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Peters, Wouter; Krol, Maarten; Dentener, Frank; Lelieveld, Jos

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Identification of an El Niño-Southern Oscillation signal in a multiyear global simulation of tropospheric ozone

Wouter Peters and Maarten Krol

Institute for Marine and Atmospheric Research Utrecht, Utrecht, Netherlands

Frank Dentener

Joint Research Centre, Ispra, Italy

Jos Lelieveld

Max Planck Institut für Chemie, Mainz, Germany

Abstract. We present the first study of the El Niño-Southern Oscillation (ENSO) interannual variability in tropical tropospheric ozone in a multiyear simulation with a global three-dimensional chemistry-transport model. A 15-year period (1979–1993) was simulated using European Centre for Medium-Range Weather Forecasts meteorological reanalysis data and a time-varying emission data set. A comparison of model calculations with observations shows good agreement for surface ozone, seasonal cycles, and ozone concentrations at remote stations, but reveals an underestimate of ozone in the free troposphere, which is most pronounced during biomass burning seasons. The ENSO signal is the most important component of interannual variability in tropical tropospheric ozone columns (TTOC), being responsible for nearly 25% of the total interannual variability of ozone in the tropics. The amplitude of the modeled ENSO signal in TTOC is 3 Dobson units, in close agreement with satellite observations. This signal is evenly distributed with height, indicating that rapid vertical transport plays an important role. The ENSO signal is also detectable at the surface, for example at the Pacific island Samoa, for which model-calculated and measured ozone agree well.

1. Introduction

The interest in tropical tropospheric ozone has intensified in the past decade, since it provides important insights into transport processes, photochemistry, and the oxidation power of the atmosphere. Photochemistry is particularly active in the tropics due to the high insolation. Measurements of ozone are conducted at only a few stations in the tropics [Logan, 1999, and references therein], while most of the in situ observations have been performed during intensive campaigns [e.g., Browell *et al.*, 1990; Diab *et al.*, 1996; Kley *et al.*, 1996; Thompson *et al.*, 1996; Fenn *et al.*, 1999; de Laat *et al.*, 1999]. These data sets, however, are insufficiently comprehensive to infer trends and large-scale distributions, as they lack spatial and temporal coverage.

Total tropospheric ozone columns (TTOC) were retrieved from satellite measurements in several studies [e.g., Fishman *et al.*, 1990; Kim *et al.*, 1996; Hudson *et al.*, 1995; Hudson and Thompson, 1998]. These studies are based on so-called residual methods, where TTOC is calculated

as the difference between total column ozone and stratospheric column ozone. The Total Ozone Mapping Spectrometer (TOMS) [McPeters and Labow, 1996] provides a 15-year record (1978–1993) of total ozone columns, while calculation of the stratospheric ozone contribution differs from one method to the other. Hudson and Thompson [1998] described the modified residual (MR) method, where stratospheric ozone is obtained from a combination of TOMS observations and ozonesondes launched near the Atlantic Ocean ozone maximum. Ziemke *et al.* [1998] used cloud observations from the TOMS instrument to estimate the stratospheric ozone content (cloud convective differential or CCD method). These two methods have been shown to be successful in reproducing TTOC values from ozonesondes [Ziemke *et al.*, 1998; Hudson and Thompson, 1998; Thompson and Hudson, 1999].

Satellite observations of TTOC have been used to describe the "zonal wave one" distribution of ozone in the tropics [Fishman and Larsen, 1987; Kim *et al.*, 1996]. This zonal wave one pattern is characterized by an ozone minimum associated with strong convective upward motions over the Pacific warm pool, and an ozone maximum associated with oceanic anticyclones over the tropical Atlantic. These motions are part of large-scale zonal transport which is in-

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duced by convection, and their effect on TTOC has been described previously [Lelieveld and Crutzen, 1994; Krishnamurti et al., 1996; Chandra et al., 1998; Wang et al., 2000]. Fishman et al. [1990] recognized that the TTOC maximum over the Atlantic Ocean is strongest in Southern Hemisphere spring (September–November), when the biomass burning intensity reaches a maximum over Africa and Brazil. Later studies from the Transport and Atmospheric Chemistry Near the Equator–Atlantic (TRACE-A) campaign [Fishman et al., 1996; Thompson et al., 1996] indicated that production of ozone from precursors in biomass burning plumes can lead to a 10–15 Dobson unit (DU) increase of ozone over the Atlantic Ocean during austral spring.

In addition, the observed mean distribution of tropospheric ozone is influenced by interannual variability in the tropics. Phenomena such as the El Niño–Southern Oscillation (ENSO) introduce variability in tropospheric transport patterns, the amount and location of biomass burning emissions, the UV flux entering the troposphere, and other parameters. Signatures of ENSO were recognized previously in measurements of various chlorofluorocarbons (CFCs) at Samoa [Prinn et al., 1992]. They noted that transport of methylchloroform (CH_3CCl_3) from the Northern Hemisphere to Samoa was inhibited by migration of the Intertropical Convergence Zone (ITCZ) during ENSO events. Ziemke et al. [1999] showed that owing to shifting convection patterns during ENSO, TTOC over the eastern part of the Pacific decreases (3–4 DU), while the western Pacific shows an increase in ozone (2–3 DU). To our knowledge, a model study of the influence of ENSO on the chemical composition of the tropical troposphere has not yet been conducted.

Most previous studies of tropical tropospheric ozone with models were largely limited to validation of off-line and on-line chemistry-transport models [e.g., Wang et al., 1998; Brasseur et al., 1998; Hauglustaine et al., 1998; Lawrence et al., 1999]. Although most models seem to generally reproduce ozone observations well, all studies report difficulties with representing tropical ozonesondes. This is usually attributed to a poor representation of biomass burning and lightning NO_x emissions, insufficient model resolution, or limitations of the chemistry scheme used. Several studies that focused on the impact of biomass burning on ozone [e.g., Chatfield et al., 1996; Roelofs et al., 1997; Galanter et al., 2000; Wang et al., 2000; Marufu et al., 2000] have yielded important insights on the interaction of (convective) transport and photochemistry during the biomass burning season. However, these model studies focussed on reproducing observed ozone distributions during specific years and for specific regions, while none was aimed at reproducing a long-term tropical ozone record, including interannual variability.

In this study we present for the first time an analysis of a 15-year tropical ozone record simulated with an off-line chemistry-transport model. European Centre for Medium-Range Weather Forecasts (ECMWF) reanalysis meteorological data have been combined with a time-varying emission data set to perform such a long-term integration. Some results from this integration were previously published by

Lelieveld and Dentener [2000], focusing on the relative roles of chemistry and transport in global tropospheric ozone. In the work presented here, we focus on tropical ozone and address two questions: (1) How well can the model reproduce the ozone distribution in the tropics? and (2) how well can the model reproduce ENSO variability?

In section 2 the chemistry-transport model (CTM) is described, as well as the details of the long-term integration. The analysis method (principal component analysis or PCA) is discussed in section 3. After analyzing the modeled tropopause heights (section 4), we compare annual cycles of ozone at several stations with climatological values of Logan [1999] (section 5). In section 6 we focus on ENSO variability in modeled TTOC, and show that this agrees well with satellite-derived observations of Ziemke et al. [1999]. We show the effects of ENSO on surface ozone at the tropical Pacific station Samoa, where a significant increase in ozone is observed during ENSO. Finally, we discuss our results in section 7 and present our conclusions in section 8.

2. Model Description

In this model study, the off-line chemical tracer transport model version 3 (TM3) is used to calculate atmospheric concentrations of 47 trace species over the period 1979–1993. Transport of chemical tracers is prescribed using ECMWF reanalysis data [Gibson et al., 1997], which encompass the period January 1979 to April 1994, as meteorological input. Six-hourly global fields of geopotential height, temperature, specific humidity, clouds, precipitation and horizontal mass fluxes are retrieved from the ECMWF archive and extrapolated to a horizontal resolution of $5^\circ \times 3.75^\circ$, corresponding to about 600×400 km in the tropics. Between the surface and 10 hPa, 19 hybrid σ - p layers are applied with approximately five in the boundary layer, nine in the free troposphere, and five in the stratosphere. Although the long-term integration spans the 1979–1997 period, only the period corresponding to the reanalysis was used for consistency. A short list of processes included in the model and further references to previous applications of the model is given in Table 1. We will limit ourselves to a description of processes that are relevant for this study. These include treatment of stratospheric ozone, calculation of photolysis rates, and the emission scenario used in this study.

In the model, stratospheric chemistry is not explicitly accounted for, because it would strongly increase the computational burden. Since ozone is produced in the stratosphere, an upper boundary condition has to be applied for this compound. For this purpose the TOMS data set from the Nimbus 7 satellite (1979–1992) has been used in combination with the ozone climatology from Fortuin and Kelder [1998]. The ozone concentrations between the top of the atmosphere and 10 hPa in the model are fixed at climatological values. Between 10 hPa and 60 hPa, zonally averaged ozone values are forced toward zonally and monthly averaged TOMS data with a relaxation time of 2.5 days. For this purpose the TOMS total ozone is distributed in the vertical direction by means of the climatology [Fortuin and Kelder, 1998]. The

Table 1. Processes Included in the Model and References to the Original Work

Process	Based on	Discussed in ^a
Advection	<i>Russel and Lerner</i> [1981]	<i>Dentener et al.</i> [1999]
Convection (subgrid)	<i>Tiedtke</i> [1989]	<i>Dentener et al.</i> [1999]
Turbulent mixing (subgrid)	<i>Louis</i> [1979]	<i>Dentener et al.</i> [1999]
Stratospheric boundary ^b		<i>Lelieveld and Dentener</i> [2000]
Photolysis	<i>Landgraf and Crutzen</i> [1998] <i>Krol and van Weele</i> [1997]	
Dry deposition	<i>Wesely</i> [1989]	<i>Ganzeveld et al.</i> [1998]
Wet deposition	<i>Guelle et al.</i> [1998]	<i>Jeuken</i> [2000]
Biomass burning emissions ^b	<i>Hao et al.</i> [1990]	<i>Marufu et al.</i> [2000]
Lightning NO _x emissions	<i>Price and Rind</i> [1992] <i>Levy et al.</i> [1996]	
Other emissions ^b	<i>J.A. van Aardenne</i> ^c	<i>Lelieveld and Dentener</i> [2000]
Chemistry, CBM-IV	<i>Gery et al.</i> [1989] <i>Houweling et al.</i> [1998]	<i>Houweling et al.</i> [1998]

^aThis column refers to previous work with the TM3 model.

^bThis process is discussed in section 2.

^cJ.A. van Aardenne, A high-resolution data set of historical anthropogenic trace gas emissions for the period 1890-1990, submitted to *Global Geochemical Cycles*, 2000

ozone between the Earth's surface and 60 hPa, as well as the zonal distribution and variability, is fully determined by transport and chemistry of the model [*Lelieveld and Dentener*, 2000]. The TOMS data of 1992 were used to constrain the model in 1993, when Nimbus 7 TOMS was no longer available. Therefore relatively little attention is given to 1993.

Photodissociation frequencies for 20 trace gases are calculated on-line in the model with a scheme based on *Landgraf and Crutzen* [1998] and *Krol and van Weele* [1997]. In this scheme, photodissociation frequencies depend on the thickness of the stratospheric ozone column. As noted above, part of the stratospheric ozone column in the model is prescribed by the 14-year TOMS record. Thus interannual variability in the stratospheric ozone column that is present in TOMS observations is also introduced in photodissociation frequencies of ozone, and in species with absorption bands overlapping with ozone. The effect of (multiple) scattering of clouds

is also incorporated in the photodissociation scheme, which allows for possible feedbacks associated with convection in the troposphere.

Trace gas emission estimates for the 1978-1993 period are based on the Emission Database for Global Atmospheric Research (EDGAR) [*Olivier et al.*, 1996]. Anthropogenic emission calculations have been performed for 10-year intervals since 1860 (J.A. van Aardenne, A high-resolution data set of historical anthropogenic trace gas emissions for the period 1890-1990, submitted to *Global Geochemical Cycles*, 2000). The emission trends for anthropogenic ozone precursors between 1979 and 1993 that were not explicitly calculated were scaled with regional trends of fossil-fuel-related CO₂ emissions [*Benkert*, 1997]. Biomass burning emissions are based on *Hao et al.* [1990], and African emissions were recently evaluated by *Marufu et al.* [2000]. Emission magnitudes of sources that are specifically important to the tropics are given in Table 2. It is important to note that in the cur-

Table 2. Estimated 15-Year Average Global Emission Magnitudes of CO, NO_x and Nonmethane Hydrocarbons (NMHC) for Categories Relevant to the Tropics^a

Source Category	CO, TgC yr ⁻¹		NMHC, Tg yr ⁻¹		NO _x , TgN yr ⁻¹	
	Range	Avg	Range	Avg	Range	Avg
Biomass burning						
Savannah burning	68-77	73	13-15	14	2.6-2.9	2.8
Tropical deforestation	43-49	46	7-8	7.5	1.0-1.1	1.0
Temperate wildfires		46		4	1.6-0.8	1.2
Agricultural waste burning	87-94	89	13-15	14	2.2-2.4	2.2
Lightning					4.4-4.9	4.63
Agricultural soil					2.7-3.5	3.2
Natural vegetation/ soils		115		403	3	3

Here Tg=10¹² g. Data are from J.A. van Aardenne (see footnote to Table 1) and *Benkert* [1997].

^aNumbers in the table signify the range and average for 1979-1993.

rent study natural biomass burning emission distributions do not vary from year to year and that the same emission distribution is used in each year of our simulation. Therefore the effect of ENSO on ozone precursors is reflected only in different transport patterns, and not in enhanced burning in unusually dry areas or prolonged duration of the burning seasons [Chandra *et al.*, 1998; Fujiwara *et al.*, 2000].

3. Principal Component Analysis

A principal component analysis (PC analysis) is used to analyze variability of TTOC in the model data set. Since a detailed description of this technique can be found in most statistical analysis textbooks, we will limit ourselves to a short description. A comprehensive comparison between different variability analysis methods was published by Bretherton *et al.* [1992] and Kim and Wu [1999].

PC analysis (sometimes called empirical orthogonal function decomposition) is a tool to investigate spatial and temporal variability in a data set. It is based on the concept that the bulk of the variability in a data set is controlled by only a few physical processes, which modify the field on certain timescales with specific spatial patterns. PC analysis uncovers these patterns and their associated timeseries. The patterns are called empirical orthogonal functions (EOFs), while the time series are called principal components (PCs). The data set is decomposed into (latitude $\times$ longitude) EOFs, and individual EOFs and corresponding PCs from this technique might relate to a physical mechanism that caused the variability. Whether this is the case for any EOF has to be decided afterward. This can be done by relating the EOF pattern to a known physical process, but also by investigating the corresponding PC. The dominant frequency in the signal, and whether or not it correlates with a known time series (such as the ENSO index) can help to isolate the physical mechanisms. A similar technique was applied by Martin *et al.* [2000] to find patterns of variability in the annual cycles of TTOC.

A second analysis technique applied in this work is that of linear regression. We use the same linear regression model as described by Stolarski *et al.* [1991], Randel and Cobb [1994] and Ziemke *et al.* [1999], which is the following:

$$X(t) = \alpha(t) + \beta(t)t + \gamma(t)QBO(t) + \delta(t)solar(t) + \epsilon(t)ENSO(t) + R(t) \quad (1)$$

In (1), t is the index for the month ($t=1, 2, \dots, 180$, corresponding to January 1979 to December 1993). The equation simply states that a given signal $X(t)$ can be decomposed into contributions from five different proxies: a seasonal cycle (α), a linear trend (β), a contribution on the timescale of the quasi-biennial oscillation (γ), a contribution on the timescale of the solar cycle (δ), and a contribution on the timescale of ENSO (ϵ), plus a residual term $R(t)$. Each of these time-varying coefficients consists of a combination of 4-month, 6-month, and 12-month sine and cosine functions. For the proxies we have used the 10.7-cm solar flux series ($solar(t)$), the Singapore zonal winds at 30 mb ($QBO(t)$), and the Tahiti-Darwin pressure difference ($ENSO(t)$).

There are two important differences between PC analysis and more traditional linear regression techniques. First of all, in linear regression the most important physical mechanisms are defined in advance, and their temporal behavior is prescribed in the analysis using indicator functions (or proxies, see also Ziemke *et al.* [1997]). Second, linear regression analysis is performed by fitting curves to all the individual time series in the domain. In contrast, PC analysis is performed on the entire temporal and spatial domain at once, and both patterns and time series are selected for their ability to explain the variance of the complete domain. These two features make PC analysis more general than a linear regression. It must be noted that to gain confidence in our results, we also applied the linear regression model (1) to the modeled TTOC time series. These results do not differ much from those presented in section 6 and are not further discussed.

Before performing the PC analysis, we removed the seasonal cycle from the signal to isolate interannual components. This was done by subtracting the 15-year average annual cycle from the actual signal for each of the 15 years. By filtering the solar cycle, the results further improved, since the number of solar cycles (± 11 years) is too small in our 15-year data set to be isolated as an independent component of variability.

4. Tropopause Heights

The first step in calculating the model TTOC is the definition of the tropopause. In contrast to satellite retrieval methods that provide only limited information on the spatial distribution of the tropopause height, the model tropopause can be defined for every grid point using the temperature profile. The main problem is the poor vertical resolution at the tropopause. At the tropopause, model levels are typically spaced approximately 2 km apart, which makes gradient-based methods [Craig, 1965; Bethan *et al.*, 1996] unreliable. Craig [1965] suggested that the level where the lapse rate of temperature increases to -2 K km^{-1} is the best definition of the tropopause. However, with the coarse vertical resolution, this level would be at approximately 13 km, which is clearly too low compared to observations as described by Logan [1999] and Ziemke *et al.* [1999]. We defined the tropopause as the altitude where the temperature lapse rate becomes positive, since this is most consistent with the dynamics of the model and shows a reasonable agreement with the observations. The results are shown in Table 3 for stations Natal, Samoa, Brazzaville, and Ascension.

The tropical tropopause in our model seems generally too low by about 10–20 hPa. This may be due to an underestimate of the depth of convective penetration. For example, the tropical convective mass fluxes in the TM3 model reach somewhat lower heights compared to the European Centre Hamburg model version 4 (ECHAM-4) climate model [Dentener *et al.*, 1999]. The underestimate of the tropopause height by 20 hPa would lead to a 1.6 DU underestimate of TTOC, when assuming an ozone mixing ratio of 100 ppbv at the tropopause. When using other definitions of the tropopause, such as the level where the ozone mixing ratio

Table 3. Pressure at the Tropopause in the TM3 model, Compared to Climatological Values From *Logan* [1999] for Four Tropical Stations^a

Months ^a	Ascension		Natal		Brazzaville		Samoa	
	Model	Climatology	Model	Climatology	Model	Climatology	Model	Climatology
DJF	105.3	91	105.8	94	106.7	104	105.7	92
MAM	109.0	95	110.0	95	109.4	104	110.4	94
JJA	118.0	106	118.4	104	117.8	93	118.3	98
SON	114.6	95	116.0	102	115.3	102	115.4	100

^a Tropopause pressures reproduced from *Ziemke et al.* [1999]. Units are hectopascals.

^b DJF denotes December-January-February; other months follow in sequence.

is 100 ppbv, the thickness of the TTOCs varies slightly but it was found that this does not affect the results presented in section 6.

5. Tropical Ozone

Before investigating interannual variability in our 15-year model data set we assess the ability of the model to simulate the climatological tropical ozone distribution. Therefore

we have compared model-calculated monthly average ozone to ozonesonde observations from the climatology compiled by *Logan* [1999] for a number of stations. In case of a partial overlap between measurements and model, we used only the model simulations from the years reported in the *Logan* [1999] climatology. In case of no overlap at all (Panama), we used all years in our model climatology.

Figure 1 shows the comparison for three continental stations near the Atlantic Ocean ozone maximum [*Cros et al.*,

Figure 1. Annual cycles of ozone for stations Natal (35°W, 6°S), Ascension (14°W, 8°S) and Brazzaville (15°E, 4°S) at 900 hPa, 500 hPa, and 200 hPa. Solid lines represent the climatological values of *Logan* [1999], including the 1- σ standard deviation. Dash-dotted lines are the model-calculated values for the same stations and averaged over the same years (when possible). Standard deviations for the model are omitted for clarity.

Figure 2. As figure 1, for stations Samoa (171°W , 14°S), Hilo (155°W , 19°N) and Panama (80°W , 9°N)

1990; Kirchhoff and Rasmussen, 1990; Diab *et al.*, 1996], while Figure 2 shows three stations at locations in the Pacific region. Although we recognize the limited coverage over the Atlantic and Pacific Oceans by these stations, it appears to be sufficient for a first analysis. In the boundary layer (900 hPa), measurements and model simulations are in close agreement for all stations. The seasonality is captured well for all the stations, and differences are generally within the $1\text{-}\sigma$ standard deviation of the measurements. Only in months where the data coverage of the Logan [1999] climatology is less than 2 years do larger differences appear.

In the lower free troposphere (500 hPa), the model underestimates ozone volume mixing ratios (VMRs) throughout the year. For remote stations (Figure 2), this underestimate is of the order of 5–10 ppbv, while at Atlantic stations (Figure 1) it is even larger (10–20 ppbv). The largest discrepancies at Atlantic stations occur during the biomass burning season (July–September), when free tropospheric ozone VMRs are enhanced due to photochemical production of ozone. Although the model shows some enhancement of ozone VMRs in the early burning season, the underestimate during these months increases up to 20–40 ppbv. For stations Natal and Brazzaville, the model seems to perform best in the months of May and April, when pristine conditions occur during the

wet season. These conditions resemble the situation at more remote stations, for which the model generally performs better.

For the upper free troposphere (200 hPa), the model performs very well at the remote stations. The model captures both the seasonality and absolute values adequately. This contrasts with Atlantic stations, for which ozone VMRs are underestimated by 10–25 ppbv. The main differences between the Atlantic and Pacific stations at this altitude are the source region and level of photochemical processing (age) of pollutant emissions. Pacific stations are mostly influenced by upward transport of boundary layer air, which is ozone depleted and relatively pristine [Kley *et al.*, 1996]. Over the Atlantic Ocean, air masses have often resided in the upper troposphere for several weeks after being lifted over continents, and these air masses are aged before descending to lower altitudes [Krishnamurti *et al.*, 1993]. We suggest that during transport in the upper troposphere, these airmasses have become enriched with ozone. One possible mechanism for this is in situ production of ozone. Calculations with a stratospheric model indicate that O_2 photolysis can give rise to net ozone production at this altitude and latitude at an average rate of about 25 pptv/h (A. Bregman, personal communication, 2000). This corresponds to 4 ppbv per week, and

since this is not incorporated in our model, it could explain part of the discrepancy in the free troposphere over the Atlantic Ocean. Other possible ozone-enhancing mechanisms in the upper troposphere are photochemical ozone production in biomass burning plumes, stratosphere-troposphere exchange (STE), and lightning. We refer to the discussion of these topics in section 7.

6. ENSO Variability

The underestimate of free tropospheric ozone in part of the tropics is reflected in tropospheric ozone columns that are too low by about 2–10 DU compared to ozonesondes and satellite observations [Thompson and Hudson, 1999]. However, this underestimate is smallest over the Pacific (2–6 DU), where it is almost uniform with longitude. Therefore an analysis of interannual variability over the 15-year period should still reflect the influence of changing transport patterns during ENSO events, since it is mostly related to changing convection patterns over the Pacific. We first describe the structure of the El Niño–Southern Oscillation in TTOC, after which surface ozone variability for the Pacific station Samoa is compared to model calculations.

The modeled TTOC analyzed by means of PC analysis indicates that the most important source of interannual variability is related to ENSO. Plate 1 shows the first EOF in TTOC, and Figure 3 shows its corresponding PC. This EOF is responsible for approximately 22% of the interannual signal in our analysis of tropical TTOC. We have correlated the PC with the ENSO index ($r=0.55$, $N=180$) which confirms that this pattern is induced by ENSO. Similar to analysis of satellite data by Ziemke *et al.* [1999], we infer a dipole structure centered on the date line. This dipole anomaly is caused by a shift in the Walker circulation, which leads to anomalous convection over the eastern Pacific and subsidence over Indonesia.

The convective redistribution of ozone and water vapor leads to the reduced TTOC over the Pacific, while enhanced TTOC over Indonesia is related to enhanced transport from the tropopause region to lower altitudes. There is possibly a contribution of ozone production following lightning flashes in the deep convective clouds. This process would cause

an increase of ozone over the Pacific and a decrease over Indonesia during ENSO, contrary to the observed signal. In our model the lightning NO_x emissions in the eastern Pacific upper troposphere increase by ± 10 pptv/d during ENSO. This small increase of the emissions has only very little impact on the ambient NO_x concentrations (10–40 pptv), most likely because the formation rate and scavenging efficiency of HNO_3 also increase under convective conditions. We believe that the small magnitude and intermittent character of the lightning NO_x source over the oceans, together with a slow ozone production rate at the ambient NO_x concentrations [Jaeglé *et al.*, 1999] and fast transport of ozone in the upper troposphere, cause this process to have a negligibly small effect on TTOC during ENSO.

The amplitude of the oscillation in Plate 1 is approximately 3–4 DU over the eastern Pacific, and 2–3 DU over Indonesia. These values agree well with the ENSO oscillation found by Ziemke *et al.* [1999], who reported TTOC anomalies of 3–4 DU during El Niño and La Niña events, based on the 20-year TOMS TTOC record. The fact that the amplitude over Indonesia in the model (without a shift in biomass burning patterns) and the satellite observations agree well, indicates that although the 1997–1998 ENSO had a great impact, the influence of biomass burning is relatively small when an analysis is made over many years (1979–1993 for the model, 1979–1998 for the satellite observations). The observed TTOC enhancement of 20 DU reported by Chandra *et al.* [1998] seems to have been unique for the 1997–1998 ENSO.

In specific locations the ENSO signal is responsible for almost 60% of interannual variability. This can be seen in Plate 2 which shows the percentage of variability explained by the ENSO-PC at each individual model column in our analysis. The highest values are seen at the equator over the eastern Pacific, while over the western Pacific ENSO explains up to 30% of the interannual signal.

The remainder of the interannual signal is composed partly of a QBO-related signal (12%, see section 7), but the other EOFs could not be related to a physical mechanism. The fact that only a relatively small fraction of the interannual signal can be explained from our analysis is related to the long lifetime of ozone relative to transport, especially

Figure 3. Temporal behavior of the dominant pattern in Plate 1 (black line) and the El Niño–Southern Oscillation index (grey line). $r=0.55$, $N=180$

Plate 1. Dominant interannual variability pattern from a principal component analysis (PCA) of tropical tropospheric ozone columns (TTOC). The contours represent the maximum anomaly in Dobson units for each location of the domain.

in the free troposphere, and the fact that it is influenced by many different processes (e.g., lightning, STE, biomass burning, deposition). The local response of the ozone concentration to a change in these processes is nonlinear due to photochemistry. More importantly, atmospheric flow patterns provide a spatial coupling between these processes on a timescale of several days. Therefore the ozone concentration is very sensitive to changes in the meteorology, and displays relatively much high-frequency variability (noise) over the 15-year time period. Filtering out this high-frequency variability increases the variability explained by the ENSO and QBO related EOFs. However, for an interpretation of the relevance of the ENSO signal in TTOC, this ENSO signal should be interpreted relative to the meteorological variability; therefore we feel that the "unfiltered" numbers are the most objective.

By performing the PC analysis on different vertical regions, the three-dimensional structure of the ENSO influence was obtained. Table 4 shows the results. The correlation with the ENSO index, as well as the variance explained by the ENSO-EOF increase with altitude, indicates that there is less noise in the ozone signal in the upper troposphere. This is related to the larger distance from precursor sources at this altitude. Remarkably, the signal of TTOC shows a higher correlation with the ENSO index than the parts separated by altitude. This means that noise at different heights in the column cancel out, giving a "cleaner" ENSO signal for the entire vertical domain. This is also reflected in the sum of the signals at different heights, which does not equal the TTOC signal.

The signal over the eastern Pacific is quite evenly distributed with height. This suggests that the signal is rapidly

transported throughout the column, as can be expected under convective conditions during El Niño. Over Indonesia the signal is clearly stronger in the free troposphere than in the boundary layer, in agreement with prevailing downward transport during El Niño. The anticorrelation between the eastern Pacific and Indonesia is strong at all altitudes, clearly connecting the two regions through the Walker circulation.

The PC analysis of both our model and of satellite data suggests that a significant fraction of interannual variability over the Pacific Ocean can be related to ENSO. Samoa (171°W, 14°S) is one of the few measurement stations located in the Pacific Ocean with a long surface ozone record. It has been shown from an analysis of surface CH_3CCl_3 concentrations [Prinn *et al.*, 1992] that interannual variability at Samoa is influenced by ENSO. Next, we address the question of whether ENSO variability is also detectable in surface ozone values.

Figure 4 shows the surface ozone record for Samoa (1979–1992) and the model-calculated surface ozone (1979–1993). The time series of model-calculated surface ozone for Samoa corresponds very well to observations (see also Lelieveld and Dentener [2000]). The deviations from the seasonal cycle in Figure 5 display a very noisy signal, which we ascribe to changes in local meteorology associated with the influence of synoptic systems. Nevertheless, the model seems to capture most features of this signal quite well.

A linear regression was performed on the surface ozone time series from measurements and model, using the previously mentioned linear regression model. As expected, the annual cycle contains about 80% of the variance of the data set for both time series. Apart from high-frequency variability, there is a 6% contribution from ENSO (Figure 5). The

Plate 2. Percentage of interannual variability explained by the ENSO-related EOF.

Table 4. The ENSO Signal at Different Heights in the Troposphere

	PCA Statistics ^a		Signal Strength ^b			
	r ($N=180$)	percentage	Eastern Pacific		Indonesia	
			Dobson Units	Dobson Units per kilometer	Dobson Units	Dobson Units per kilometer
Boundary Layer (0–1.4 km)	0.44	10	-0.31	-0.22	+0.08	0.06
Lower Free Troposphere (1.4–7.1 km)	0.45	15	-1.28	-0.22	+1.18	0.21
Upper Free Troposphere (7.1–16.0 km)	0.50	30	-1.53	-0.17	+1.21	0.13
Total tropospheric Ozone Column	0.55	22	-2.23	-0.14	+1.98	0.12

^aStatistics shown are the correlation of the principal component with the ENSO index and percentage of the signal explained by the ENSO related empirical orthogonal function for the entire tropics.

^bOzone anomalies during El Niño over the eastern Pacific (120°W, Eq) and Indonesia (120°E, Eq).

correlation between the modeled and measured linear regression signal is excellent ($r=0.93$, $N=180$). The signal shows an increase in surface ozone of about 2 ppbv during the 1983 ENSO. The increase in other ENSO years is smaller (± 1 ppbv), while the decrease during the 1989 La Niña is quite pronounced. In agreement with the analysis by *Oltmans and Levy* [1994], a small but statistically significant component of variability related to QBO was obtained.

To ensure that the ENSO signal is not an artifact of the linear regression technique, we also performed a PC analysis on the surface ozone field of the model in the tropics. Although ENSO variability does not dominate the ozone field at the surface, we obtain a high correlation between the ENSO-PC and the measurements ($r=0.57$, $N=180$). However, the absolute amplitude in the PC analysis was smaller than in the linear regression because this technique has more

Figure 4. Time series and annual cycle of surface ozone at station Samoa (171°W,14°S). Grey lines represent the measurements; black lines are the model calculations. Measurements are by courtesy of the National Oceanic and Atmospheric Administration (NOAA) and S. Oltmans [Oltmans and Levy, 1994].

Figure 5. The (top) interannual variability ($r=0.61$, $N=168$) and (bottom) ENSO signal ($r=0.93$, $N=168$) in surface ozone at station Samoa (171°W , 14°S) obtained by linear regression. Grey lines represent the measurements; black lines represent the model calculations.

degrees of freedom (latitude $\times$ longitude), and is based on many more concurrent time series. Yet, the fact that both statistical techniques yield an increase of surface ozone during ENSO emphasizes the robustness of the results.

The increase in surface ozone contrasts with the behavior of TTOC at Samoa, which slightly decreases during ENSO. The explanation for this is that surface ozone measured at Samoa has normally resided in the marine boundary layer for an extended period. The strong inversion at the top of the marine boundary layer isolates sampled air masses from the free troposphere where ozone mixing ratios are higher. During an El Niño, anomalous convection in the vicinity of Samoa mixes free tropospheric air to lower altitudes [Lu *et al.*, 2000], thus increasing ozone mixing ratios toward the surface. For the entire tropospheric column, however, transport of ozone-poor air and increased photochemical destruction of ozone [Kley *et al.*, 1996] dominate over downward transport of ozone-rich air [Lelieveld and Crutzen, 1994], which explains the TTOC decrease during an El Niño event.

7. Discussion

Many processes in our model contribute to uncertainties in the simulation of ozone. Sensitivity analyses have shown that it is not possible to isolate a single process responsible for the free tropospheric ozone underestimate in the model.

The comparison with observations at 500 hPa nevertheless clearly shows that the model underestimates ozone, which is likely caused by an underestimate of the effects of biomass burning in combination with convective transport and associated lightning NO_x . Owing to the relatively long lifetime of ozone in the upper troposphere, this might also explain part of the discrepancy in other months and at higher altitudes. Other possible causes for the ozone underestimate are the previously discussed omission of the O_2 photolysis, and other shortcomings of the chemistry scheme such as too low in situ lightning NO_x production, or a misrepresentation of stratosphere-troposphere exchange at low latitudes. We will briefly discuss some of these uncertainties and indicate possible directions for future research.

The CBM-IV mechanism we use was originally developed for studies of tropospheric photochemistry under polluted conditions. Houweling *et al.* [1998] have improved the description of several biogenic compounds in the mechanism, as well as the performance under unpolluted (low NO_x) conditions. Nevertheless, the reaction rates and branching ratios used in the mechanism are mostly biased toward freshly polluted conditions. Although this will have an impact on the performance of the scheme at larger distances from the sources, the overall effect on the upper tropospheric ozone concentrations will probably be localized and relatively small. A similar argument can be made for the effects

of trace gases that are not included in the model, such as acetone and several hydroperoxides and alkylnitrates. Sensitivity studies using more elaborate schemes indicated that the effect on ozone of using such a scheme in GCMs, was very local and less than 10% (R. von Kuhlmann and G.J. Roelofs, personal communication, 2000).

Recent discussions of the influence of tropical biomass burning on ozone, NO_x , and CO were presented by *Galanter et al.* [2000] and *Marufu et al.* [2000]. The latter authors focused on African biomass burning emissions in the same model as used in this study. However, the current work includes extended time series and covers larger regions than *Marufu et al.* [2000].

Large uncertainties exist in emission estimates of NO_x from fires, and the discussion of whether these emissions can directly influence the free troposphere has not been resolved. It is possible that biomass burning plumes are NO_x depleted before they reach the free troposphere due to rapid formation of HNO_3 or by deposition at the surface. Ozone production from this direct NO_x source would then occur close to the fires only, unless NO_x would be recycled or added to the aged plume. Conversion of HNO_3 on soot aerosols has been suggested; however, *Disselkamp et al.* [2000] showed that this process is not important under atmospheric conditions. A much more likely candidate is the NO_x produced from lightning, which has been shown to significantly influence tropospheric ozone concentrations [*Lamarque et al.*, 1996; *Martin et al.*, 2000; *Lelieveld and Dentener*, 2000]. However, the emission strength and distribution of NO_x from lightning are highly variable and poorly quantified [*Pickering et al.*, 1993; *Levy et al.*, 1996; *Price et al.*, 1997; *Pickering et al.*, 1998].

Distributions and magnitudes of NO emissions, but also of other important tropospheric compounds (CO, nonmethane hydrocarbons) are highly variable in both time and space. They often depend on many parameters, including meteorological conditions. Concerning biomass burning, arid regions can shift from one year to the next, and the onset and duration of the biomass burning season change from year to year. The model includes the biomass burning emission distribution of *Hao et al.* [1990] for the entire period, without interannual or geographical variability. This emission database was constructed on a coarse resolution ($5^\circ \times 5^\circ$), which implies that local differences in timing and magnitude of the sources are not included. A comparison of the *Hao et al.* [1990] emission data set with satellite observations showed that the timing of the burning peak is not always accurate [*Cooke et al.*, 1996]. This was confirmed by *Galanter et al.* [2000], who also mentioned the relatively long duration of the biomass burning season in the *Hao et al.* [1990] data. The overall effect is that emissions are more widespread temporally, which leads to lower peak values of ozone in the model.

To analyze emission-related uncertainties further, we performed several sensitivity studies. By varying the magnitude of NO_x emissions from biomass burning and lightning, and the emission altitude of biomass burning products, we tried to improve the comparison in section 5. Although the com-

parison sometimes improved locally, the situation at other stations would deteriorate, in agreement with similar experiments conducted by *Galanter et al.* [2000]. This suggests that the cause of the underestimate is a combination of several poorly modeled processes, but it also leaves open the possibility of an ozone-producing mechanism in biomass burning plumes that is not understood at the moment.

In the tropical upper troposphere, stratosphere-troposphere exchange contributes significantly to the ozone budget [*Lelieveld and Dentener*, 2000]. Besides the suggested role of O_2 photolysis, transport by STE can also be a direct source of ozone to the tropical upper troposphere [*Baray*, 1999; *Zachariasse et al.*, 2000]. The current contribution of STE to the tropical ozone budget in our model is controlled by horizontal transport from the extratropics. In our simulation the stratospheric contribution to ozone VMRs is smaller over the Atlantic than over the tropical Pacific Ocean. This contrasts with the situation in the subtropics. A. Kentarchos et al. (Altitude distribution of tropospheric ozone over the Northern Hemisphere during 1996, simulated with a high resolution chemistry-GCM, submitted to *J. Geophys. Res.*, 2000) showed that the influence of STE is greater at Izaña (Tenerife, 3°E , 26°N) than at Hilo (155°W , 19°N) because filaments of stratospheric air can penetrate further equatorward in the gradual subsidence over the Atlantic Ocean than over the convective Pacific. It is therefore quite possible that we currently underestimate horizontal transport of filaments of ozone-rich air to the tropical Atlantic region. Based on analysis of ozonesonde data from Indonesia, *Fujiwara et al.* [2000] also suggested a stratospheric source of ozone in the tropics. Although tropopause-folding events do not occur in the tropics [*Elbern et al.*, 1996], a direct tropical source due to compensation of deep convective overshoots by downward transport of stratospheric air should be considered [*Tuck et al.*, 1997; *Lu et al.*, 2000; *Fujiwara et al.*, 2000]. For now, the underestimate of free tropospheric ozone over the Atlantic Ocean remains a problem that requires further study.

On the other hand, detection of the ENSO signal in a modeled chemical tracer is a very promising result. Other studies have suggested a possible influence of ENSO on measurements during El Niño years, while a quantification of this influence was impossible due to a lack of spatial coverage of the measurements. The results presented in this work suggest that multiyear model simulations can offer an alternative. Although the presence of the ENSO signal in our model is introduced by the off-line ECMWF reanalysis, effects of convection, changing UV fluxes, and photochemistry are calculated on-line by the model. The fact that all of these processes play an important role in the ozone abundance, and that the ENSO signal was found both in surface ozone data and in TTOC, motivates the extension of our model efforts to other trace gases.

Apart from ENSO, *Ziemke et al.* [1999] also found a contribution by the quasi-biennial oscillation to interannual variability over the Atlantic Ocean. They showed an anticorrelation between stratospheric and tropospheric ozone columns on the timescale of QBO, which they suggested to

be caused by changing UV fluxes to the troposphere during QBO. An increase (decrease) in stratospheric column ozone would lead to a decrease (increase) in UV flux, causing a decrease (increase) in ozone. This implies that the photochemical regime over the Atlantic Ocean causes net ozone production. They stressed the important role that three-dimensional photochemical models could play in further study of this phenomenon. In our model the stratospheric QBO is reflected well in the wind fields, and application of the TOMS upper boundary conditions ensures that upper stratospheric ozone is modeled adequately. Our model results indicate that this introduces a 20% fluctuation in tropospheric ozone photolysis rates on the timescale of QBO, which leads to a small (1–2 DU) QBO signal in the troposphere. In contrast to the results of Ziemke *et al.* [1999], this signal correlates positively with the stratospheric QBO, indicating that a net ozone destruction regime prevails in our model. This suggests that our model underprediction of free tropospheric ozone is related to underestimated in situ photochemical formation rather than transport from the stratosphere. A further analysis of the QBO signal has been planned for the future, since we first want to investigate the accuracy of our stratospheric ozone relaxation method for the tropics (see section 2), as it was shown to work well for middle and high latitudes.

8. Summary and Conclusions

We presented model simulations of tropospheric column ozone for 1979–1993 based on 15 years of ECMWF meteorological reanalyzed data and an emission data set that accounts for the temporal development of anthropogenic emissions. From a comparison of the results with ozonesondes in the Logan [1999] climatology, we identify an ozone VMR underestimate, which is most pronounced over the Atlantic Ocean at higher altitudes in the troposphere and during the biomass burning season. The model captures surface ozone values and seasonal cycles of ozone in the tropics well. Owing to the underestimate of free tropospheric ozone and an underestimate of tropopause heights, TTOC is underestimated by 2–10 DU. This does not affect interannual variability, and the model reproduces observed signals of ENSO in the 15-year TTOC record. The ENSO signal in model-calculated tropospheric ozone columns is very similar in structure and amplitude (3–4 DU) to that observed in tropospheric ozone retrieved from satellites. Furthermore, an analysis of the ENSO signal in surface ozone at station Samoa showed excellent agreement between measurements and model. This consistency of the model-calculated ENSO signal with two independent data sets lends credibility to the ability of the model to capture effects of ENSO on the ozone concentration, and the underlying processes, that is convective redistribution of ozone within the troposphere. Besides improvement of the simulation of tropical ozone over the Atlantic Ocean, future work will focus on the three-dimensional structure of the ENSO signal, as well as the ENSO signal in other important trace gases (CO and hydrocarbons, including CH₄). The quantification of this vari-

ability will be an important consideration when analyzing tropical trace gas measurements.

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F. Dentener, Joint Research Centre, Environment Institute, I-21020 Ispra (Va), Italy, (e-mail: frank.dentener@jrc.it)

M. Krol and W. Peters, Institute for Marine and Atmospheric Research Utrecht, P. O. Box 80005, NL-3508TA Utrecht, Netherlands, (e-mail: M.Krol@phys.uu.nl; W.Peters.phys.uu.nl)

J. Lelieveld, Max Planck Institut für Chemie, Joh.-J.-Becherweg 27, D-55128, Mainz, Germany, (e-mail: lelieveld@mpch-mainz.mpg.de)

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