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Significance of long-range transport from continental locations in determining oxidant mixing ratios and budgets over the tropical Pacific Ocean

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ABSTRACT

Our project with EPA is aimed at further development and applications with the three-dimensional chemical-transport model, MOZART, we are developing in coordination with Guy Brasseur and others at NCAR. The primary objective of the calculations to be presented here is to evaluate the impact of long-range transport from continental source regions on the oxidative capacity of the troposphere using this model. Transport from the Eastern United States and Western Europe is known to significantly influence the north Atlantic and biomass burning in South America on the southern Atlantic Ocean the oxidant mixing ratios. More recently the influence of the Pacific rim countries and south and Central America on the northern tropical and southern tropical Pacific and southern Asia on the tropical Indian oceans oxidant mixing ratios has been under intensive investigation. We use results from the MOZART (Version 2) to evaluate the impacts of long-range transport from the Pacific rim countries and south and central America on the oxidant levels over the tropical Pacific Ocean. Measurements made by NASA during the past decade in the North-Central and Southern tropical Pacific will be used for evaluating the model results. Key questions addressed include evaluation of the factors controlling the ozone budget in the tropical pacific, and determination of the significance of transported fluxes of ozone and precursors into the tropical pacific basin from source regions in the western Pacific rim countries, west coast of USA, Mexico and biomass burning in south America and Africa.

INTRODUCTION

Our STAR program project with the U.S. Environmental Protection Agency (EPA) is aimed at further development, testing, and applications with the three-dimensional chemical-transport model, MOZART of the global atmosphere. This model is of particular interest to EPA for its potential to address key issues such as the long range transport of pollutants, concerns about global scale tropospheric and stratospheric ozone, and concerns about climate change. Along with further development and testing of the MOZART model in coordination with Guy Brasseur (now at the Max Planck Institute in Hamburg) and with colleagues at the National Center for Atmospheric Research, we have already used the model to examine concerns about future emissions of short-lived brominated gases that can affect stratospheric ozone (1), an issue of special interest to EPA. In this study, the objective is to evaluate the impact of long-range transport from continental source regions on the oxidative capacity of the troposphere using this model. The focus in this study is the south Pacific region because of the availability of data from the PEM-TROPICS A (PT-A) and PEM-TROPICS B (PT-B) campaigns. The South Pacific Basin likely represents the cleanest region of the tropical troposphere, making a

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detailed baseline survey of great importance. However, initial studies during these campaigns indicated much higher ozone levels than originally expected, suggesting that the region is being influenced by long range transport of pollutants.

Ozone is a product of atmospheric chemistry and also is a useful indicator of precursor trace gas emissions into the troposphere from anthropogenic and natural sources. The impact of anthropogenic emissions on the chemistry of the atmosphere has been evaluated in terms of ozone (2). It was shown that ozone is not only a key component of smog, but also a significant and pervasive constituent in the chemistry of the troposphere. The primary net source of ozone in to the troposphere is the subsidence of stratospheric air and its primary net sink is the physical removal at the surface of the earth by dry deposition. The gross production and loss terms due to chemical reactions in the atmosphere are larger than these net production and loss terms by factors of 4 to 5, though the net increase in ozone due to the chemical process is expected to be much smaller than stratospheric import (3).

The impact of anthropogenic emissions on the chemistry for the different regions of the atmosphere is currently under evaluation based on limited data sets collected in the recent past and modeling activity. The main focus of the NASA PEM (Pacific Exploratory Mission) program is to evaluate the atmospheric conditions in selected remote locations in the Pacific using aircraft platform based measurements in collaboration with limited ground level data sets. Data collected during these measurement campaigns provide a snapshot of the atmospheric conditions prevailing in these regions during the limited time periods (typically 1 to 2 months). Developing relationship of these limited data sets to seasonal and climatic variability of the atmosphere is also important. This can be done by either performing extensive comparison of these data sets with few available long-term monitoring for limited number of species, such as ozone and carbon monoxide, or using global scale models for generating chemical climatology. Here we employ the latter approach to evaluate the ozone budgets in the southern tropical Pacific Ocean and identify the key control factors in the model and compare it with the measurements. PT-A and PT-B field measurement experiments conducted by NASA under the GTE program offer such an opportunity by providing us with a database of intensive measurements of ozone and its precursors in the tropical southern Pacific during two different periods of the year. PT-A was conducted during August-October of 1996 in what would be the spring period in the Southern Hemisphere and PT-B was conducted during the fall period of March-April 1999.

MODEL DESCRIPTION

The latest version (version 2) of the global-scale 3-D chemistry-transport model MOZART (**M**odel for **O**zone **a**nd **R**eactive **T**race gases; the original version of the model described in reference 4) was used to analyze the PT-A and PT-B measurements and compare the measurements with results calculated from the model by using dynamic inputs generated with a climate model. A 0-D box photochemical model with a local equilibrium assumption was also developed and used to calculate the ozone production and loss tendencies for comparison with numbers generated by the 3-D model. Below is a

brief description of the models used.

MOZART Model

The 3-D GCTM MOZART (version 2) has an approximate horizontal resolution of 2.8° latitude by 2.8° longitude and extends vertically from the surface to approximately 38 km. Physical variables (wind fields, pressure, temperature, and convection) derived from the NCAR Community Climate Model version 3 (CCM3) are stored every 3 hrs and used to run the CTM off-line (although eventually the models could be coupled for more detailed studies of the interactions between climate and atmospheric chemistry). The vertical grid resolution varies from60 meters near the surface to approximately 2 km at the top of the model domain.

Advective transport of the trace gases is simulated by using the flux-form semi-Lagrangian formulation of a Eularian scheme ofLin and Rood (5. This algorithm is conservative and upstream biased. In addition, it contains monotonic constraints and conserves tracer correlations. The chemistry scheme currently includes 107 gas-phase, 5 heterogeneous,and 29 photochemical reactions affecting global scale tropospheric chemistry. Heterogeneous reactions involving N_2O_5 and NO_3 on ammonium sulfate and other particles are included. Wet and dry deposition rates are included as first-order loss processes. Both in- cloud and below-cloud scavenging of trace gases are included. For highly soluble gases, below-cloud scavenging by raindrops is also included. Dry deposition is specified as a sum of species independent aerodynamic resistance and a species- dependent surface resistance. The CTM has fluxes for anthropogenic and biogenic emissions prescribed according to the EDGAR data base. The model provides spatial and temporal distributions for 52 species at present.

Box Model

The box photochemical model is based on the our 2-D zonal averaged model of the global atmosphere. The current version has 72 species, 132 thermal reactions, and 52 photolysis rates. The model has full representation of CH_4, C_2H_6, and C_3H_8 chemistries, condensed set of reactions for isoprene, C_2H_4 and C_3H_6. The model can treat heterogeneous chemistry and includes N_2O_5, $BrNO_3$ and $ClNO_3$ reactions on sulfate aerosol. In addition, it has a full representation of ClOx, BrOx, HOx and NOx chemistries. The photolysis rates are calculated by using a two-stream radiative transfer model with 128 bins for calculating absorption cross sections ranging from 170 -450 nm.

MODEL ANALYSES

In this study, we use the MOZART 3-D model for three separate runs. A one-year run with mixing ratios, fluxes and chemical tendency terms saved once a day was initially carried out. Results from this run were used to initialize two additional runs: one for the August-September period and the second for the March-April period in accordance with PT-A and PT-B time. Results from these runs were saved at a much higher frequency at once every hour for comparison with the PT-A and PT-B measurements.

The box-photochemical model was used to calculate the photochemical production and loss tendencies of ozone with constraints on radiation and trace gas mixing ratios measured from the PT-A and PT-B data sets. The one-minute averaged merged data files generated by the Harvard research group were used to make the calculations. Below is a detailed description of the results from these calculations.

Results

Figure 1 shows the modeled and measured profiles of ozone at Fiji in the southern tropics. A typical data points from Fiji for the SHADOZ program of ozone sonde measurements would include several launches in a month for 2 to 5 years. In general, the model is in good agreement with the data for both spring and fall seasons. MOZART is slightly under-estimating mid-tropospheric ozone during the months of March/April in Fiji.

Figure 1. SHADOZ ozone sonde profiles, compared with MOZART (v2) calculations for Fiji.

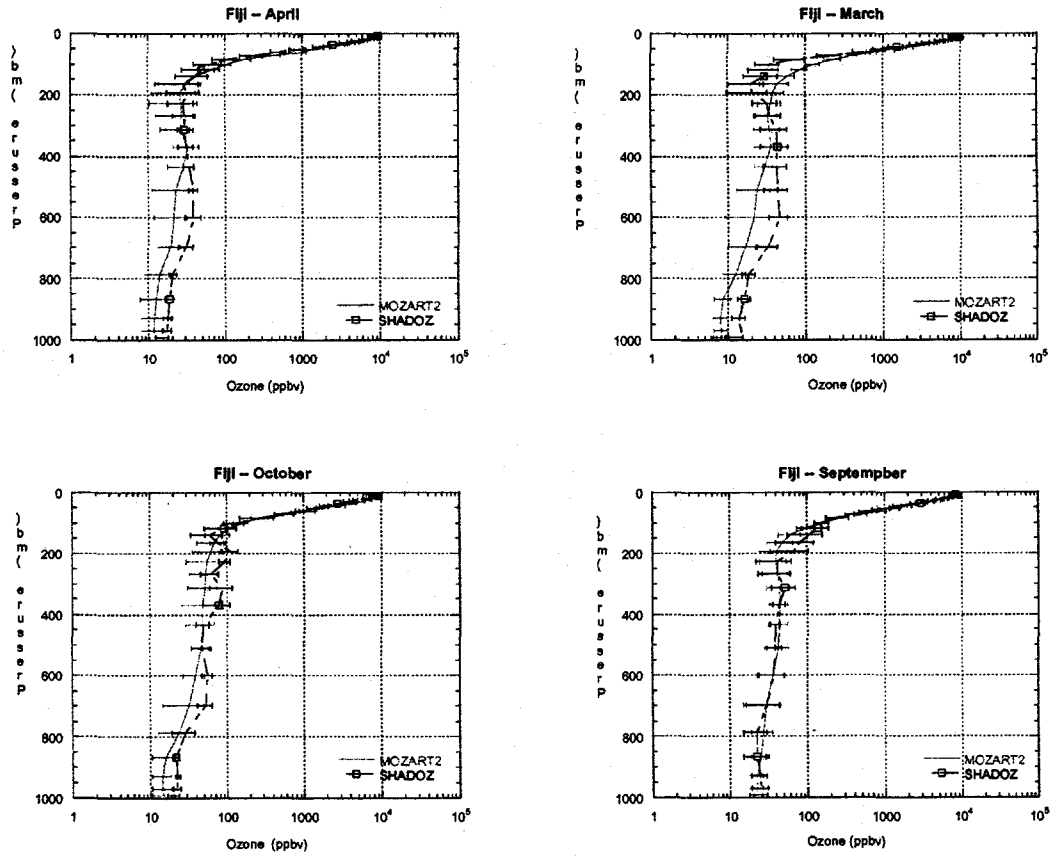
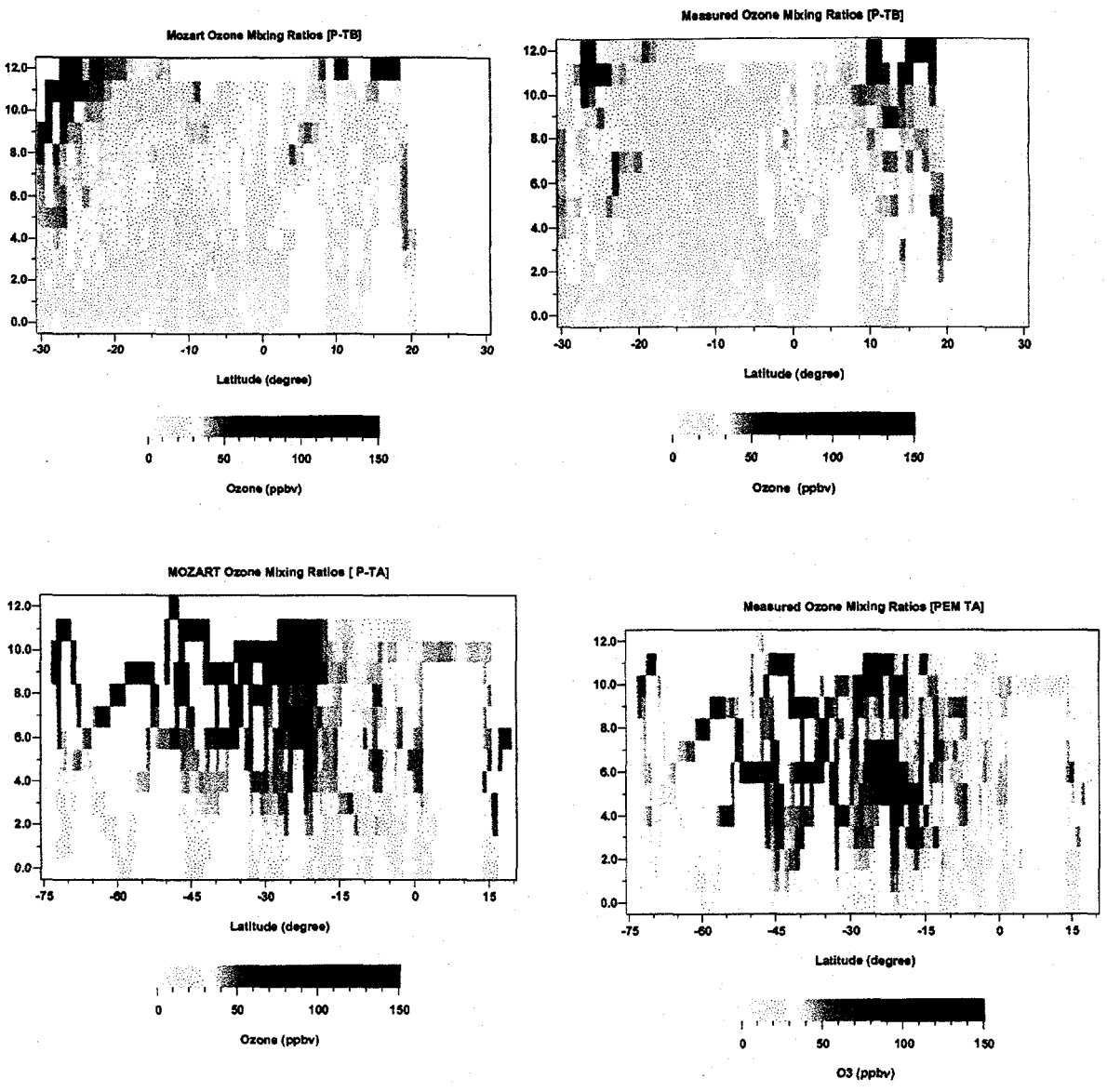


Figure 2 shows the ozone mixing ratio from MOZART and that measured during the PT-B (Fig 2a) and PT-A (Fig.2b) periods as a function of latitude and altitude. The model

was sampled in the same way as the data from the aircraft flights. If there are several data points in a particular altitude-latitude bin, the average of these values is used for plotting. In Fig 2a, the results from the model calculation is able to reproduce the relatively low ozone values throughout the depth of the troposphere in the tropical Southern Hemisphere; however, several pockets of high ozone in the data set at 10-12 km are not captured in the model. These pockets of high ozone represent episodes of long-range transport of ozone from East Asia to the northern tropical Pacific and possibly from South Africa or South America to the extra tropical regions of the South Pacific (5).

Figure 2. (a) top panels, MOZART calculated ozone (average, left panel) for March and April and sampled at the same locations from DC-8 aircraft flights during PT-B (right panel); (b) bottom panels, MOZART calculated ozone (average, left panel) for September and sampled at the same locations from DC-8 flights during PT-A (right panel).



In Figure 2b for the PT-A period, the model result shows only a slight elevation in ozone mixing ratios in the 25 to 15 S latitudes as compared to the significant elevations in the observed data set. Based on sensitivity studies with the model, the reason for this difference may be due to underestimation of the biomass burning sources of pollutants from South America and from the southern tip of Africa. A similar comparison of model results with PEM-TROPICS data was performed for CO as an indicator of biomass/anthropogenic influence on the air masses. In general, there is an excellent agreement between the model calculated and measured CO for this period, although again there appears to be an underestimation of the biomass burning sources used in the model.

Advective, convective, and diffusive fluxes across each of the grid boundaries were calculated and saved once every hour for the limited in time calculations for the March/April and August/September model calculations. The mass change in each of the grid cells due to processes in the model, such as due to chemical production and chemical

loss were also saved as one hour averages for these calculations. The fluxes derived from the model were analyzed for the central pacific zone and defined as follows. The central Pacific region (CP) extends from 165 E to 120 W longitudes and from 30 N to 30 S latitude. The boxes were further divided in the vertical plane in to the lower tropospheric box extending from 0 to 2 km, mid tropospheric box extending from 2 to 7 km and upper tropospheric box extending from 7 to 12 km. Table 1 lists the model calculated fluxes averaged over a month in the central Pacific region for both PT-A and PT-B periods. Overall, the model is able to simulate the pattern of general circulation in this region. For example, the lower tropospheric box (surface layer) ozone fluxes are directed from east to west, whereas the mid-tropospheric box (MT) and upper tropospheric box (UT) the flux direction is from east to west in alignment with the prevailing wind directions of subtropical jet. The diagram also shows ozone subsidence in this region for the vertical fluxes. As a result, there is a net ozone increase in the central Pacific mainly due to zonal transport mechanisms.

Table 1: Central Pacific Region (165E~135W, 30N~30S) Fluxes Analysis

Monthly Averaged Fluxes (kg/sec)		Directional Fluxes						Processes.				
		West	East	South	North	Bottom	Top	Adv	Depos	Conv.	Diff	Chem
PEM-Tropics A (Sep.)	UT	22,470	20,340	-2,402	-1,896	-1,718	-972	877.6	216.9	-1,268	4.329	917.3
	MT	6,486	4,144	-1,456	-2,424	-2,589	-1,718	2,440	174	-1,443	-2.824	-1,262
	LT	-3,059	-5,060	-28.52	-754.5	0	-2,589	5,316	75.78	2,715	-1,287	-6,584
PEM-Tropics B (Mar.)	UT	18,840	27,650	-1,550	-10,510	-654.9	-1,221	710.2	301.4	-1,906	6.303	650
	MT	4,551	5,678	-694	-3,484	-571.6	-654.9	1,746	157.2	-62.86	-1.879	-1,554
	LT	-2,674	-4,219	-69.02	-1,465	0	-571.6	3,512	95.56	1,972	-1,029	-4,167

Net Fluxes		Latitudinal	Longitudinal	Vertical	% change = (B-A)/A x100%	E-W	N-S	Vert.
PEM-Tropics A (Sep.)	UT	2,130	-506	-746	UT	-514%	1871%	176%
	MT	2,342	968	-871				
	LT	2,001	726	2,589	MT	-148%	188%	110%
PEM-Tropics B (Mar.)	UT	-8,810	8,960	566.1				
	MT	-1,127	2,790	83.3	LT	-22.8%	92%	-78%
	LT	1,545	1,396	571.6				

Note:

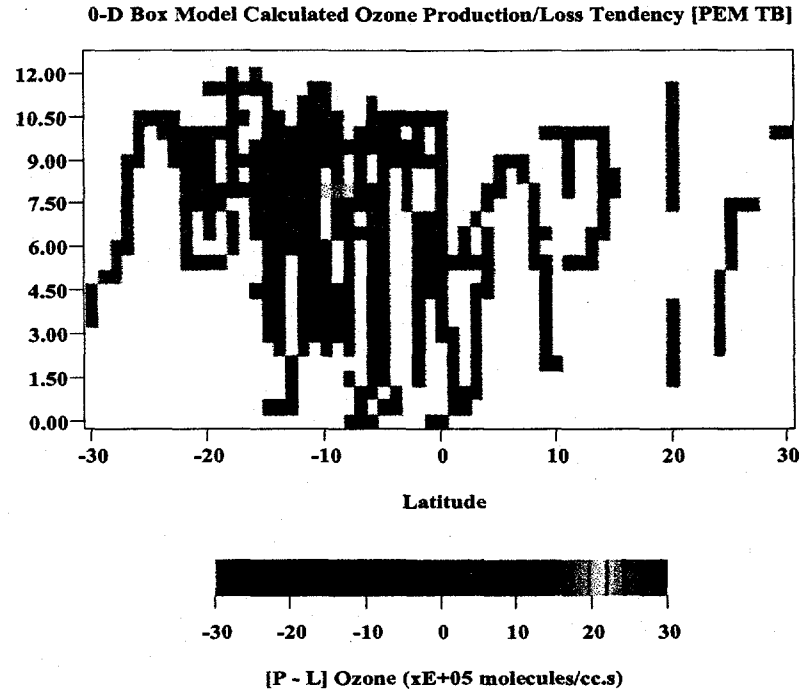
UT: Upper tropospheric Box (7~12 km), MT: Middle tropospheric Box (2~7 km), LT: Lower tropospheric Box (0~2 km)

Adv: Advective Flux
Depos.: Depositional Flux
Conv.: Convective Flux
Diff.: Diffusive Flux
Chem.: Chemistry Rate

Figure 3 presents the results of odd oxygen (O_x) production/loss term from the box-model and the MOZART 3D model for the PT-B period as a function of altitude and latitude for the Southern Hemisphere. The box model analyses use the observed concentrations of other important constituents in deriving the ozone production and loss terms. Overall, the

3D model has the same tendency as the box model results for most of the altitude and latitude bins. However, the model is much less likely to produce ozone in the upper troposphere (8-12 km) than the data from the box model. As we have seen in other analyses of the MOZART model, this is likely due to the model deriving levels of NOx that are too low in comparison with observations.

Figure 3. 0D box model (upper panel) and MOZART(lower panel) calculated ozone production/loss tendency for the period of PT-B.



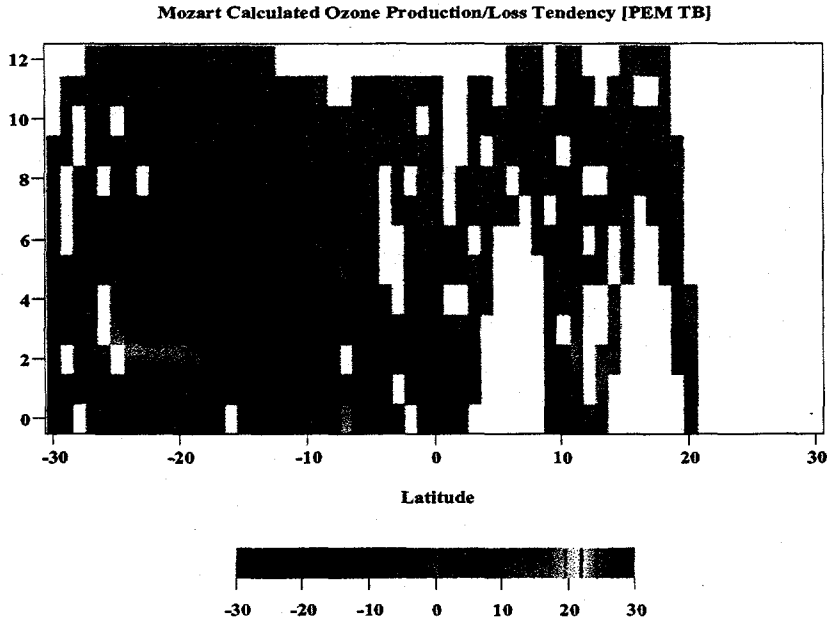
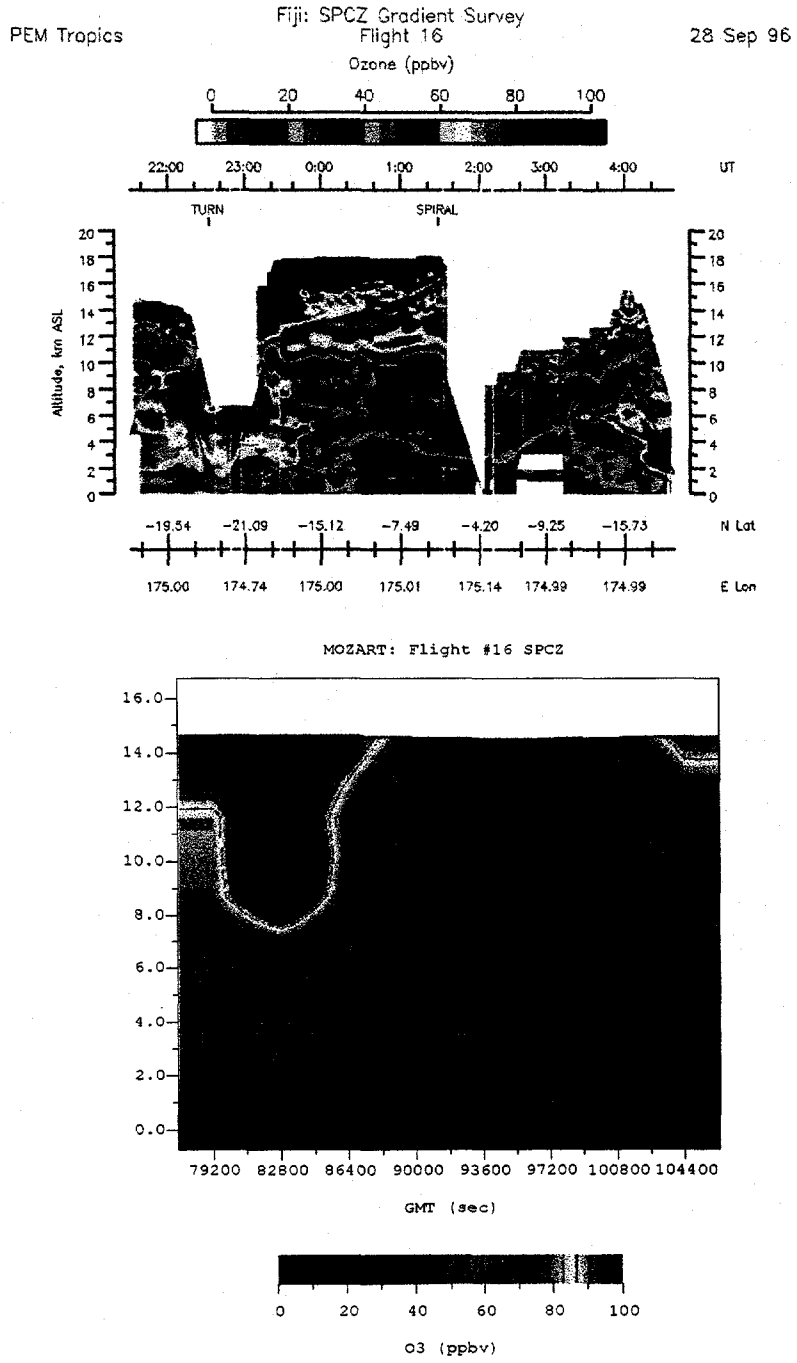


Figure 4 shows the flight 16 data from PT-A and model calculated comparison for analysis of the South Pacific Convergence Zone (SPCZ). Basically, the model is able to distinguish a well-defined SPCZ as compared to the observation, and the stratospheric intrusion at around 20 degree south from the lidar measurement is also captured in the model. Thus this inversion may be a climatological feature for this time of year in the SPCZ region.

Figure 4. Ozone profile from Flight 16 in PT-A (upper panel) and MOZART calculation (lower panel)



CONCLUSIONS

A 3-D GCTM was used to analyze the significant seasonal variations in the concentrations of ozone observed in the southern tropical Pacific during the PT-A (spring) and PT-B (fall) measurement campaigns. Diurnal average ozone values from a one-year model calculation were used for comparison with measured ozone profiles at SHADOZ ozone sonde measurement sites. The model shows considerable skill in reproducing the observed ozone profiles, including the seasonal variability. Another set of model calculations was performed for the period s August-September and March-April corresponding to the PT-A and PT-B periods, respectively, to produce additional hourly diagnostic outputs, including ozone fluxes across the model grid surfaces and *in situ* production and loss for the O_x group. The O_x production and loss tendencies were also calculated by using a 0-D box photochemical model constrained with observations. Results were compared with MOZART-calculated values. In general, the various analyses indicated that transport of pollutants from East Asia and from biomass burning sources in South America and southern Africa all play a significant role in explaining the ozone observed over the South Pacific Basin.

Fluxes of ozone across grid boundaries were computed and analyzed for the PT-A and PT-B periods. In general, the period corresponding to PT-B in the model experienced much stronger north-south flux transport of ozone than did the PT-A period. The budget analysis reveals a net decrease in the ozone burden in the box during the PT-B period, reflecting the net loss in ozone from east-to-west fluxes, compared to a net increase during the PT-A period from this zonal transport mechanism. The grid-scale net vertical fluxes for both the PT-A and PT-B periods in the central Pacific are negative, implying subsidence of ozone in this region. However, the strength of this subsidence in the model is much smaller during the PT-B period than in the PT-A period and is smaller by a factor of 3.5 for the LT box in PT-B than in PT-A. The subgrid convective flux during PT-B was entirely a result of deep convection taking air from the LT box to the UT box. The same analysis for the PT-A period shows an even distribution of convective exchange between the LT and the MT boxes and the LT and UT boxes.

The O_x production and loss tendencies calculated from the 3-D model were compared with those from a box photochemical model constrained with PT-A and PT-B measurements. Overall, the 3-D GCTM shows the same tendency (i.e., production or loss) as the box model results for most of the altitude and latitude bins. However the model is much less likely to produce ozone in the upper troposphere (8- 12 km) than the data. This pattern partially results from low NOx in the model compared to measurements for the PT-B period in these altitudes. This observation is also reflected in the higher-than-measured net destruction rates of O_x in the middle and lower troposphere.

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