Ozone production in transpacific Asian pollution plumes and implications for ozone air quality in California

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[1]   We examine the ozone production efficiency in transpacific Asian pollution plumes, and the implications for ozone air quality in California, by using aircraft and surface observations in April–May 2002 from the Intercontinental Transport and Chemical Transformation 2002 (ITCT 2K2) campaign off the California coast and the Pacific Exploration of Asian Continental Emission–B (PEACE-B) campaign over the northwest Pacific. The observations are interpreted with a global three-dimensional chemical transport model (GEOS-CHEM). The model reproduces the mean features observed for CO, reactive nitrogen oxides (NO_y), and ozone but underestimates the strong (~20 ppbv) stratospheric contribution to ozone in the middle troposphere. The ITCT 2K2 aircraft sampled two major transpacific Asian pollution plumes, one on 5 May at 5–8 km altitude with CO up to 275 ppbv but no elevated ozone and one on 17 May at 2.5–4 km altitude with CO up to 225 ppbv and ozone up to 90 ppbv. We show that the elevated ozone in the latter plume is consistent with production from peroxyacetylnitrate (PAN) decomposition during subsidence of the plume over the northeast Pacific. This production is particularly efficient because of the strong radiation and low humidity of the subsiding environment. We argue that such PAN decomposition represents a major and possibly dominant component of the ozone enhancement in transpacific Asian pollution plumes. Strong dilution of Asian pollution plumes takes place during entrainment in the U.S. boundary layer, greatly reducing their impact at U.S. surface sites. California mountain sites are more sensitive to Asian pollution because of their exposure to the free troposphere. Model results indicate a mean Asian pollution enhancement of 7 ppbv ozone at Sequoia National Park in May 2002 on those days when the 8-hour average ozone concentration exceeded 80 ppbv.   INDEX TERMS: 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); KEYWORDS: ozone, Asian pollution, ITCT 2K2, PEACE-B, transpacific transport

1.   Introduction

[2]   Rapid industrialization of the Asian continent may have important implications for global tropospheric ozone [*Berntsen et al.*, 1997; *Gupta et al.*, 1998; *Wild and Akimoto*, 2001] and surface ozone air quality in the United States [*Jacob et al.*, 1999; *Fiore et al.*, 2002]. Several aircraft campaigns over the NW Pacific (PEM-West, TRACE-P, BIBLE, PEACE) have characterized the Asian outflow of ozone and its precursors [*Hoell et al.*, 1996, 1997; *Jacob et al.*, 2003; *Kondo et al.*, 2002; *Parrish et al.*,

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2004b]. The PHOBEA aircraft campaigns over the NW coast of the United States observed a number of transpacific Asian pollution plumes with elevated carbon monoxide (CO) and dust, and with variable enhancements of ozone [*Jaffe et al.*, 1999, 2003a, 2003b; *Price et al.*, 2003, 2004; *Bertschi et al.*, 2004]. The ITCT 2K2 aircraft campaign [*Parrish et al.*, 2004b], conducted in April–May 2002 off the California coast, provided a detailed chemical characterization of these transpacific Asian pollution plumes including ozone, its precursors, and a number of other species. The PEACE-B mission conducted concurrently out of Japan characterized the outflow of ozone and its precursors from the Asian continent [*Parrish et al.*, 2004b]. We use here a global three-dimensional (3-D) model of tropospheric chemistry to interpret the ITCT 2K2 and PEACE-B observations in terms of ozone production during transpacific transport of Asian pollution, and to assess the implications for surface ozone air quality in the United States.

[3] Ozone (O_3) is produced in the troposphere by the photochemical oxidation of CO and volatile organic compounds (VOCs) in the presence of nitrogen oxides ($NO_x \equiv NO + NO_2$). Transport from the stratosphere is also a source of tropospheric ozone, much less important on a global scale but responsible for large ozone enhancements in regions of subsidence [*Cooper et al.*, 2002]. Loss of ozone is mostly photochemical, with lifetimes ranging from as short as a few days in the boundary layer to several months in the upper troposphere [*Wang et al.*, 1998]. Tropospheric production of ozone is limited in general by the supply of NO_x [*Chameides et al.*, 1992], which is emitted by combustion, microbial processes in soils, and lightning. Anthropogenic emissions from fuel combustion and biomass burning account presently for 75% of the global NO_x emissions of 52 Tg N yr^{-1} according to *Ramaswamy et al.* [2001]. *Streets et al.* [2003] estimate that the present-day anthropogenic NO_x emission from Asia is 8.2 Tg N yr^{-1}, accounting for 20% of the global anthropogenic source. Future emission projections from *Ramaswamy et al.* [2001] estimate a 50–100% rise in Asian anthropogenic NO_x emissions from 2000 to 2020, while North American and European emissions are most likely to decrease. Understanding the impact of Asian NO_x emissions on ozone is therefore a matter of great interest.

[4] A critical issue in relating NO_x emissions to global ozone production is the fraction of emitted NO_x that is ventilated out of the continental boundary layer [*Jacob et al.*, 1993]. Oxidation of NO_x to nitric acid and peroxyacetylnitrate (PAN) in the boundary layer takes place on a timescale of a few hours. The ozone production efficiency per unit NO_x consumed (OPE) decreases as the NO_x concentration increases [*Liu et al.*, 1987], hence ozone production within the continental boundary layer is relatively inefficient because of the high-NO_x conditions. Nitric acid is removed rapidly by deposition, but PAN (which is thermally unstable and not water-soluble) can be vented from the boundary layer and transported on a global scale at cold temperatures, eventually decomposing to release NO_x as air masses subside. The resulting NO_x produces ozone with high efficiency because background NO_x concentrations are low. Aircraft observations in Asian and North American outflow indicate that 5–10% of emitted NO_x is

ventilated out of the boundary layer as PAN [*Koike et al.*, 2003; *Li et al.*, 2004; *Parrish et al.*, 2004a]. Observations of aged Asian plumes over the tropical Pacific during the TRACE-P campaign have offered the first evidence of ozone production driven by PAN decomposition [*Heald et al.*, 2003]. We will use here the ITCT 2K2 observations to examine the contribution of this mechanism to elevated ozone in plumes reaching the United States.

[5] We will also use a combination of ITCT 2K2 and surface ozone data to examine how transpacific pollution plumes subsiding from the free troposphere can affect U.S. ozone air quality. Model simulations suggest that surface ozone in the western United States in April–May is enhanced by 3–6 ppbv on average as a result of Asian anthropogenic emissions [*Jacob et al.*, 1999; *Yienger et al.*, 2000]. Surface observations in that region and season indicate a significant rise of background ozone over the past two decades [*Lin et al.*, 2000; *Jaffe et al.*, 2003c]. Transpacific transport of Asian ozone pollution mainly takes place in the free troposphere where winds are strong and the ozone lifetime is long [*Liang et al.*, 2004; *Price et al.*, 2004]. Observations from the PHOBEA campaigns show that Asian pollution plumes in the free troposphere over the U.S. West Coast can contain large ozone enhancements, up to 27 ppbv [*Jaffe et al.*, 2003a; *Price et al.*, 2004]. This raises the issue of whether such enhancements could be observed in surface air as the plumes subside, with possibly important implications for meeting air quality standards. We will address that issue here.
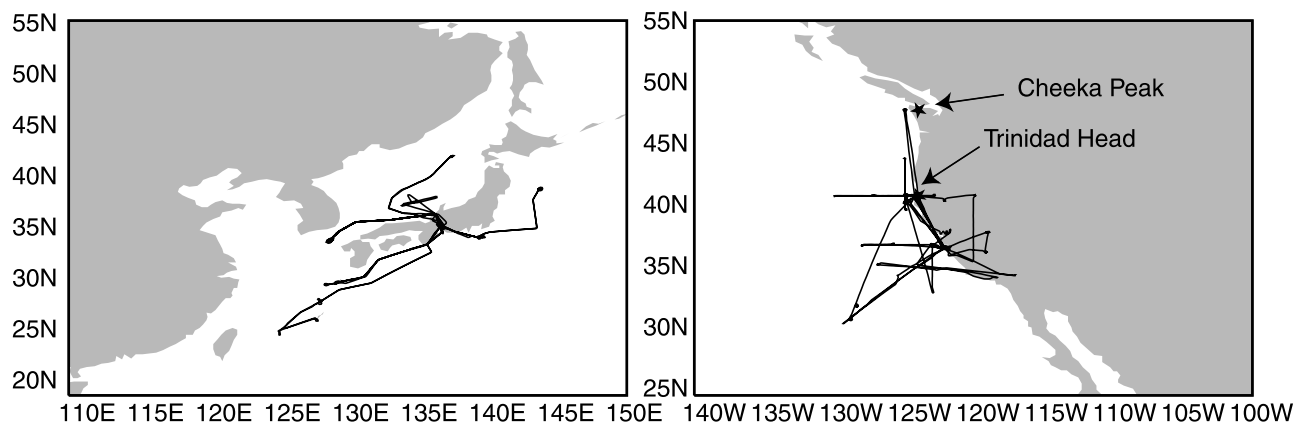
2. Observations

[6] The Japanese PEACE-B campaign took place from 21 April to 17 May 2002 over the NW Pacific out of Tokyo (Figure 1). It used a Gulfstream-II aircraft with a ceiling of 14 km and equipped with instrumentation for CO, ozone, NO, NO_2, NO_y (sum of NO_x and its gas-phase oxidation products), and speciated hydrocarbon concentrations [*Parrish et al.*, 2004b]. This mission characterized Asian outflow and offered upwind information for interpretation of ITCT 2K2 data.

[7] The NOAA ITCT 2K2 campaign took place from 22 April to 19 May 2002 over the NE Pacific and the western United States out of Monterey, California (Figure 1). It used a WP-3D aircraft (ceiling 8 km) equipped with extensive chemical instrumentation [*Parrish et al.*, 2004b]. We make use here of 1-min average measurements of ozone, CO, NO, NO_2, HNO_3, PAN, NO_y, acetonitrile, and total aerosol number concentrations. Ground-based measurements, including daily ozonesondes, were made at Trinidad Head in northern California [*Goldstein et al.*, 2004; *Oltmans et al.*, 2004]. Additional aircraft measurements out of Seattle, Washington were made by the PHOBEA 2002 campaign from 29 March to 23 May 2002 [*Bertschi et al.*, 2004] including measurements of ozone, CO, aerosols, and speciated hydrocarbons.

3. Model Description

[8] We use the GEOS-CHEM global three-dimensional model of tropospheric chemistry (version 6.03; http://www.as.harvard.edu/chemistry/trop/geos/) driven by assim-

Figure 1. Flight tracks for the PEACE-B and ITCT 2K2 aircraft campaigns. The locations of Trinidad Head and Cheeka Peak are also shown.

ilated meteorological observations from the Goddard Earth Observing System (GEOS-3) of the NASA Global Modeling and Assimilation Office (GMAO). The model is applied to a global simulation of O_3-NO_x-VOC chemistry including a fully coupled H_2SO_4-HNO_3-NH_3-H_2O aerosol mechanism. A general description of the GEOS-CHEM model is given by *Bey et al.* [2001a] and a specific description of the coupled oxidant-aerosol simulation as used here is given by *Park et al.* [2004]. A full listing of the chemical mechanism is available from the above web site.

[9] Meteorological fields in the GEOS-3 data have a temporal resolution of 6 hours (3 hours for surface variables and mixing depths) and a horizontal resolution of $1° \times 1°$, with 48 vertical sigma levels between the surface and 0.1 hPa (including about 20 in the troposphere and 9 in the boundary layer up to 2 km). For input to GEOS-CHEM we degrade the horizontal resolution to $2° \times 2.5°$. The simulations are conducted for April–May 2002 and are initialized on 1 April 2002 with GEOS-CHEM fields generated by an 18-month spin-up simulation with $4° \times 5°$ resolution.

[10] Transport of ozone from the stratosphere is simulated using the "Synoz" (Synthetic Ozone) flux boundary condition of *McLinden et al.* [2000], in which a constant net ozone source of 495 Tg ozone yr^{-1} is applied in the tropical upper stratosphere and transported downward by the model. One enforces in this manner a cross-tropopause flux of 495 Tg ozone yr^{-1}, consistent with observational constraints [*McLinden et al.*, 2000], with the location and timing of this flux determined by the model transport. The Synoz flux boundary condition corrects globally for the factor of 2–3 excessive cross-tropopause transport of air in the GEOS fields [*Liu et al.*, 2001], which appears to be due to noise in vertical winds resulting from the data assimilation [*Tan et al.*, 2004]. However, cross-tropopause transport of ozone in preferred regions of downwelling may then be underestimated to compensate for the excess of transport elsewhere. This appears to affect our simulation of the PEACE-B and ITCT 2K2 data, as discussed in the next section.

[11] We use a global anthropogenic emissions inventory for 1998 (the last year of available statistics) as described by *Bey et al.* [2001a]. The global fossil fuel NO_x emissions are 26 Tg N yr^{-1}. Of these the United States contribute 6.3 Tg N yr^{-1} and Asia contributes 8.8 Tg N yr^{-1}. The global lightning source is 6 Tg N yr^{-1}. Biofuel emissions

are as described by *Yevich and Logan* [2003]. Biomass-burning emissions are climatological means as described by *Duncan et al.* [2003], with the addition of large fires in Siberia identified from satellite data [*Bertschi et al.*, 2004]. Plumes from these fires affected the PHOBEA observations off the Washington coast but did not extend sufficiently far south to affect the ITCT 2K2 observations [*Bertschi et al.*, 2004; *de Gouw et al.*, 2004].

[12] GEOS-CHEM has been applied previously to investigate the Asian outflow of ozone and its precursors in spring [*Bey et al.*, 2001b] and in other seasons [*Liu et al.*, 2002], as well as the transpacific transport of CO and ozone [*Heald et al.*, 2003; *Jaeglé et al.*, 2003]. It has also been used to examine background ozone over North America in spring, both in surface air [*Fiore et al.*, 2003] and in ozonesonde data [*Li et al.*, 2002b]. Extensive comparisons to observations presented in these papers show no obvious model biases for features of interest here except for an overestimate of background HNO_3 [*Bey et al.*, 2001a; *Li et al.*, 2004]. Other applications of GEOS-CHEM to analysis of the PEACE-A, PEACE-B and ITCT 2K2 data, using the same version of the model as is used here, are presented by Y. Kondo et al. (manuscript in preparation, 2004) for source attribution of NO_y in Asian outflow, *Goldstein et al.* [2004] for interpretation of ozone and CO time series at Trinidad Head, *Liang et al.* [2004] for study of transpacific transport of CO, and *Bertschi et al.* [2004] for the impact of Siberian fires on transpacific transport. We will refer to these studies in the context of our analysis.

[13] We present results from two principal simulations. The first is our standard simulation as described above. The second is a sensitivity simulation without Asian anthropogenic emissions (i.e., excluding fossil fuel, biofuel, and biomass-burning emissions), which allows us to derive Asian pollution enhancements in the standard simulation by difference. We also conduct a CO-only simulation using archived OH concentrations from the standard simulation, and including 10 tagged CO tracers to resolve source regions contributing to transpacific transport [*Bey et al.*, 2001b]. Finally, we conduct single-tracer simulations of odd oxygen (O_x = O_3 + NO_2 + $2NO_3$ + $3N_2O_5$ + HNO_3 + HNO_4 + peroxyacylnitrates), using archived 3-D fields of daily production rates and loss frequencies from the above simulations, to resolve the ozone source regions. This ozone
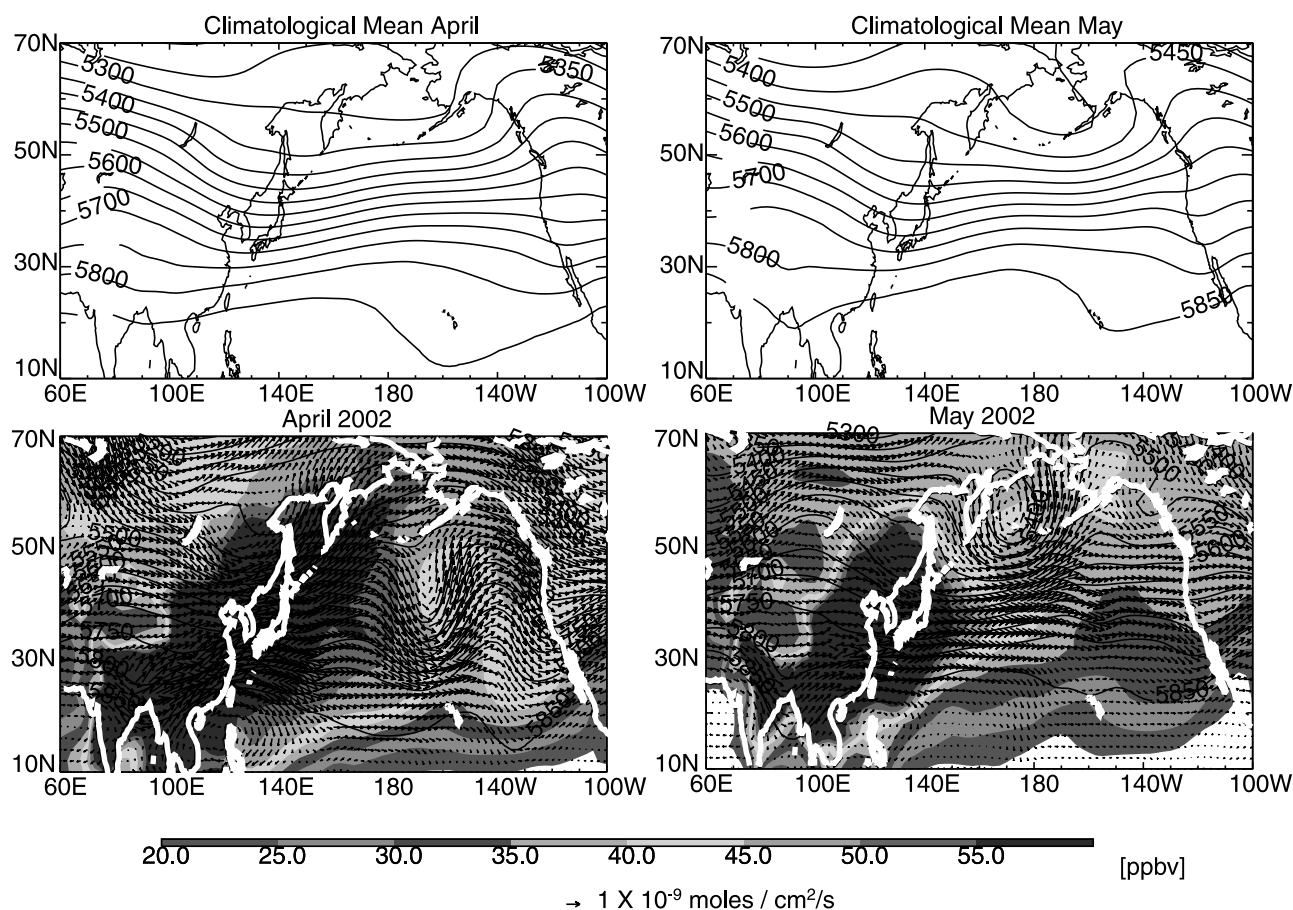
Figure 2. Mean patterns of transpacific transport of Asian pollution in April–May. The top panels show NCEP climatological values (1948 to present) of geopotential heights (m) at 500 hPa. The bottom panels show conditions for 2002 including NCEP geopotential heights at 500 hPa (line contours) and GEOS-CHEM model results for the Asian anthropogenic CO tracer: fluxes in the surface to 150 hPa column (arrows, moles/cm^2/s) and mean mass-weighted concentrations in the 0–6 km column (solid contours). See color version of this figure at back of this issue.

tracer technique was first described by *Wang et al.* [1998] and has been applied since in a number of GEOS-CHEM studies [e.g., *Li et al.*, 2002a].

4. Mean Transport Patterns and Concentrations

[14] Asian outflow to the Pacific is particularly strong in spring because of frequent cyclonic activity and associated warm conveyor belts (WCBs) that sweep across east Asia and lift pollution to the free troposphere and into the westerlies [*Stohl*, 2001; *Liu et al.*, 2003; *Miyazaki et al.*, 2003]. Figure 2 shows contours of 500 hPa geopotential heights over the Pacific in April–May, for the long-term climatology and for year 2002. The climatology shows zonal flow from Asia to the United States. The May 2002 flow is indeed near zonal but the April 2002 flow has strong meridional structure, with a ridge at 160°E present for most of April that deviated Asian outflow to higher latitudes and then split it into northern and southern branches over the NE Pacific.

[15] Also shown in Figure 2 are the simulated column concentrations and fluxes of Asian anthropogenic CO, i.e., CO emitted from fuel and biomass burning. Asian pollution in April was mostly directed toward Alaska and Canada by

the mid-Pacific ridge. The fraction that circulated around the ridge then encountered a persistent trough at 160W that resulted in further dilution. Over the month of April only one weak Asian pollution plume was observed by the ITCT 2K2 aircraft [*Nowak et al.*, 2004] and none was observed at the Trinidad Head site [*Goldstein et al.*, 2004], although several events were observed at the Cheeka Peak site on the Washington coast [*Liang et al.*, 2004]. We see from Figure 2 that the Asian pollution traversing the Pacific at high latitudes in April is eventually transported south over the United States, but by then it has lost much of its structure and represents effectively an enhanced background. In May, the normal zonal flow resulted in several Asian pollution plumes with CO > 190 ppbv observed by the ITCT 2K2 aircraft [*Nowak et al.*, 2004]. However, background CO levels are lower than in April because of higher OH concentrations and hence faster chemical loss. Thus we find greater average Asian CO influence over the United States in April than in May (Figure 2).

[16] Figure 3 compares simulated and observed mean vertical profiles of CO, NO$_y$, and ozone concentrations in the PEACE-B data north of 30°N, where the bulk of observations were made. Here and elsewhere, model results are sampled along the flights tracks at the time of the flights,
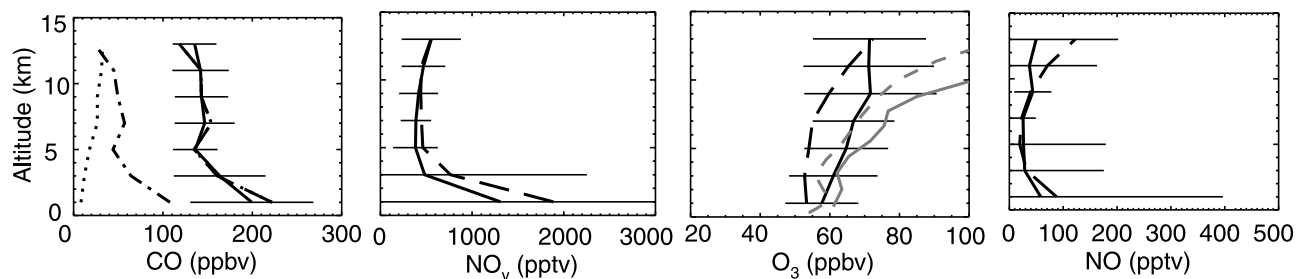
Figure 3. Vertical profiles of CO, NO$_y$, ozone, and NO concentrations for the ensemble of PEACE-B flights north of 30°N (Figure 1) covering the period 21 April to 17 May 2002. Observations are shown as solid lines (means for ozone and CO, medians for NO and NO$_y$, with standard deviations about the means shown as horizontal lines). Mean model results sampled along the flight tracks are shown as dashed lines. The CO panel also shows model results for the Asian fuel tracer (dash-dotted line) and the Southeast Asian biomass-burning tracer (dotted line). The ozone panel also shows mean ozonesonde measurements (May climatology in the period from January 1985 to December 2000, 38 profiles, solid grey line) and May 2002 mean model profile (dashed grey line) for Tateno, Japan (36°N, 140°E). The measurements are averages of ozonesondes, obtained from World Ozone and Ultraviolet Data Center (WOUDC) at http://www.msc-smc.ec.gc.ca/woudc.

and observations are averaged over the model gridboxes. The CO observations show strong Asian outflow below 4 km altitude, a minimum at 5 km, and a secondary bulge at 5–9 km. The model reproduces these features. The tagged CO tracers in the model indicate that most of this structure is due to Asian fossil fuel outflow, although biomass-burning outflow from Southeast Asia lifted in WCBs and in deep convection makes a significant contribution in the upper troposphere (Figure 3). The Siberian fires have negligible impact on the CO concentrations observed in PEACE-B.

[17] Observed concentrations of NO$_y$ also decrease rapidly with altitude but do not show a secondary bulge at 5–10 km. This is again captured by the model and reflects the scavenging of inorganic nitrate (HNO$_3$ gas and NO$_3^-$ aerosol) during moist lifting in WCBs [*Koike et al.*, 2003; *Miyazaki et al.*, 2003]. As a result NO$_y$ in the free tropo-

sphere is not correlated with CO, either in the model or in the observations, although PAN in the model is correlated with CO (Figure 4). The PEACE-B aircraft made no measurements of PAN. Observed NO shows similar structure and is well simulated by the model except for an overestimate above 10 km.

[18] Mean ozone increases with altitude, both in the model and in the observations; the model is about 10 ppbv too low. A similar discrepancy is found in ITCT 2K2 profiles and appears to be partially due to stratospheric influence, as discussed further in the context of the ITCT 2K2 comparison. Strong transport from the stratosphere to the troposphere is known to take place over Japan in association with tropopause folding along the strong jet stream located over Japan [*Austin and Midgley*, 1994; *Stohl*, 2001]. Figure 3 also shows mean May ozone profiles at Tateno, Japan (36°N, 140°E), from ozonesonde observa-
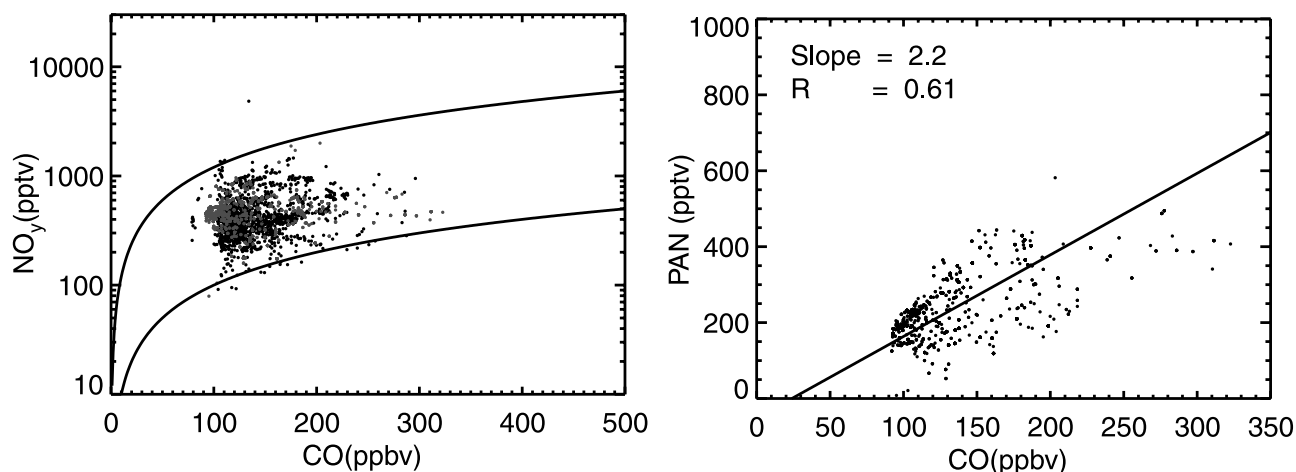
Figure 4. Relationship of NO$_y$ with CO concentrations at 2.5-10 km altitude over the NW Pacific during PEACE-B. The left panel shows NO$_y$ versus CO in the aircraft observations (red) and in the GEOS-CHEM model (black). Curves correspond to NO$_y$/CO ratios of 1 and 12×10^{-3} mol mol^{-1}. The right panel shows PAN versus CO in the model sampled along the PEACE-B flight tracks (no measurements of PAN were made on the aircraft). See color version of this figure at back of this issue.
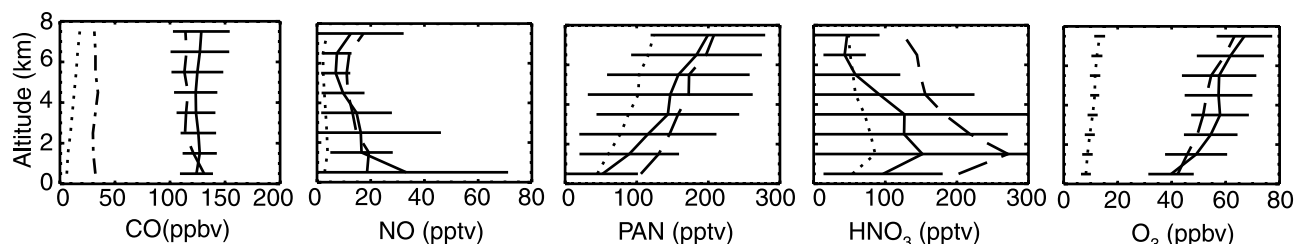
Figure 5. Mean vertical profiles of CO, NO, PAN, HNO_3, and ozone concentrations for the ensemble of ITCT 2K2 flights covering the period 22 April to 19 May 2002, excluding data with local pollution influence or collected in the stratosphere (see text). Observations (solid lines, with standard deviations as horizontal bars) are compared to model results sampled along the flight tracks (dashed lines). The CO panel also shows model results for the Asian fuel tracer (dash-dotted line) and the Southeast Asian biomass-burning tracer (dotted line). The other panels show as dotted lines the simulated Asian anthropogenic enhancements, as determined by the difference from results from a sensitivity simulation with Asian anthropogenic sources turned off.

tions (climatology) and from the model. The model is too low by 5 ppbv in the free troposphere, a bias that is consistent though smaller than for the PEACE-B data.

[19] Figure 5 compares simulated and observed mean vertical concentration profiles of CO, NO_y components, and ozone along the ITCT 2K2 aircraft flight tracks. In this comparison we have excluded data from transit flights, flights targeted at local ship and urban plumes (flights 7, 10, and 13), observations in the continental boundary layer (CBL) over land, fresh combustion plumes (diagnosed by aerosol concentrations higher than 2000 cm^{-3} and either NO or NO_2 greater than 500 pptv), and stratospheric air (diagnosed by O_3 > 100 ppbv and CO < 100 ppbv). The profile of CO is featureless, both in the model and in the observations; observations average 125 ppbv in the 0–8 km column and the corresponding model average is 8 ppbv too low. Higher CO concentrations, averaging above 150 ppbv at 3–6 km altitude, were observed by the PHOBEA 2002 campaign off the coast of Washington State. These higher values were mainly due to three fire plumes of Siberian origin [*Bertschi et al.*, 2004]. By contrast, we find negligible Siberian fire influence along the ITCT 2K2 flight tracks. Asian fossil fuel combustion contributes 32 ppbv CO on average at all altitudes in the model. Biomass burning in Southeast Asia is far less important, although its influence increases with altitude up to 18 ppbv at 8 km because of lofting over the source region by deep convection [*de Gouw et al.*, 2004].

[20] Mean observed concentrations of NO observed in ITCT 2K2 range from 33 pptv in the boundary layer (with high variability) to 6 pptv at 6 km. As shown in Figure 5, these values are well reproduced by the model. The Asian anthropogenic enhancement is 3 pptv, as determined by difference with a sensitivity simulation with this source shut off. PAN concentrations increase with altitude, up to 200 pptv at 8 km, because of the strong thermal dependence of the lifetime. The model reproduces this trend but is too high, by 10–20% in the free troposphere. Asian anthropogenic emissions enhance PAN by about a factor of 2 at all altitudes. Nitric acid concentrations are highest in the lower free troposphere, both in the model and in the observations, for reasons previously discussed by *Staudt et al.* [2003] in their analysis of aircraft observations over the Pacific in the

PEM-Tropics B campaign. Model values for HNO_3 are a factor of 2 too high, a problem apparent in previous global simulations of HNO_3 concentrations in the remote troposphere, both in GEOS-CHEM [*Bey et al.*, 2001a] and in other models [*Hauglustaine et al.*, 1998; *Mickley et al.*, 1999; *Horowitz et al.*, 2003; *Rotman et al.*, 2004]. Insufficient scavenging may be an explanation. This has little implication for the simulation of NO_x since HNO_3 is mainly removed by deposition and provides only a minor recycling source for NO_x even in subsiding air masses [*Staudt et al.*, 2003].

[21] Mean ozone concentrations observed in ITCT 2K2 increase with altitude, from 40 ppbv near the surface to 67 ppbv at 8 km altitude, reflecting the strong subsidence over the northeastern Pacific. The model shows a similar gradient but is slightly low, by up to 6 ppbv at 4 km altitude. The Asian pollution enhancement in the model ranges from 8 ppbv in the boundary layer to 13 ppbv at 8 km.

[22] We compare model results in Figure 6 to the mean daily ozonesonde profiles at Trinidad Head during the ITCT 2K2 period. The model is 10 ppbv too low in the lower free troposphere, a pattern of discrepancy that is similar but somewhat larger than that found in the aircraft data. Inspection of the ozonesonde data for individual days indicates that the model underestimate is due to its failure to reproduce high-ozone layers of stratospheric origin. 75% of the observed ozonesonde profiles show high-ozone layers (enhancements > 10 ppbv) at 1–5 km altitude, and the majority of these layers appear to originate from the stratosphere (based on low humidity, back-trajectories, and potential vorticity). This is illustrated in Figure 7 with data for two particular days featuring stratospheric ozone enhancements of about 30 ppbv in the lower free troposphere. The model reproduces qualitatively these layers, as indicated by the stratospheric ozone tracer profile, but the enhancement is a factor of 2–3 too low, consistent with the expected model bias in resolving stratospheric layers (section 3). The mean simulated concentration of the stratospheric ozone tracer over Trinidad Head ranges from 5 ppbv in the boundary layer to 15 ppbv at 8 km altitude (Figure 6). As shown in Figure 6, scaling up this stratospheric contribution by a factor of 2 in the model would correct
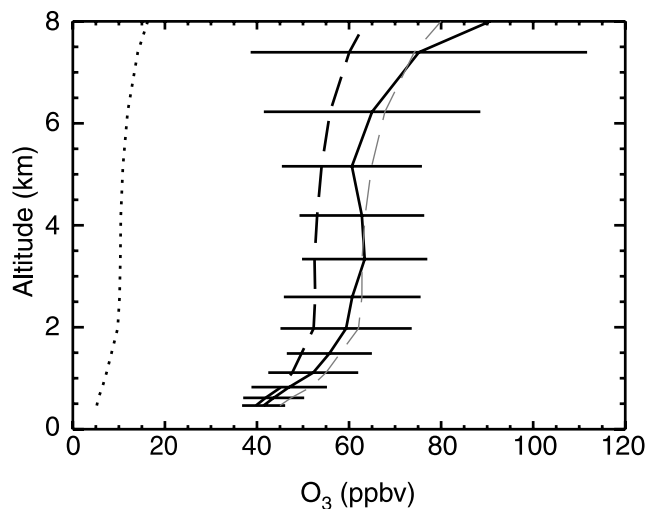
Figure 6. Mean ozone concentration profile over Trinidad Head, California, during the ITCT 2K2 campaign. The solid line shows statistics (means and standard deviations) of daily ozonesonde data for the period 17 April to 17 May 2002. The black dashed line shows the corresponding model results. The dotted line shows the stratospheric contribution to the model concentrations as determined from the stratospheric ozone tracer (see text). The grey dashed line shows the model results with the stratospheric contribution doubled.

the discrepancy between model and observations. It thus appears that the North Pacific in April–May is a region of strong stratospheric influence on ozone, contributing about 20 ppbv in the free troposphere. O. R. Cooper et al. (A springtime comparison of tropospheric ozone and transport pathways on the east and west coasts of the United States, submitted to *Journal of Geophysical*

Research, 2004) argue that this strong stratospheric influence in the midtroposphere extends throughout the 38°–43°N latitude band.

5. Ozone Production in Transpacific Pollution Plumes

5.1. The 5 May and 17 May Plumes

[23] *Nowak et al.* [2004] identified seven Asian pollution plumes in the ITCT 2K2 aircraft data with CO > 150 ppbv and back-trajectories extending to Asia. The three most important (CO >190 ppbv) were observed on 5, 10, and 17 May. The 10 May plume was interleaved with a stratospheric intrusion that made the ozone data difficult to interpret [*Cooper et al.*, 2004b, *Nowak et al.*, 2004]. We focus our attention on the 5 and 17 May plumes and interpret the large differences in ozone behavior between the two plumes.

[24] The 5 May plume (6 May, 0000 UTC) was observed at 33°–37°N, 123°E, and 5–8 km altitude (Figure 8). The lower section (5.5 to 6.5 km) showed enhancements in propane (>700 pptv) suggesting a fossil fuel source [*Nowak et al.*, 2004] while elevated CH_3CN (>500 pptv) was seen above 7 km suggesting a biomass-burning source [*de Gouw et al.*, 2004]. There was no significant ozone enhancement correlated with CO (Figure 8). The plume was transported across the Pacific at altitudes above 4 km ahead of a midlatitude cyclone that had entrained remnants of an upwind decaying WCB as well as fresh pollutants from the Asian lower troposphere [*Cooper et al.*, 2004a].

[25] Figure 9 shows the GEOS-CHEM simulation of the 5 May transport event. The model identifies the fossil fuel and biomass-burning components of the plume but places the plume 5°–10° north of the observations. The simulated Asian pollution enhancement of CO is 67 ppbv, for a total CO concentration in the plume of 155 ppbv; while the observed concentration was up to 275 ppbv (Figure 9); we attribute the difference to numerical diffusion in the model.
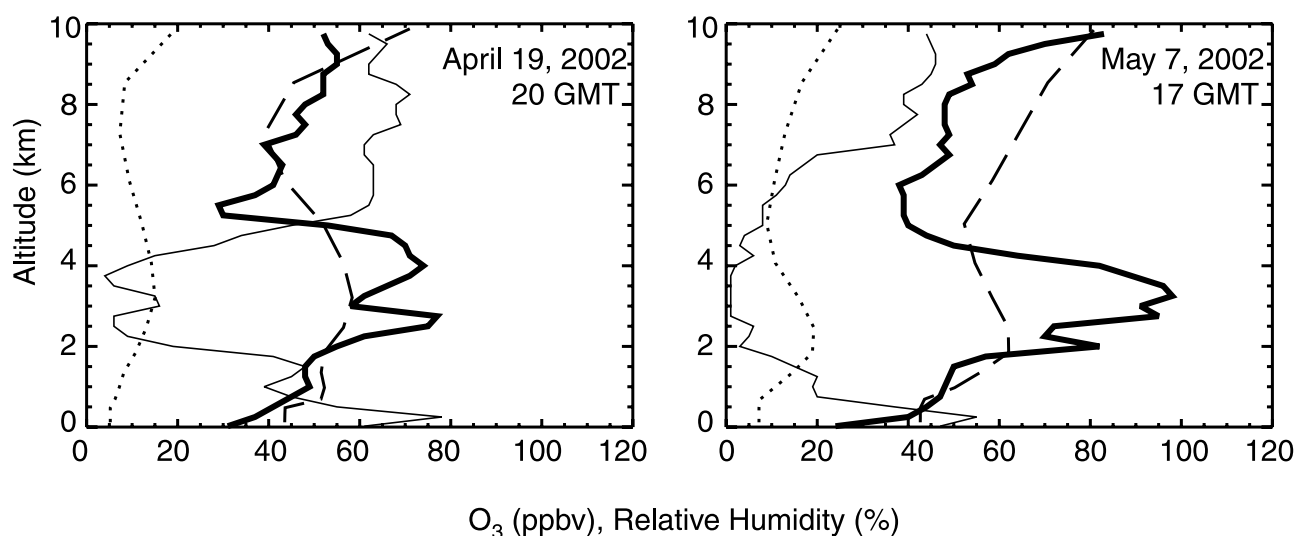
Figure 7. Ozonesonde profiles at Trinidad Head for 19 April and 7 May 2002: ozone concentrations (bold lines, ppbv) and relative humidity (thin lines, %). Also shown are model results for the standard simulation (dashed lines, ppbv) and for the stratospheric contribution as determined from the corresponding ozone tracer (dotted lines, ppbv).
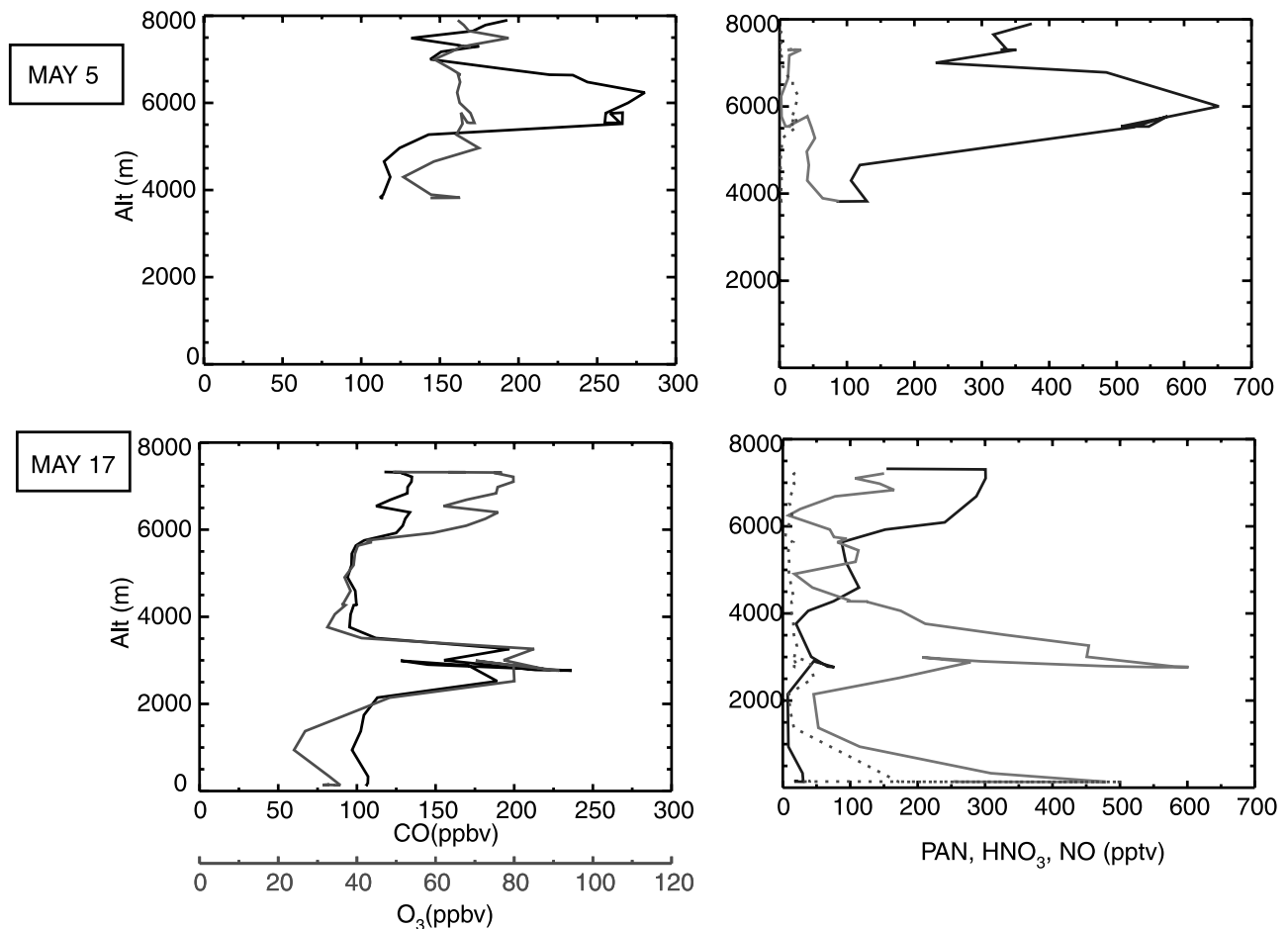
Figure 8. Observed vertical profiles of concentrations for the 5 May and 17 May Asian pollution plumes sampled by the ITCT 2K2 aircraft. (left) CO (black) and O_3 (red). (right) NO_y components: PAN (solid blue), HNO_3 (solid green), and NO (purple). The 5 May data are for the time interval 2345–2421 UTC, and the 17 May data are for the time interval 2218–2314 UTC. See color version of this figure at back of this issue.

Heald et al. [2003] previously noted the inability of the model to capture the magnitude of high-CO events in transpacific plumes over the northeast Pacific observed during TRACE-P. Also shown in Figure 9 are the CO column data from the MOPITT instrument aboard the EOS-Terra satellite. The left panels show the MOPITT observations for 4 and 6 May, and the central panels show the corresponding GEOS-CHEM fields with MOPITT averaging kernels applied, as given by *Heald et al.* [2003]. The averaging kernels are weighted toward the middle and upper troposphere. MOPITT observes the Asian pollution plume transported south of Alaska on 4 May and to the California coast on 5 May (6 May, 0000 UTC), consistent with the corresponding patterns in the model (circles in Figure 9).
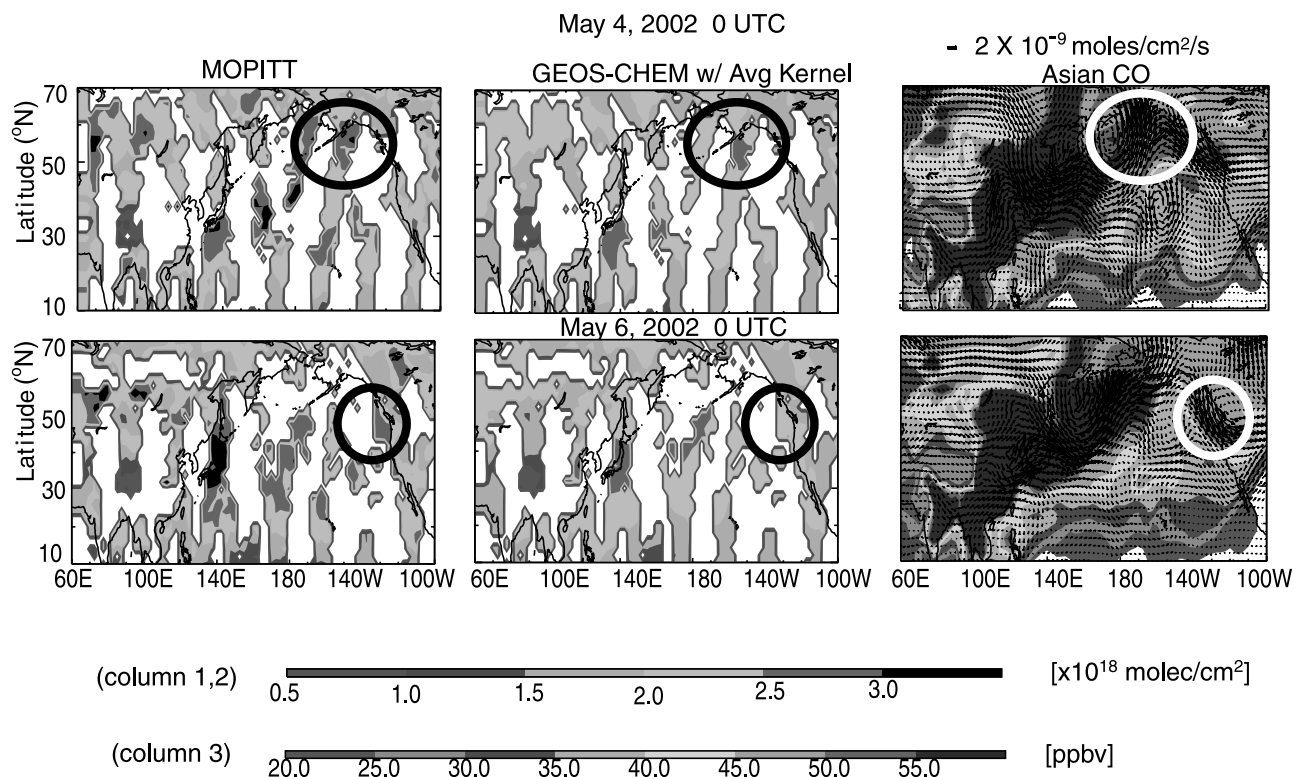
[26] The 17 May plume was intercepted west of California at 31°–37°N, 129°–121°W, and 2–4.5 km altitude, with CO and ozone mixing ratios reaching 225 and 90 ppbv respectively (Figure 8). MOPITT does not see the 17 May plume, presumably because of its low altitude [*Crawford et al.*, 2004]. Figure 10 shows the progression of the plume across the Pacific in GEOS-CHEM. It originated from the northeastward progression of a midlatitude cyclone with Asian pollution in its WCB airstream. On 11 May this polluted air mass left the WCB above the central Pacific, because of the rounding of a weak upper level ridge directing the flow to the southeast. The air mass then subsided for the next 6–7 days before it was observed by the aircraft on 17 May. *Brock et al.* [2004] show that SO_2 conversion to sulfate aerosol in the ITCT 2K2 observations is consistent with slow subsidence over the Pacific for ~8 days. The northeast Pacific is known as a region of preferred cyclone decay, as WCBs round upper level ridges and subside on their eastward side into the northwesterly jet [*Cooper et al.*, 2004a]. Such descent also took place for the 5 May plume but eastward of the 17 May plume and not as dramatically.

5.2. Ozone Production in the 17 May Plume

[27] The 5 May plume sampled at 5–8 km altitude had no significant ozone enhancement, while the 17 May plume sampled at 2.5–4 km had a positive O_3-CO correlation (0.2 mol mol^{-1}) corresponding to an ozone enhancement of about 50 ppbv relative to the local background of 30–40 ppbv. This O_3/CO enhancement ratio is at the low end of those observed in springtime transpacific fossil fuel and biomass-burning plumes transported in the free troposphere and in the absence of mineral dust (O_3/CO = 0.2–

Figure 9. Asian anthropogenic CO concentrations and mass fluxes during the transpacific Asian pollution event sampled by the ITCT 2K2 aircraft on 5 May (6 May, 0000 UTC). The left panels show MOPITT observations of CO columns on 4 May and 6 May at 0000 UTC. The central panels show the corresponding GEOS-CHEM model results sampled along the MOPITT orbit tracks and with MOPITT averaging kernels applied. The circles show the plume location on 4 May, 0000 UTC, and 6 May, 0000 UTC. The right panels show the simulated mass-weighted mean CO concentrations at $0-6$ km altitude of anthropogenic Asian CO including contributions from fuel and biomass burning. The arrows represent mass fluxes (moles/cm^2/s) for the surface to 150 hPa column. See color version of this figure at back of this issue.
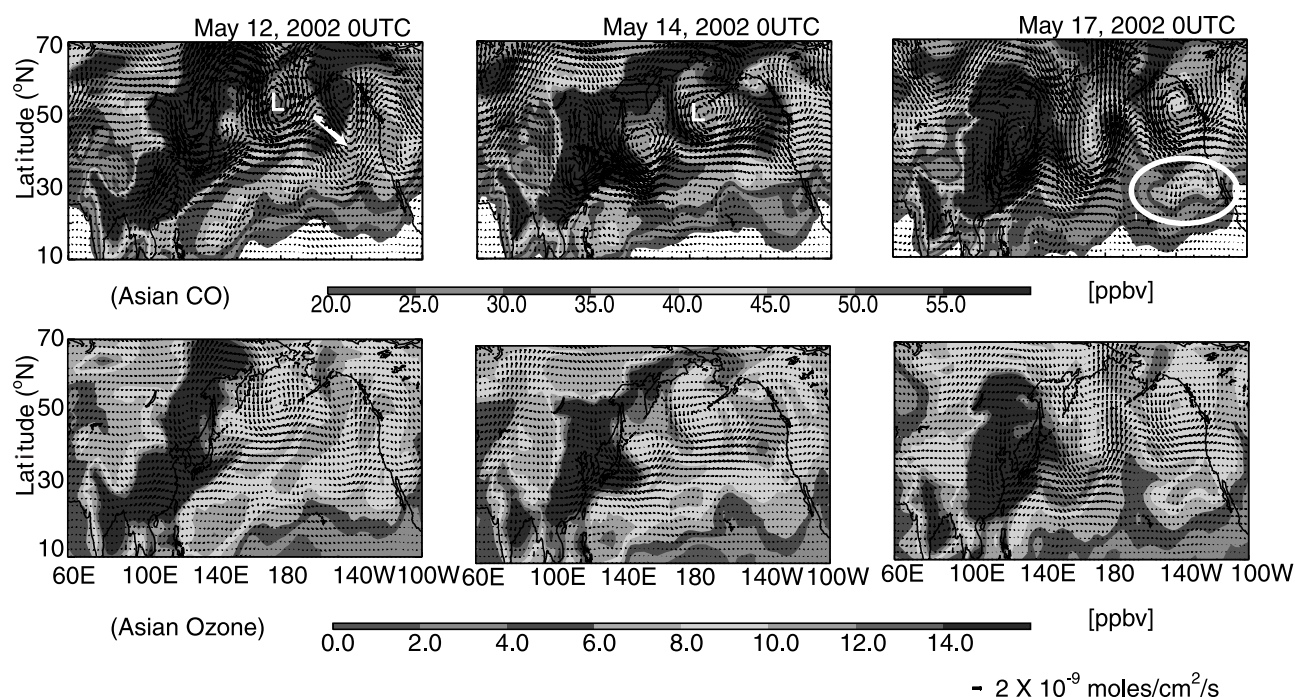
0.5 mol mol^{-1}) [*Price et al.*, 2004]. The 17 May plume was very dry, with a RH of only 2%, implying subsidence from the upper troposphere. The observed speciation of NO$_y$ (Figure 9) suggests an explanation for the difference in ozone enhancement between the 5 and 17 May plumes. In the 5 May plume, PAN was strongly correlated with CO and accounted for 65% of the observed NO$_y$. The observed PAN/CO enhancement ratio (2.5 $\times$ 10^{-3} mol/mol) is consistent with that simulated by the model for the PEACE-B Asian outflow (Figure 4). PAN has a lifetime in excess of a month at that altitude [*Talukdar et al.*, 1995], so it would be conserved during transpacific transport. In the 17 May plume, by contrast, PAN accounted for only 14% of the total NO$_y$ concentration of 630 pptv (Figure 9). The NO concentration was 20 pptv. It thus appears that PAN decomposed during subsidence of the 17 May plume, releasing NO$_x$ that drove ozone production.

[28] We can estimate the ozone production efficiency (OPE) per unit PAN decomposed in the 17 May plume by using the 5 May plume to characterize the initial conditions before subsidence. Mean ozone concentrations in the 5 and 17 May plumes were 67 and 84 ppbv [*Nowak et al.*, 2004], respectively, corresponding to an enhancement of 17 ppbv driven by PAN decomposition in the 17 May plume.

Assuming that NO$_y$ was conserved during subsidence in the 17 May plume and that PAN accounted initially for 65% of NO$_y$ (based on the 5 May plume data), we conclude that 17 ppbv ozone was produced from the decomposition of 320 pptv PAN. This corresponds to an OPE of about 53 mol mol^{-1}. The OPE per unit PAN decomposed is equivalent to the more standard definition of the OPE per unit NO$_x$ oxidized to HNO$_3$ [*Liu et al.*, 1987] if we assume that NO$_x$ in the subsiding plume is in chemical steady state between the source from PAN decomposition and the loss from oxidation to HNO$_3$. This assumption seems to be applicable to subsiding air masses in the middle troposphere [*Jacob et al.*, 1996].

5.3. Importance of PAN Decomposition for Ozone Production in Transpacific Asian Plumes

[29] We can compare this observational estimate of the OPE with that obtained from the GEOS-CHEM model for the subsiding region of the northeast Pacific. We compute the OPE in the model as the gross ozone production per NO$_x$ molecule oxidized to HNO$_3$ and show in Figure 11 the mean values at $2-4$ km altitude in May. The mean OPE is 80 mol mol^{-1} over the northeast Pacific, consistent with our observational estimate. We see from

Figure 10. Simulated Asian anthropogenic enhancement to CO and ozone concentrations and mass fluxes during the Asian pollution event sampled by the ITCT 2K2 aircraft on 17 May. The Asian pollution enhancements are obtained from a simulation with Asian anthropogenic sources shut off. The figure shows mass-weighted mean (top) CO and (bottom) ozone concentrations at 0–6 km altitude. The black arrows represent mass fluxes (moles/cm^2/s) for the surface to 150 hPa column. The white "L" shows the progression of the low-pressure center whose warm conveyor belt (WCB) airstream uplifted pollutants associated with the 17 May event. The white arrow shows the route of the plume as it left the warm conveyor belt over the Pacific and descended toward the southeast. See color version of this figure at back of this issue.

Figure 11 that the OPE is much higher over the northeast Pacific than at other longitudes; this is because of intense radiation, low humidity, and relatively low NO_x concentrations. Considering that typical OPEs in the continental boundary layer are 5–10 mol mol^{-1} [*Liang et al.*, 1998] and that 5–10% of Asian NO_x emissions are exported from the boundary layer as PAN [*Koike et al.*, 2003], we conclude that PAN decomposition during subsidence is a substantial and perhaps dominant contributor to ozone enhancements observed in transpacific Asian pollution plumes.

6. Asian Pollution Influence on Surface Ozone in California

[30] The large Asian ozone pollution enhancement observed in the 17 May plume sampled by the ITCT 2K2 aircraft raises the issue as to whether such large enhance-
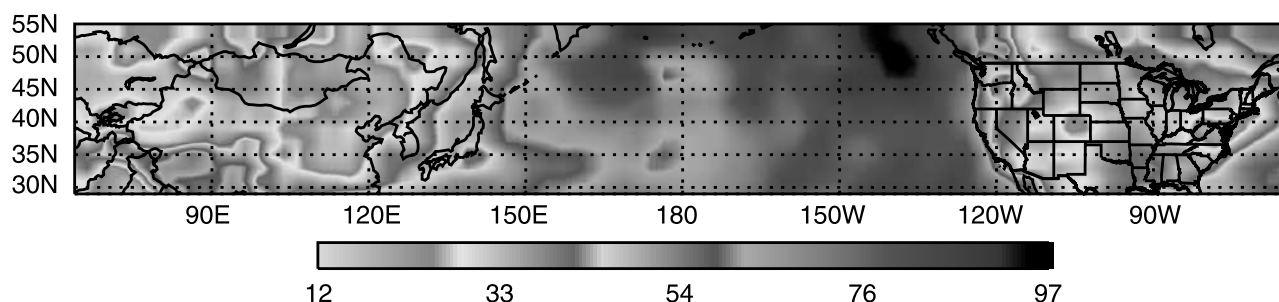
Figure 11. Mean simulated ozone production efficiency per unit NO_x consumed (OPE) for May 2002 in the lower free troposphere (average between 2 and 4 km altitude). See color version of this figure at back of this issue.
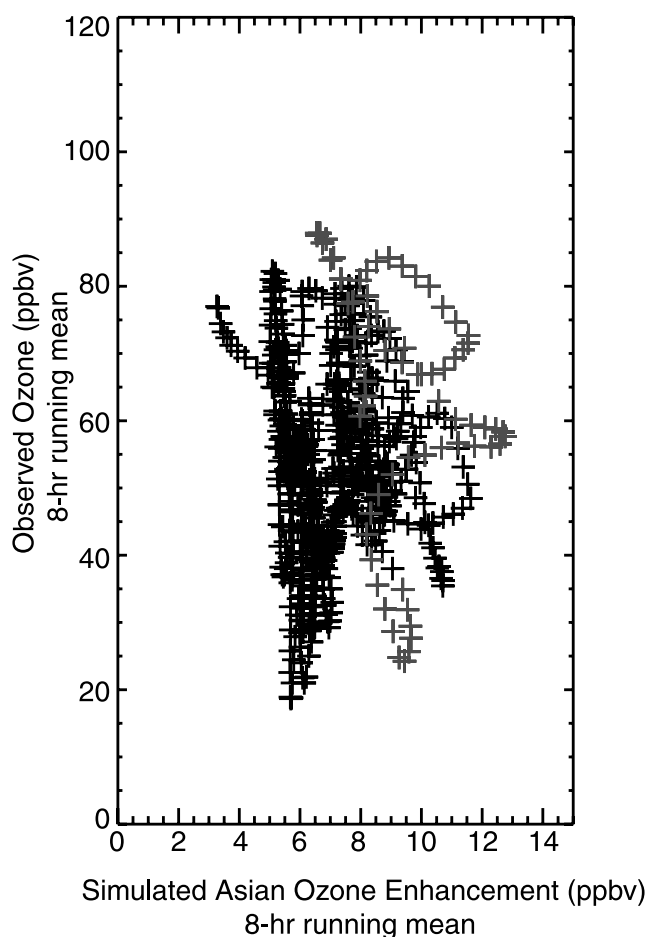
Figure 12. Ozone concentrations observed at Sequoia National Park (36°N, 118°W, 1890 m altitude) in May 2002 versus the corresponding Asian pollution enhancements simulated by the GEOS-CHEM model. Values are 8-hour running means. Red symbols indicate the 17–20 May period, during which a major transpacific pollution event was observed by the ITCT 2K2 aircraft. See color version of this figure at back of this issue.

ments could be observed at surface sites in the western United States, with major implications for air quality. *Goldstein et al.* [2004] presented an analysis of the ozone surface air observations at Trinidad Head during ITCT 2K2 and used GEOS-CHEM to diagnose Asian ozone enhancements at that site. They found good agreement between simulated and observed ozone; production over the Asian continent (as diagnosed from an O_x tracer simulation) accounted for 4.5 ± 1.1 ppbv ozone in the model fields. There was no indication of episodic enhancements in Asian influence, either in the model or in the observations.

[31] The Asian influence as estimated by *Goldstein et al.* [2004] does not discriminate between anthropogenic and natural contributions to ozone production over the Asian continent, nor does it account for ozone production downwind of the continent. A better calculation of the Asian pollution enhancement at Trinidad Head can be obtained from our simulation with Asian anthropogenic sources shut off. We obtain in this manner an Asian pollution

enhancement of 6 ± 2 ppbv ozone, somewhat less than the simulated mean Asian pollution enhancement of 8 ppbv for the ITCT 2K2 observations in the marine boundary layer (Figure 5). The difference reflects the short lifetime (~3 days) of O_x in the continental mixed layer [*Fiore et al.*, 2002].

[32] The temporal variability of Asian influence simulated by the model is small, consistent with the previous GEOS-CHEM analysis by *Fiore et al.* [2003], which examined the time series of Asian influence on observed ozone concentrations at a number of U.S. surface sites. Asian pollution influence in U.S. surface air in the model mostly reflects a hemispheric-scale enhancement of ozone in subsiding air masses rather than the direct transport of pollution plumes from Asia to North America. It is likely that GEOS-CHEM underestimates the variability of transpacific pollution influence over the United States because it excessively dilutes transpacific plumes, as discussed in section 5.1. Nevertheless, it is consistent with the lack of detectable ozone enhancements in Asian pollution plumes sampled at Trinidad Head and Cheeka Peak [*Goldstein et al.*, 2004; *Jaffe et al.*, 2001].

[33] Transpacific transport of Asian ozone pollution takes place mainly in the free troposphere, where winds are strong and the lifetime of ozone is long. The lack of detectable Asian plume influence in the surface observations can be understood in terms of the large dilution effect as the plumes subside to the surface. Observations of large Asian dust events sampled in the free troposphere and at the surface over the western United States suggest a dilution by an order of magnitude during subsidence to the surface [*Jaffe et al.*, 2003a, 2003b]. Applying this dilution factor to the ~20 ppbv ozone enhancement observed in the 17 May plume implies a surface ozone enhancement of only 2 ppbv. Such a small enhancement would not be detectable in the Trinidad Head time series.

[34] A larger Asian influence on ozone might be expected at California mountain sites, which are more subjected to free tropospheric influence. We examined April–May 2002 observations and model results at several such sites from the CASTNET network [*Lavery et al.*, 2001]: Yosemite National Park, Pinnacles National Monument, Sequoia National Park, and Joshua Tree National Park. Simulated ozone enhancements from Asian pollution at these sites during the ITCT 2K2 period average 8 ± 2 ppbv, higher than at surface sites but with similarly low temporal variability. Figure 12 shows the simulated 8-hour average Asian pollution enhancements at Sequoia National Park (1890 m) for May 2002, plotted against the observed 8-hour average concentrations at that site. The 17 May plume sampled by the ITCT 2K2 aircraft corresponds to a model peak in Asian pollution influence at Sequoia National Park on 18 May. On that day, the observed ozone concentration at Sequoia National Park exceeded 84 ppbv (the U.S. air quality standard) with Asian pollution contributing a 7–10 ppbv enhancement according to the model. Overall, for the 8-hour periods at Sequoia National Park in May 2002 when observed ozone concentrations were in excess of 80 ppbv, the Asian pollution enhancement in the model was 7 ± 2 ppbv. Unlike at surface sites [*Fiore et al.*, 2002], there is no negative correlation between Asian pollution enhancements and total ozone concentrations. Model results previously presented by *Fiore et al.*

[2002] for U.S. surface sites indicated 2–7 ppbv of combined Asian and European pollution influence under the stagnation conditions leading to ozone pollution episodes. It appears that high-ozone events at California mountain sites are far more sensitive to Asian pollution influence.

7. Conclusions

[35] We have used a global 3-D model of tropospheric ozone chemistry (GEOS-CHEM) to interpret observations of transpacific transport of Asian pollution in April–May 2002 from the ITCT 2K2 aircraft campaign out of California and the PEACE-B campaign out of Japan. The model reproduces the mean vertical profiles of CO and NO_y concentrations observed for both Asian outflow (PEACE-B) and North American inflow (ITCT 2K2). Asian fuel (fossil and biofuel) influence on CO in the model averages 32 ppbv in North American inflow, with little vertical variability, and 50 ppbv for Asian outflow in the free troposphere. Observed concentrations of NO average 10 pptv in North American inflow in the free troposphere, of which 3 pptv are of Asian anthropogenic origin according to the model.

[36] The model underestimates observed ozone concentrations in the free troposphere from both PEACE-B and ITCT 2K2 by up to 10 ppbv. We show that this is due to insufficient accounting of the strong stratospheric influence over the North Pacific. Ozonesonde observations at Trinidad Head, California, during April–May 2002 reveal frequent occurrences of high-ozone stratospheric layers extending down to the lower free troposphere (2 km). Increasing the stratospheric contribution by a factor of 2 (to ∼20 ppbv) in the model would correct the discrepancy with the ITCT 2K2 and Trinidad Head observations in the free troposphere. The Synoz flux boundary condition for cross-tropopause transport of ozone [McLinden et al., 2000], implemented in the model to correct for excessive cross-tropopause transport of air in the GEOS fields [Bey et al., 2001a; Liu et al., 2001; Tan et al., 2004], is effective on the global scale but would underestimate stratospheric influence in regions of preferential downwelling.

[37] We examined in more detail the two major transpacific Asian pollution plumes sampled by the ITCT 2K2 aircraft offshore from California, on 5 May (5–8 km altitude) and on 17 May (2.5–4 km altitude). The 5 May plume had elevated CO (up to 275 ppbv) but no correlated ozone enhancement (67 ppbv, which is typical for that altitude); most of the NO_y in that plume was present as PAN, consistent with observations in Asian outflow. The 17 May plume had both elevated CO (up to 225 ppbv) and elevated ozone (up to 90 ppbv); NO_y levels were comparable to the 5 May plume but most of that NO_y was present as HNO_3. We show that the ozone enhancement in the 17 May plume is consistent with production from PAN decomposition during subsidence of the plume over the northeast Pacific. We derive an ozone production efficiency (OPE) per unit NO_x consumed of 50 mol mol^{-1}, consistent with the model value for the region (80 mol mol^{-1}). We find in the model that the subsiding northeast Pacific atmosphere is a region of unusually high OPEs because of strong radiation and low humidity, thus promoting ozone production in subsiding Asian plumes reaching the United States in the lower free troposphere.

[38] We went on to investigate the potential of these Asian plumes to elevate ozone in surface air over California. Observations at Trinidad Head during the ITCT 2K2 campaign show good agreement with the model [Goldstein et al., 2004]. The simulated Asian pollution enhancements of ozone at that site, as determined by difference with a simulation with anthropogenic Asian emissions shut off, are relatively large but show little variability (6.4 ± 1.9 ppbv). The Trinidad Head observations do not show detectable ozone pollution associated with Asian pollution plumes [Goldstein et al., 2004]. This may be explained by the large dilution (factor of 10) of Asian pollution plumes as they are transported from the free troposphere to the surface. We find in the model a larger Asian pollution influence at California mountain sites, for example at Sequoia National Park (1890 m altitude) where it ranges from 2 to 14 ppbv in April–May 2002. During periods when observed ozone concentrations at Sequoia National Park exceeded 80 ppbv, the Asian pollution enhancement averaged 7 ± 2 ppbv. Asian pollution influence could thus make a significant contribution to exceedances of the air quality standard at California mountain sites.

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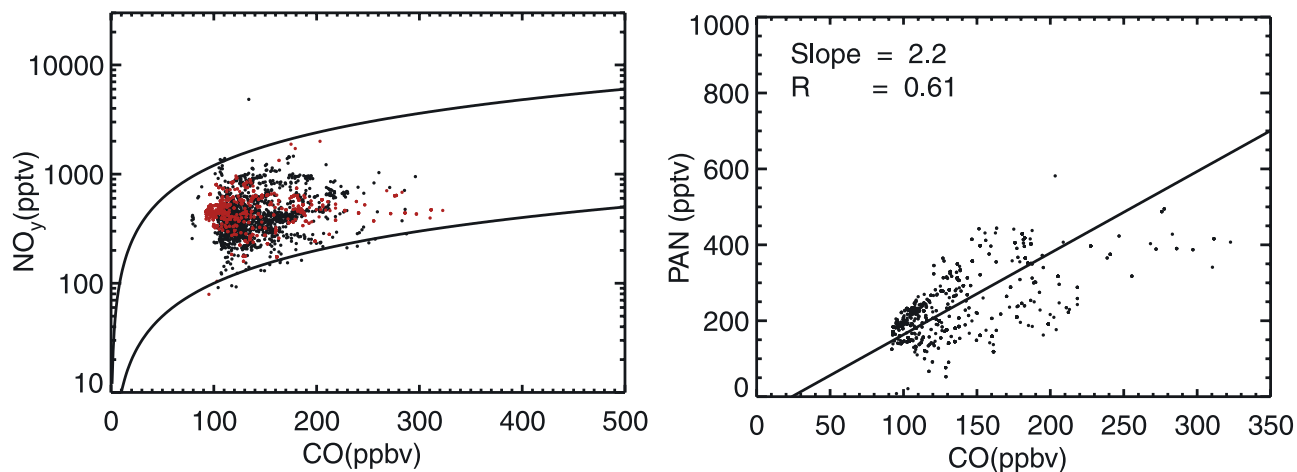
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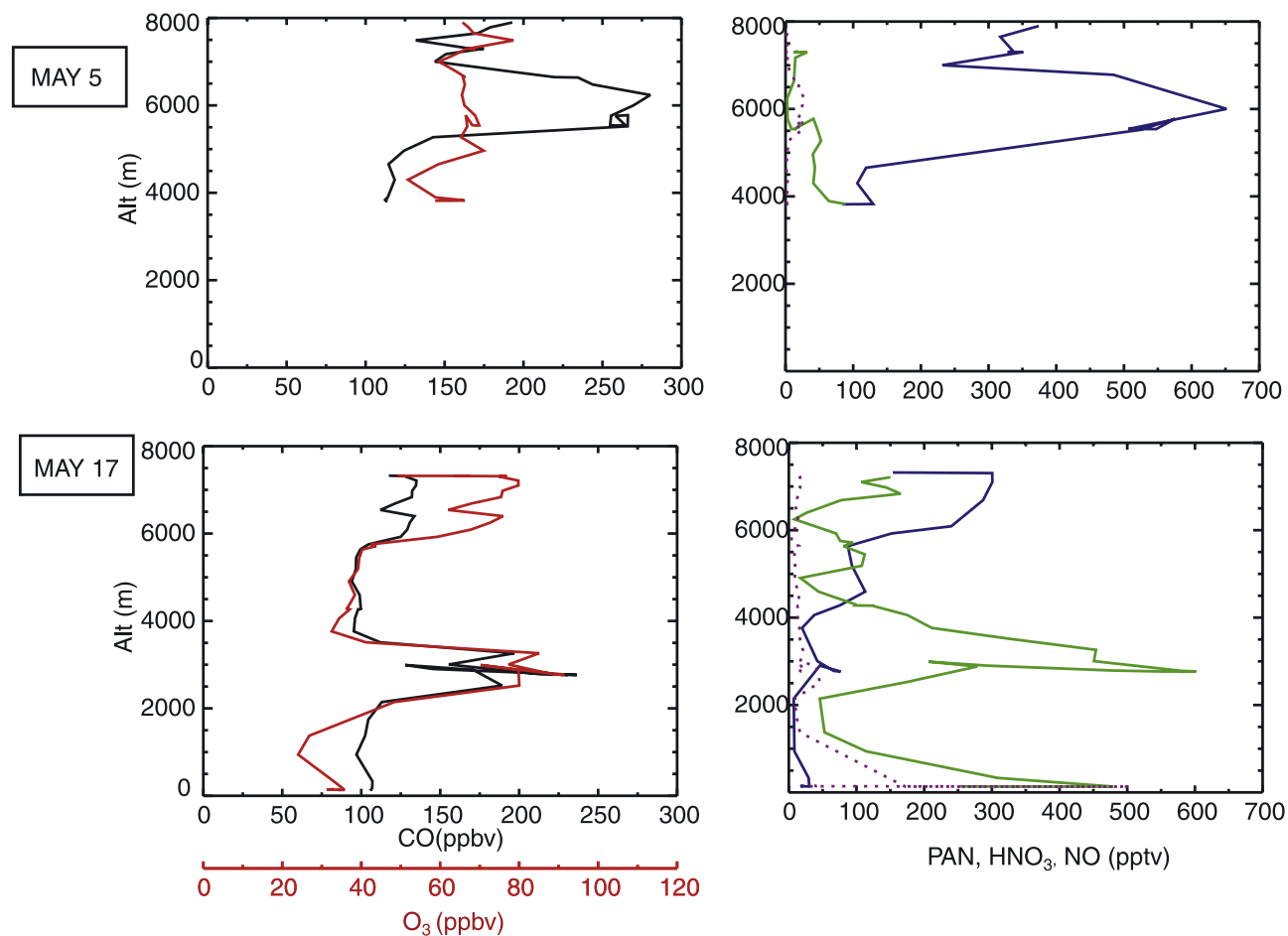
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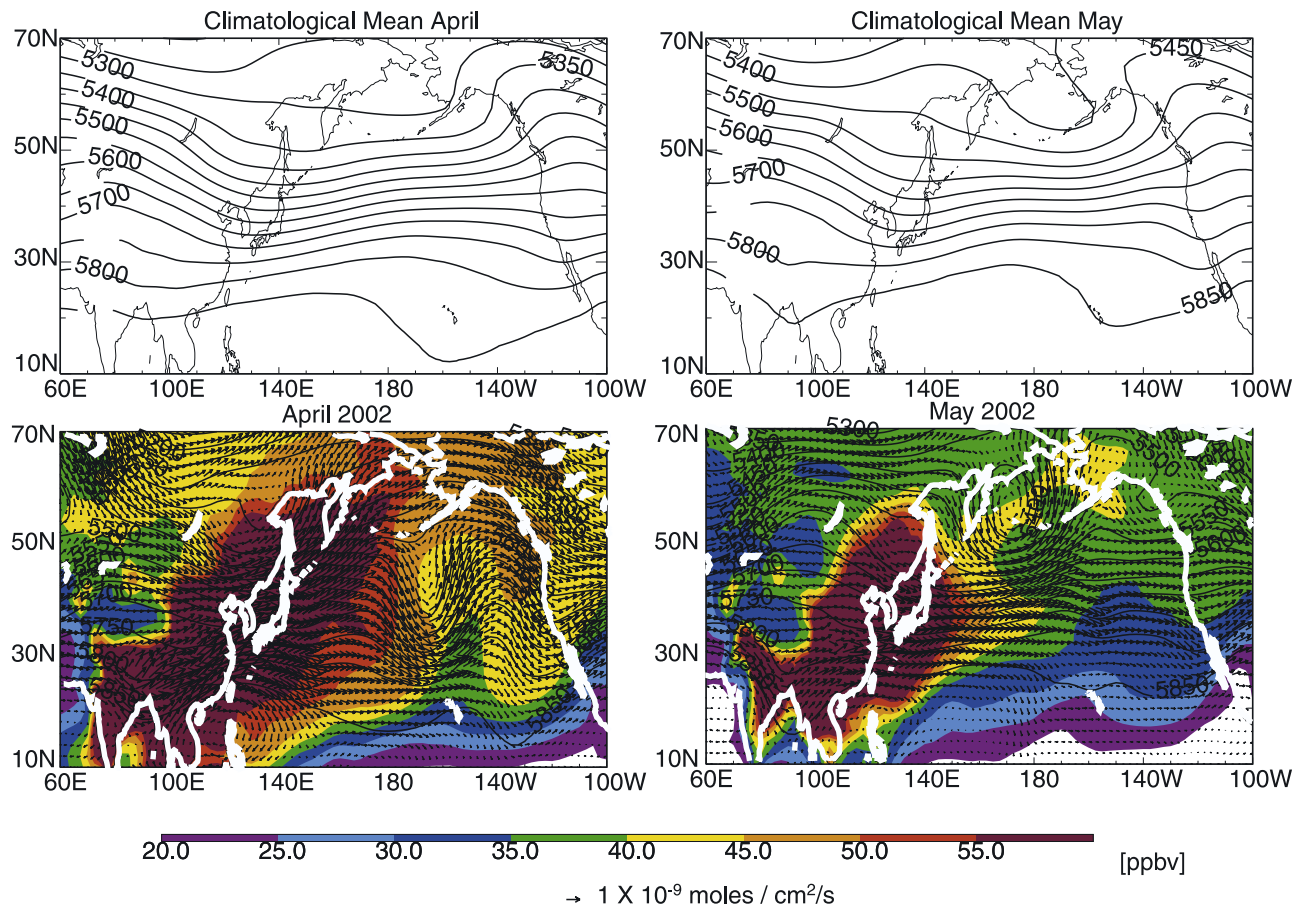
Figure 2. Mean patterns of transpacific transport of Asian pollution in April–May. The top panels show NCEP climatological values (1948 to present) of geopotential heights (m) at 500 hPa. The bottom panels show conditions for 2002 including NCEP geopotential heights at 500 hPa (line contours) and GEOS-CHEM model results for the Asian anthropogenic CO tracer: fluxes in the surface to 150 hPa column (arrows, moles/cm^2/s) and mean mass-weighted concentrations in the 0–6 km column (solid contours).
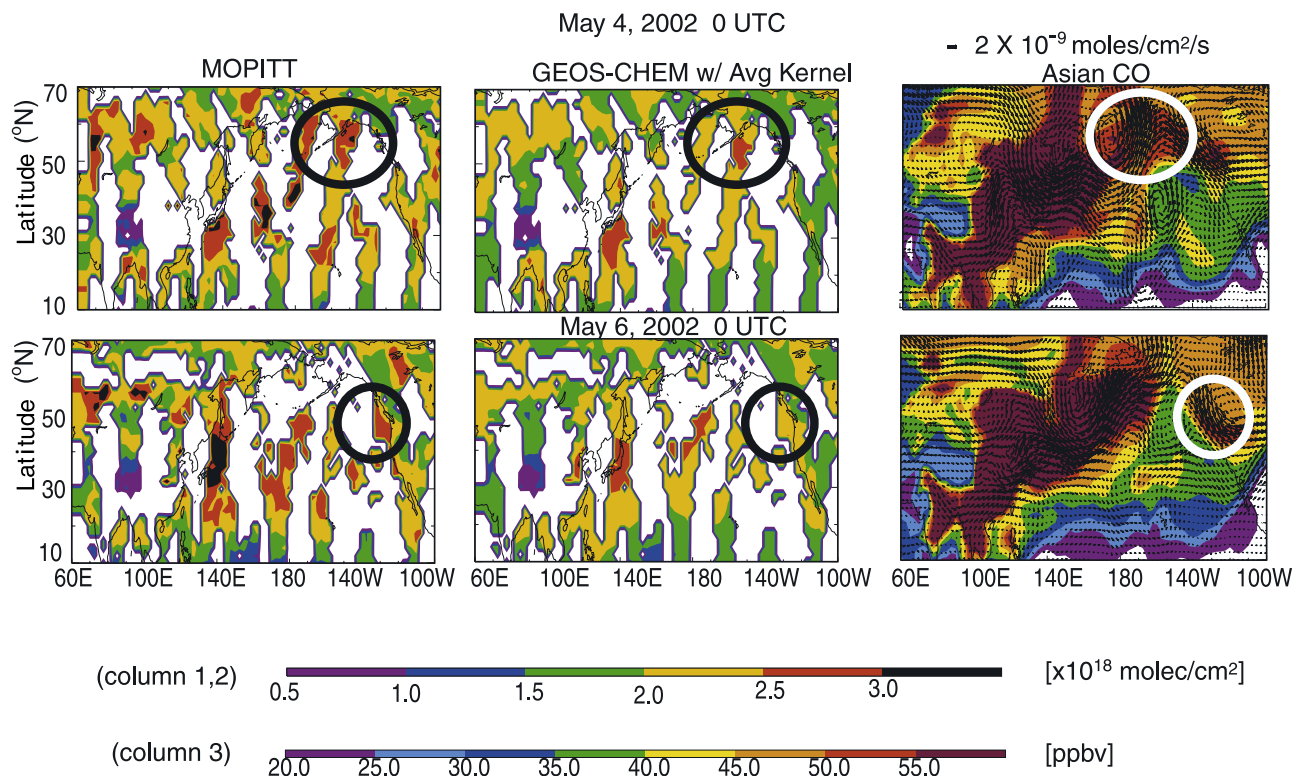
Figure 4. Relationship of NO_y with CO concentrations at 2.5-10 km altitude over the NW Pacific during PEACE-B. The left panel shows NO_y versus CO in the aircraft observations (red) and in the GEOS-CHEM model (black). Curves correspond to NO_y/CO ratios of 1 and 12×10^{-3} mol mol^{-1}. The right panel shows PAN versus CO in the model sampled along the PEACE-B flight tracks (no measurements of PAN were made on the aircraft).
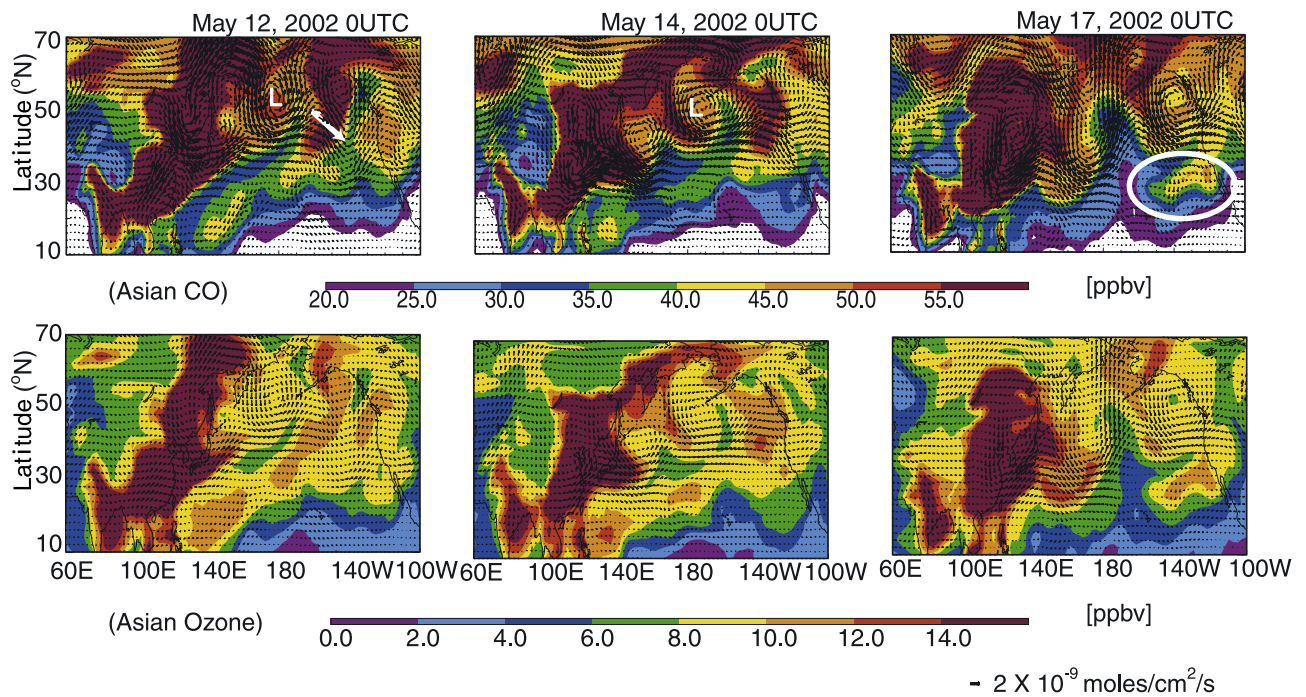

Figure 8. Observed vertical profiles of concentrations for the 5 May and 17 May Asian pollution plumes sampled by the ITCT 2K2 aircraft. (left) CO (black) and O_3 (red). (right) NO_y components: PAN (solid blue), HNO_3 (solid green), and NO (purple). The 5 May data are for the time interval 2345–2421 UTC, and the 17 May data are for the time interval 2218–2314 UTC.
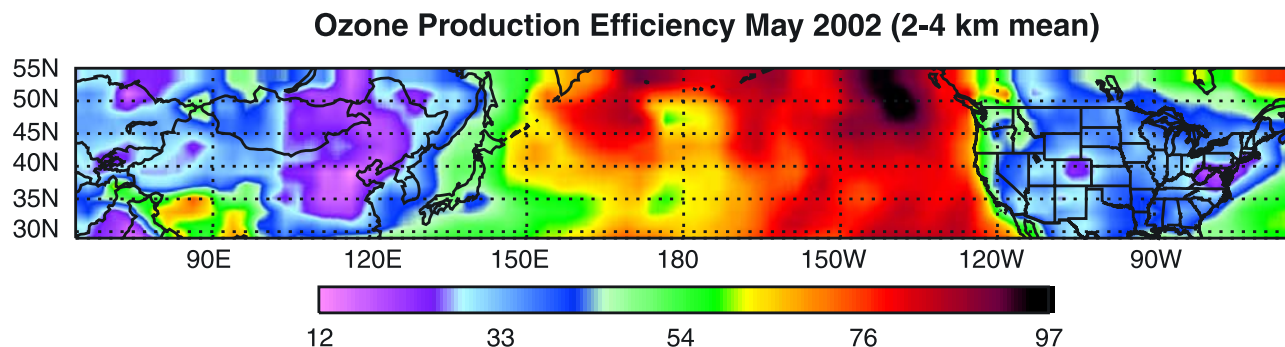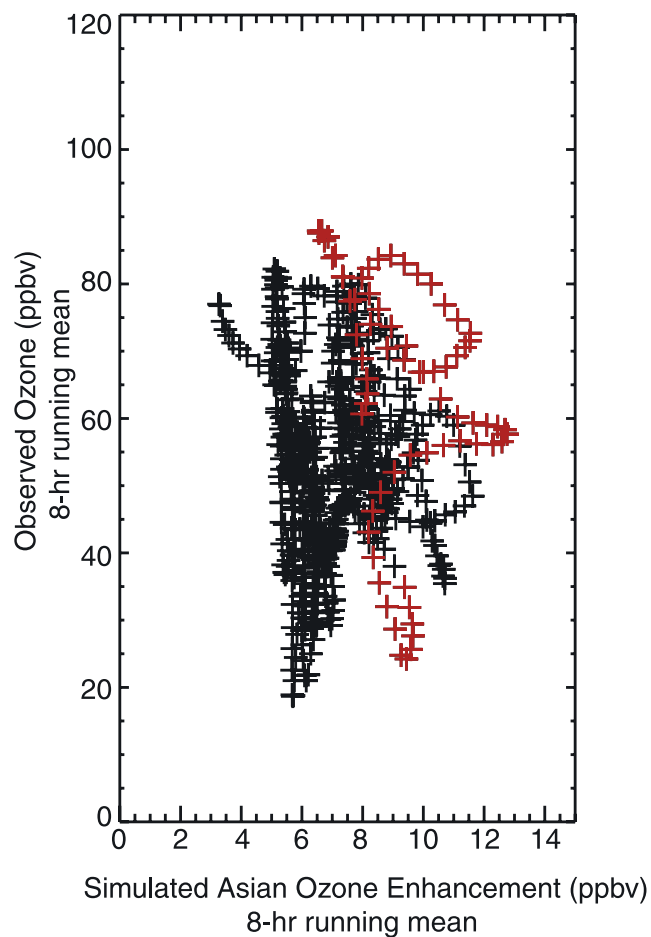
Figure 9. Asian anthropogenic CO concentrations and mass fluxes during the transpacific Asian pollution event sampled by the ITCT 2K2 aircraft on 5 May (6 May, 0000 UTC). The left panels show MOPITT observations of CO columns on 4 May and 6 May at 0000 UTC. The central panels show the corresponding GEOS-CHEM model results sampled along the MOPITT orbit tracks and with MOPITT averaging kernels applied. The circles show the plume location on 4 May, 0000 UTC, and 6 May, 0000 UTC. The right panels show the simulated mass-weighted mean CO concentrations at 0–6 km altitude of anthropogenic Asian CO including contributions from fuel and biomass burning. The arrows represent mass fluxes (moles/cm^2/s) for the surface to 150 hPa column.

Figure 10. Simulated Asian anthropogenic enhancement to CO and ozone concentrations and mass fluxes during the Asian pollution event sampled by the ITCT 2K2 aircraft on 17 May. The Asian pollution enhancements are obtained from a simulation with Asian anthropogenic sources shut off. The figure shows mass-weighted mean (top) CO and (bottom) ozone concentrations at 0–6 km altitude. The black arrows represent mass fluxes (moles/cm^2/s) for the surface to 150 hPa column. The white "L" shows the progression of the low-pressure center whose warm conveyor belt (WCB) airstream uplifted pollutants associated with the 17 May event. The white arrow shows the route of the plume as it left the warm conveyor belt over the Pacific and descended toward the southeast.

Ozone Production Efficiency May 2002 (2-4 km mean)

Figure 11. Mean simulated ozone production efficiency per unit NO_x consumed (OPE) for May 2002 in the lower free troposphere (average between 2 and 4 km altitude).

Figure 12. Ozone concentrations observed at Sequoia National Park (36°N, 118°W, 1890 m altitude) in May 2002 versus the corresponding Asian pollution enhancements simulated by the GEOS-CHEM model. Values are 8-hour running means. Red symbols indicate the 17–20 May period, during which a major transpacific pollution event was observed by the ITCT 2K2 aircraft.