only at the cloud tops in the model, so that the fall-off from MT maximum to UT minimum values will tend to begin at too high an altitude.

In the free troposphere the western CEPEX region has the lowest O$_3$ mixing ratios, due to the more intense convective activity there. At the surface, however, the mean observed O$_3$ mixing ratios are lowest in the central and eastern CEPEX regions, largely due to O$_3$ depletion during travel along the lower branch of the Walker cell (Fig. 3). In the central CEPEX region the westerly and easterly flows converge and produce an upwelling. This carries the low-O$_3$ surface air into the lower free troposphere, which
can be seen in Fig. 4: O₃ stays below 10 nmol mol⁻¹ until well above 800 hPa in the central CEPEX region in both the observations and the model, whereas it exceeds 10 nmol mol⁻¹ already by 800 hPa in the western and eastern regions. In addition, the higher average surface O₃ levels in the west may have been in part due to recent convective activity: while updraughts produce the strong UT O₃ minima, downdraughts can simultaneously bring large amounts of high-O₃ MT air into the MBL. MATCH-MPIC clearly overestimates the mean surface O₃ levels in the central and eastern CEPEX regions. Whether this is due to a missing sink near the surface (e.g. halogen chemistry), or perhaps due to the non-entraining nature of the downdraughts in MATCH-MPIC, carrying high-O₃ MT air directly to the near-surface layers, remains to be determined. In either case, this has an important implication: if the model cannot reproduce the very low surface O₃ mixing ratios, it will not be able to predict extremely low UT O₃ levels. This point is returned to in section 5.

(c) O₃ above Christmas Island

Since a series of soundings was made above Christmas Island, it is possible to look at the mean and short-term variability of the O₃ profile at a single location. The mean and standard deviation of the observed and simulated soundings are plotted in Fig. 5. Near the surface the two curves diverge, with MATCH-MPIC predicting much higher levels than observed, similar to what was previously noted for the profiles in the central and eastern CEPEX regions (Fig. 4). Throughout the rest of the troposphere the simulated mean profile remains within about one standard deviation of the observed mean and displays the main features: an MT maximum (at about 8 km), a UT minimum (about 2 km too high), and the rapid increase at the tropopause. Thus, it would appear that though MATCH-MPIC is not able to reproduce the individual CEPEX soundings on a one-by-one basis, it does indeed capture the overall photochemical and meteorological characteristics of the free troposphere of this region well enough to be able to reproduce the mean profile on a longer time-scale (in this case about a week).

In Fig. 5(b), the observed and simulated relative standard-deviation profiles (relative to the March mean) are plotted. (Note that O₃ is not actually normally distributed, though it is generally close enough that the standard deviation can provide a good approximate diagnostic of its variability.) The standard deviation based on the observations is highest in the UT and near the surface. This is presumably due to the stochastic nature of convective outflow into the UT (updraughts) and MBL (downdraughts). The standard-deviation profile computed from the ten MATCH-MPIC O₃ profiles differs significantly from the observed variability. In the lower free troposphere the simulated variability is much greater, while in the MBL and UT it is much less. This may be in part due to the coincidence of the specific week chosen for sampling; during the first two weeks of March, the standard deviation of O₃ in MATCH-MPIC is much more in line with what was observed during CEPEX than the profiles from the last weeks, when the sampling took place (this is seen later in Fig. 8(d)). The standard-deviation profile computed from the model ozone values over the whole of March is also plotted in Fig. 5(b); it is also much closer to the observed temporal variability in the UT. However, even the longer-term variability in the simulation in the UT is generally less than that observed during the brief Christmas Island sampling. Thus the temporal variability is likely somewhat underestimated in the MATCH-MPIC simulations. This point is important for the next section, which makes use of the temporal variability in MATCH-MPIC to analyse the CEPEX observations.
Figure 5. Comparison with Christmas Island O₃ data: (a) mean O₃ profiles above Christmas Island based on the ten observed soundings (squares with 1 standard deviation error bars) and the ten corresponding MATCH-MPIC simulated profiles (triangles). The observed soundings were unevenly spaced in height; they were binned into 50 hPa intervals before computing the mean and standard deviation; (b) O₃ relative standard-deviation profiles (relative to the March mean) above Christmas Island based on the observed soundings (squares with connecting solid lines for data binned in 50 hPa intervals, solid line with no markings for data binned into 5 hPa intervals), and based on the corresponding MATCH-MPIC simulated profiles (triangles). The March standard-deviation profile for MATCH-MPIC is also plotted (diamonds).
4. Do the CEPEX O$_3$ soundings represent the regional mean O$_3$ distribution?

The CEPEX O$_3$ soundings are unquestionably a valuable addition to our knowledge of photochemistry in the tropical Pacific troposphere. However, from the soundings alone it cannot be determined whether they are representative of the regional mean O$_3$ distribution, or whether they instead provide us with an indication of the degree of variability of O$_3$ in this region. In particular, it would be interesting to know whether the mean UT O$_3$ mixing ratio in the western UT is actually below 5 nmol mol$^{-1}$, or if instead these measurements represent a short-term phenomenon that CEPEX was fortunate to encounter. The answer to this will not be known with certainty until many more O$_3$ observations are made in the equatorial Pacific over an extended period of time. In the meantime, it is possible to get a glimpse at what this answer might be by using MATCH-MPIC. To do so, in this section we will compare the March mean O$_3$ distribution computed by MATCH-MPIC with the model output sampled in the same way as the atmosphere was sampled during CEPEX. The quality of this assessment is of course limited by the ability of MATCH-MPIC to simulate ozone in this region; this should be borne in mind throughout this section. In particular, it was pointed out in the previous section that the temporal variability in MATCH-MPIC appears to be somewhat less than indicated by the observations. This would imply that the model assessment presented in this section will tend to give a lower limit to the differences expected between the sampled O$_3$ and the actual mean O$_3$ distribution in this region.

(a) RV Vickers cruise O$_3$ data

The March mean O$_3$ profiles computed by MATCH-MPIC for the western, mid, and eastern CEPEX regions (along the RV Vickers route) are shown in Fig. 6(a). The O$_3$ profiles show the same character in all three regions, with low MBL O$_3$, increasing into the free troposphere, and falling off to a minimum in the UT. The distribution also fits with the circulation pattern shown in Fig. 3: surface O$_3$ is lowest in the central region due to the long transport times from the continents. Furthermore, the UT O$_3$ levels are lowest in the west due to the stronger mean convective activity there. The variability in O$_3$ computed by MATCH-MPIC for March is depicted in Fig. 6(b). The relative standard deviation is generally about 20–30%. Thus one would expect most individual O$_3$ samples taken in this region to be typically within 20–30% of the mean. On the other hand, this can also be interpreted as indicating that at least 1/3 of the sampled values should be more than 20–30% away from the mean. Even larger deviations would be expected just below the tropopause, where the relative variability is highest due to stochastic outflow of O$_3$-depleted air from convective events (especially in the western part of the region).

The next task is to use the MATCH-MPIC data to see what this variability might mean for the particular case of the CEPEX sampling. Figure 7 depicts the ratio of the computed profiles in Fig. 4 to those in Fig. 6(a). The figure indicates that most of the MATCH-MPIC data in Fig. 4 fall within some 20% of the March mean, which is basically consistent with the relative standard deviations shown in Fig. 6(b). However, there are two significant exceptions to this. In the UT above 15 km, especially in the west, the computed O$_3$ mixing ratios during CEPEX are much lower than the March mean; in the eastern and central UT around 12 km they are much higher. In other words, the weak longitudinal gradient seen in Fig. 6(a) (the simulated March mean O$_3$ distribution) is significantly exaggerated when the model results are sampled like the CEPEX cruise (Fig. 4). Processes like stochastic convective pumping and variability in the tropopause level and stratosphere–troposphere exchange can lead to differences
Figure 6. MATCH-MPIC computed profiles for the three sub-domains defined in Fig. 4 showing: (a) the mean \(O_3\) profiles during March, and (b) the \(O_3\) relative standard deviations for March (relative to the March mean).
such as these in a model. Since models tend to smooth out extreme variations due to their finite grid sizes, one would generally expect that even larger differences between individual samples and the longer-term mean would frequently show up in observed data.

(b) Christmas Island \(O_3\) data

The atmosphere above Christmas Island was sampled for \(O_3\) repeatedly over several days. This raises the question of whether or not the mean of the samples is likely to be representative of: (a) the actual mean during the sampled period, and (b) the actual mean over a longer period (e.g. March). The same question can be asked of the MATCH-MPIC data. Figure 8(a) indicates that—for the MATCH-MPIC data—the answer is yes (to both parts). For the comparison with the mean of the six days during which the sampling took place, the profiles are nearly indistinguishable. This is due to the fact that the diurnal cycle of \(O_3\) is small in this region, so that sampling once or twice daily is sufficient to capture the mean during the sampling period. There are also only minor differences compared with the March mean. In this case, one could expect that this probably also applies to the observations, since MATCH-MPIC fairly closely reproduces the mean \(O_3\) profile above Christmas Island (the mean of the observed \(O_3\) profiles is also plotted in Fig. 8(a) for reference).

This might not always be the case, however. Convective activity and synoptic winds change over the course of a month; thus, the mean \(O_3\) profile during one particular week might not always be representative of the mean over a month. This can also be examined with the MATCH-MPIC \(O_3\) data. The weekly-mean simulated \(O_3\) profile over Christmas Island is plotted for four weeks in March in Fig. 8(b) (starting with 1–7 March, etc.). The
Figure 8. Analysis of the Christmas Island O₃ profiles: (a) comparison of MATCH-MPIC data for the mean of the ten model profiles corresponding to the CEPEX soundings versus the mean profile during the 6-day sampling period, along with the March mean profile (the observed mean profile is also plotted for reference); (b) MATCH-MPIC O₃ mean profiles for each of the first four weeks in March; (c) comparison of MATCH-MPIC data for the relative standard deviation of the ten model profiles corresponding to the CEPEX soundings versus the March standard-deviation profile and the standard deviation profile for the six-day sampling period; and (d) MATCH-MPIC O₃ relative standard-deviation profiles for each of the first four weeks in March.
mean profile during the first week differs significantly from the profiles during the other weeks, with considerably more ozone in the UT. Thus it is clear that caution should be exercised in extrapolating the mean over a sampled period to being representative of the mean over a longer period.

The shifts in the O$_3$ profile seen in Fig. 8(b) also bring out another point: the temporal variability sampled over a shorter period will not include any long-term trends or shifts in the data. This can lead to a difference between the variability estimated from a limited set of soundings and the actual variability over a longer period of time, as shown for the MATCH-MPIC data in Fig. 8(c). The standard-deviation profile computed from the ten simulated soundings is very close to the standard deviation during only the week which was sampled (due to the small diurnal cycle). However, in the UT the temporal variability for March is much higher than the variability for the week sampled. This is in part due to the shift in UT O$_3$ between weeks 1 and 2, which is, of course, not seen during weeks 3–4 (when the actual sampling took place). It is also due to changes in the short-term variability itself over the course of the month. This is shown in Fig. 8(d), where the standard deviation for the simulated O$_3$ is seen to vary substantially from week to week (up to a factor of four difference in the UT). Thus, caution must also be exercised in extrapolating the standard deviation estimated from a set of O$_3$ measurements to a time frame beyond the sampling period.

5. WHAT CAUSES THE UPPER TROPOSPHERIC O$_3$ MINIMA?

This section considers the causes of the UT O$_3$ minima. As indicated in the introduction, previous analyses (Kley et al. 1996, 1997; Lawrence 1996) concluded that convective transport played the main role in producing these minima during CEPEX. We add to this assessment by considering the results from a MATCH-MPIC run in which convective transport of O$_3$ was turned off. In Fig. 9, the March mean O$_3$ profiles for this run are shown for the CEPEX region, along with their ratios to the modelled profiles in Fig. 6(a). Without convective transport of O$_3$ the UT minima vanish, and the overall O$_3$ levels in the UT increase, while the surface O$_3$ levels decrease considerably (by 30–35%). Thus, convective overturning is responsible for driving up the MBL O$_3$ levels, and is simultaneously the major factor in producing the O$_3$ minima in MATCH-MPIC.

However, as seen in Fig. 2, this only produces O$_3$ minima of just below 10 nmol mol$^{-1}$ for the CEPEX sampling scenario. At other times and locations the modelled O$_3$ falls to much lower values. To demonstrate this, in Fig. 10(a), we show the minimum O$_3$ mixing ratio computed during March in the CEPEX region at about 13.5 km (model level 10). O$_3$ is computed at times to fall as low as 5 nmol mol$^{-1}$, and the minimum values are below 6 nmol mol$^{-1}$ for an extended region; interestingly, this region corresponds almost perfectly to the first segment of the RV Vickers route during CEPEX, indicating that the region that was sampled could certainly have been expected occasionally to have very low UT O$_3$ levels. However, values are never computed by MATCH-MPIC to be much below 5 nmol mol$^{-1}$. One could argue that the observed values that were well below 5 nmol mol$^{-1}$ are not really valid since the instrumental uncertainty during CEPEX was about 5 nmol mol$^{-1}$ in the UT (Smit et al. 1994). On the other hand, the fact that such low values were observed on several occasions during CEPEX, and have also been observed over Europe (Reichardt et al. 1996; Davies et al. 1998), suggests that there may be some validity to these extremely low mixing ratios. If so, then it is clear that in the context of a current global photochemical model, the mechanism of convective pumping of MBL air is not sufficient by itself to explain the extremely low UT O$_3$
Figure 9. Results from a MATCH-MPIC run with convective transport of O$_3$ turned off: (a) March mean O$_3$ profiles for the three sub-domains defined in Fig. 4, and (b) the ratios of these profiles to the profiles in Fig. 6(a).
Figure 10. Minimum O₃ volume mixing ratios (nmol mol⁻¹) computed by MATCH-MPIC during March in the CEPEX region at: (a) approximately 13.5 km (or about 170 hPa, model level 10) and (b) the surface model level (about 1000 hPa).
levels (<5 nmol mol\(^{-1}\)) observed during CEPEX. Since we have employed a model at relatively high spatial resolution, and used a non-entraining convective transport parametrization that could be considered 'optimal' for the production of UT O\(_3\) minima, it is doubtful that much lower O\(_3\) mixing ratios would be produced in other global photochemical models at present. Thus, alternate explanations need to be considered.

Previous analyses have considered additional in situ losses for O\(_3\) in the UT to explain this. In particular, Kley et al. (1996) proposed that an additional in situ loss of O\(_3\) might occur if HO\(_2\) sticks to cirrus ice particle surfaces and dissociates to form O\(_2\), which will then readily react heterogeneously with O\(_3\). Lawrence (1996) considered this possibility in more detail via two MATCH-MPIC simulations in which a parametrization for this loss was included in the model. It was found that this mechanism could present a significant additional loss, provided the reaction probability (\(\gamma\)) for O\(_3\) with dissociated HO\(_2\) on ice exceeds \(\gamma = 10^{-5}\). The reaction probability is still unknown. Lawrence (1996) also discussed another possibility. Convective transport may well be sufficient to reduce O\(_3\) to essentially MBL levels in the outflow region of convective storms. In a global model framework, however, the outflow region is generally much smaller than the dimensions of a grid cell. Thus, the outflow air has to be mixed with the air in the rest of the grid cell, where convection is not taking place, so that the low-O\(_3\) signal from convection becomes 'smeared out' and thus less severe. Whether this is the case will become clearer once we are able to do simulations of the CEPEX region at higher horizontal and vertical resolution.

However, even at higher resolution we would not expect computed UT O\(_3\) levels to fall much below 3 nmol mol\(^{-1}\). This is because the minimum O\(_3\) mixing ratio computed by MATCH-MPIC at the surface never falls below about 3 nmol mol\(^{-1}\), as shown in Fig. 10(b). This figure is particularly important because it indicates that transport alone, no matter how extreme, would not be capable of producing the near-zero O\(_3\) levels in MATCH-MPIC as observed during CEPEX. As was seen in Figs. 4 and 5, MATCH-MPIC tends to overestimate the mean MBL O\(_3\) levels compared with CEPEX observations, and Fig. 2 showed that near-zero MBL O\(_3\) levels were occasionally observed during CEPEX. Furthermore, there are other observations of equatorial Pacific MBL O\(_3\) mixing ratios well below 3 nmol mol\(^{-1}\) (e.g. Johnson et al. 1990; Singh et al. 1996). Therefore, some additional in situ loss process in the MBL of MATCH-MPIC seems necessary. One possibility is that the turnover rate for air in the model's MBL is too rapid, so that insufficient time is being allowed for photochemical depletion as discussed in section 3(a). Another possibility is that important reactions are missing from the model, such as the set of halogen-family reactions, which are believed to provide a significant additional loss of O\(_3\) in the MBL (Sander and Crutzen 1996; Vogt et al. 1996), and thus might also play an important role in indirectly contributing to the presence of near-zero O\(_3\) levels in the upper tropical troposphere. Future studies in which these reactions are included in a 3D model would help shed some light on whether this could contribute to producing the extremely low observed UT O\(_3\) levels.

6. Conclusions

The comparison between our O\(_3\) profiles computed with MATCH-MPIC and those observed during CEPEX gave mixed results. We are clearly not yet to the state of being able to reproduce observed profiles on an individual basis, at least not in remote regions like the equatorial Pacific. Part of this is certainly due to the discretization of the physical atmosphere in the model into grid cells with dimensions of about 200 km per side. Given the large degree of variability in O\(_3\) evident in the observations, one cannot really
expect the mean O$_3$ mixing ratio over tens of thousands of square kilometers to be always representative of the measurements at a given point within that domain. One can also expect the simulated variability of O$_3$ averaged over these grid dimensions to be less than the variability indicated by point measurements, as was indeed generally found to be the case. However, obtaining a high degree of agreement between modelled and observed O$_3$ profiles would require more than just an improvement in the spatial resolution; significant advances on several fronts of atmospheric modelling would need to be made. For instance, the synoptic meteorology of these regions would need to be far better constrained by extending the current network of observing stations. Even then, it is not clear whether models like MATCH-MPIC would be able to predict critical processes such as the evolution of individual convective storm events at the right times and places; determining this would require extensive comparisons with satellite cloud images. In addition, once the horizontal and vertical resolution of atmospheric models is further refined so that several important processes (mainly at the cloud scale) can be resolved, the parametrizations of these processes would need to be improved to capture their physics more realistically. Furthermore, one would need to ascertain whether all important photochemical reactions and trace-gas sources and losses are being adequately represented by the simulations. These are enormous tasks that would require many years of concerted effort.

On the more positive and immediate side, we are apparently already at the stage where we can reproduce many key features of remote O$_3$ observations obtained over a relatively short time period, as seen in this study. Although some of this agreement was likely to have been fortuitous, other parts fit well with our understanding of physical processes active in the tropics. Some examples of this are: the presence of UT minima and MT maxima, lower UT O$_3$ levels in the more convective western Pacific, upwelling in the central Pacific associated with the (El Niño period) Walker cell, and a sharp tropical tropopause. This type of agreement should help support conclusions that are made from modelling studies, such as assessing the impact of lightning and anthropogenic NO$_x$ emissions on the photochemistry of the tropical troposphere.

One of the primary features of the CEPEX observations, the presence of UT O$_3$ minima, was qualitatively but not quantitatively reproduced by MATCH-MPIC. Based on both the model and observations, the occurrence of UT O$_3$ minima appears to be a basic part of the general character of equatorial Pacific O$_3$ profiles, rather than an isolated phenomenon. The causes of these minima were considered in this study. It was shown that convective transport of O$_3$-depleted MBL air masses into the UT, especially without mixing along the updraught column, is capable of producing substantial O$_3$ minima in the UT in MATCH-MPIC. However, these still do not fall below the 5 nmol mol$^{-1}$ level, while in the observations the UT O$_3$ mixing ratios were often well below 5 nmol mol$^{-1}$. Thus, the model is missing some critical process (or processes). One of these may be a loss process for O$_3$ in the MBL, since the surface O$_3$ mixing ratios only fall to some 3 nmol mol$^{-1}$ in the model, higher than commonly observed, and insufficient to be able to produce near-zero O$_3$ via transport to the UT. A strong candidate for an additional loss process in the MBL is halogen-mediated O$_3$ destruction (Sander and Crutzen 1996; Vogt et al. 1996). Other possibilities of model deficiencies include smearing out of the convective effect due to the nearly 200 x 200 km grid cell horizontal dimensions, or possibly heterogeneous loss of O$_3$ on cirrus ice particles. These will all hopefully become clearer in ongoing studies.

This study also addressed the question of how likely it is that the CEPEX data are representative of the mean O$_3$ distribution in this region. This was done by using the
MATCH-MPIC O₃ data as a surrogate, and comparing the MATCH-MPIC O₃ data sampled like CEPEX with the modelled March mean. A similar question was posed by Ehhalt et al. (1997) for the PEM-West A and B datasets. During those campaigns, a much more extensive sampling of the photochemistry of the western Pacific took place than what was possible during CEPEX. Ehhalt et al. (1997) performed their study with three surrogate tracers with uniform 5, 20, and 100-day lifetimes. They found that the regional mean distributions computed for these three tracers were closely reproduced when they sampled their model data like the atmosphere was sampled during the two PEM-West campaigns. We instead used O₃ from our tropospheric photochemistry model, with its strongly variable lifetime due to photochemical destruction processes, and arrived at somewhat different conclusions for the CEPEX dataset.

For our study, the CEPEX data were broken down into two parts. For the Christmas Island part, it was seen that sampling once or twice daily appears to be sufficient to capture the mean O₃ profile and its standard deviation in this region during the sampling period (due to the small diurnal cycle). However, the MATCH-MPIC results also indicate that one cannot generally extend this conclusion to periods beyond the time during which sampling takes place. The model data showed that strong shifts in the O₃ profile on time-scales of a week could result in significantly different mean O₃ profiles over a longer period. Thus, for the open-ocean cruise part of the CEPEX sampling, which only allowed one sample to be taken at each location along the route, one would anticipate potentially large differences between the observed O₃ profiles and the longer-term mean. For this particular case, MATCH-MPIC predicted significantly less O₃ in the UT (i.e. more intense UT minima) than the March mean levels. Since the temporal variability in the MATCH-MPIC O₃ data was apparently less than in the observations, it is likely that even larger deviations may exist between the observed O₃ levels and the actual mean. In the long run, this issue will only be resolved by extended O₃ measurements in this region, which would establish the long-term mean O₃ distribution. In the meantime, the results of this study indicate that the CEPEX open-ocean cruise data are likely to be within some 20% of the actual mean regional distributions during the sampling period for much of the troposphere, though on the other hand it is also likely that some features of the observed profiles are not representative of the mean state of the atmosphere in this region, particularly in the UT. We wish to emphasize, however, that this should not be taken negatively. The troposphere is rich in variability—otherwise it would not be nearly so difficult to simulate—and the CEPEX data, which are indicative of the effects of convection, have provided a valuable step towards expanding our awareness of the tremendous degree of variability in the photochemistry of the remote troposphere.

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