Asian outflow and trans-Pacific transport of carbon monoxide and ozone pollution: An integrated satellite, aircraft, and model perspective

The Harvard community has made this article openly available. Please share how this access benefits you. Your story matters

Citation

Published Version
doi:10.1029/2003JD003507

Citable link
http://nrs.harvard.edu/urn-3:HUL.InstRepos:14061860

Terms of Use
This article was downloaded from Harvard University’s DASH repository, and is made available under the terms and conditions applicable to Other Posted Material, as set forth at http://nrs.harvard.edu/urn-3:HUL.InstRepos:dash.current.terms-of-use#LAA
Asian outflow and trans-Pacific transport of carbon monoxide and ozone pollution: An integrated satellite, aircraft, and model perspective

Colette L. Heald,1 Daniel J. Jacob,1 Arlene M. Fiore,1 Louisa K. Emmons,2 John C. Gille,2 Merritt N. Deeter,2 Juying Warner,2 David P. Edwards,2 James H. Crawford,3 Amy J. Hamlin,3,4 Glen W. Sachse,3 Edward V. Browell,3 Melody A. Avery,3 Stephanie A. Vay,3 David J. Westberg,5 Donald R. Blake,6 Hanwant B. Singh,7 Scott T. Sandholm,8 Robert W. Talbot,9 and Henry E. Fuelberg10

Received 14 February 2003; revised 21 July 2003; accepted 24 September 2003; published 31 December 2003.

[1] Satellite observations of carbon monoxide (CO) from the Measurements of Pollution in the Troposphere (MOPITT) instrument are combined with measurements from the Transport and Chemical Evolution Over the Pacific (TRACE-P) aircraft mission over the northwest Pacific and with a global three-dimensional chemical transport model (GEOS-CHEM) to quantify Asian pollution outflow and its trans-Pacific transport during spring 2001. Global CO column distributions in MOPITT and GEOS-CHEM are highly correlated ($R^2 = 0.87$), with no significant model bias. The largest regional bias is over Southeast Asia, where the model is 18% too high. A 60% decrease of regional biomass burning emissions in the model (to 39 Tg yr$^{-1}$) would correct the discrepancy; this result is consistent with TRACE-P observations. MOPITT and TRACE-P also give consistent constraints on the Chinese source of CO from fuel combustion (181 Tg CO yr$^{-1}$). Four major events of trans-Pacific transport of Asian pollution in spring 2001 were seen by MOPITT, in situ platforms, and GEOS-CHEM. One of them was sampled by TRACE-P (26–27 February) as a succession of pollution layers over the northeast Pacific. These layers all originated from one single event of Asian outflow that split into northern and southern plumes over the central Pacific. The northern plume (sampled at 6–8 km off California) had no ozone enhancement. The southern subsiding plume (sampled at 2–4 km west of Hawaii) contained a 8–17 ppbv ozone enhancement, driven by decomposition of peroxyacetylnitrile (PAN) to nitrogen oxides (NO$_x$). This result suggests that PAN decomposition in trans-Pacific pollution plumes subsiding over the United States could lead to significant enhancements of surface ozone.

INDEX TERMS: 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; KEYWORDS: TRACE-P, MOPITT, Asian pollution, trans-Pacific transport, carbon monoxide, O$_3$ production


1. Introduction

[2] Quantifying the continental outflow and intercontinental transport of air pollutants is one of the major challenges of atmospheric chemistry today. Integration of satellite and aircraft observations with three-dimensional (3-D) models is a promising new approach for addressing this challenge. We present here such an integration through a combined model interpretation of aircraft observations of
Asian pollution outflow and trans-Pacific transport from the Transport and Chemical Evolution Over the Pacific (TRACE-P) aircraft mission, together with satellite observations of carbon monoxide (CO) from the Measurement of Pollution in the Troposphere (MOPITT) instrument. In the process we demonstrate the value of the MOPITT observations for mapping intercontinental transport of pollution, and we present the first observationally based analysis of the production of pollution outflow-origin from China, Japan and the United States. We also provide the first observations of NOx emissions from east Asia.

2. Observations and Model

2.1. TRACE-P Observations

The TRACE-P mission involved two NASA aircraft (DC-8 and P3-B) deployed from bases in Hong Kong and Japan to sample outflow from Asia. Transit flights from the United States sampled a major event of trans-Pacific transport of Asian pollution on 26 and 27 February, described in section 4. The aircraft payload included instrumentation to measure O3, CO, reactive nitrogen oxide (NOy) species, and a suite of hydrocarbon and halocarbon tracers [Jacob et al., 2003]. Observations of CO were made continuously with 1 Hz frequency using the Differential Absorption of CO Measurement (DACOM) instrument [Sachse et al., 1987]. The measurement accuracy is approximately 2%.

Fuehrberg et al. [2003] give an overview of the meteorological conditions during TRACE-P. Asian pollution was primarily exported to the Pacific in WCBs ahead of cold fronts [Liu et al., 2003]. This pollution included both anthropogenic (defined herein as fossil fuel and biofuel sources only) and biomass burning influences, the latter due to seasonal biomass burning in Southeast Asia [Heald et al., 2003]. The two influences were often mixed in the outflow [Carnicale et al., 2003; Ma et al., 2003]. Following standard practice we distinguish “anthropogenic” from “biomass burning” sources, even though biomass burning here is largely due to human activity. The distinction is useful because biomass burning has a separate geographical and seasonal signature, and because the inventories are constructed from very different types of bottom-up information.

Detailed inventories for anthropogenic emissions [Streets et al., 2003] and daily biomass burning emissions [Heald et al., 2003] were constructed for the TRACE-P period from bottom-up economic and fire information, respectively. These inventories were used by Palmer et al. [2003] in an inverse model analysis to determine the constraints from the TRACE-P CO observations toward better quantifying CO sources from east Asia. They concluded that anthropogenic emissions from China in the Streets et al. [2003] inventory were underestimated by 35%, and that biomass burning emissions from Southeast Asia in the Heald et al. [2003] inventory were a factor of three too high.

Other TRACE-P studies examined the Asian outflow of ozone and of NOy. Large NOx enhancements were observed downwind from Asia and consisted mainly of HNO3 and PAN [Miyazaki et al., 2003; Talbot et al., 2003]. PAN was the dominant form of NOy in outflow associated with WCBs [Miyazaki et al., 2003]. Examination of NOy-CO correlations by Koike et al. [2003] indicated an NOy export efficiency to the free troposphere from northeastern China of 15%, with only 0.5% of the emitted NOy remaining as NOx in the free tropospheric outflow. Significant ozone production in Asian outflow during TRACE-P appeared to be limited to biomass burning plumes originating from low latitudes [Tang et al., 2003]. Ozone production in anthropogenic plumes was generally insignificant, reflecting the weak photochemical activity at that time of year [Pierce et al., 2003].

2.2. MOPITT Observations

The MOPITT instrument is a nadir IR correlation radiometer launched aboard the NASA Earth Observing System Terra spacecraft in 1999 [Drummond, 1992; Edwards et al., 1999]. It has solar backscatter channels to measure total CO columns, and IR emission channels to measure CO vertical profiles. Correlation spectroscopy
The MOPITT retrieval uses a single profile of kernel matrix $A$ at 250 hPa and less than 60 ppbv at 150 hPa, as described by Deeter et al. [2000]. The vertical profile $x$ retrieved by the instrument is related to the true vertical profile $x_a$ by the averaging kernel matrix $A$, as described by Rodgers [2000]:

$$\hat{x} = x_a + A(x - x_a) + G\varepsilon,$$

(1)

where $\varepsilon$ is the measurement error and $G$ is the gain matrix. The MOPITT retrieval uses a single profile of $x_a$ (and $S_a$) with mixing ratio decreasing from 120 ppbv at the surface to 75 ppbv at 250 hPa and less than 60 ppbv at 150 hPa [Deeter et al., 2003]. The averaging kernel matrix is given by

$$A = I - \hat{S}S_a^{-1},$$

(2)

where $I$ is the identity matrix and $\hat{S}$ is the retrieval error covariance matrix, different for each retrieval and supplied with the MOPITT retrieval product. The rows of $A$ (averaging kernels) describe the vertical resolution of the retrieval. A sample set of averaging kernels for the North Pacific is shown in Figure 1. The column averaging kernel (right panel of Figure 1) specifies the total column sensitivity to a change in the true mixing ratio at each level and is calculated as follows:

$$a = t^TA,$$

(3)

where $t$ is the transfer operator which includes both the conversion from volume mixing ratio to number density and the integration over pressure. Figure 1 shows roughly two independent regions of information in the MOPITT retrieved profile: one in the middle troposphere (300–800 hPa) and one in the upper troposphere (pressure < 500 hPa) [Deeter et al., 2003]. For details on how the averaging kernels vary with land types and time of day, see Deeter et al. [2003]. We find that the global average number of degrees of freedom for signal in the MOPITT vertical profiles, which is the total of the eigenvalues of the averaging kernel and describes the number of independent pieces of information inferred from the retrieval [Rogers, 2000], is $1.21 \pm 0.45$ for 1 sample day (15 March 2001). One can think of this value as the number of modes of vertical structure retrieved by MOPITT [Rogers, 1990]. The first eigenmode for MOPITT is representative of a broad column-like signal with an eigenvalue close to one.

The remaining contribution to $d_a$, which can exceed 0.5 in the tropics but is generally less than 0.2 in the extratropics, can be thought of as the contribution from a broad vertical gradient. We choose to focus on the column data in our analysis.

Seven MOPITT validation profiles for a range of conditions were performed during TRACe-P underneath coincident MOPITT overpasses. Four were conducted under sufficiently clear-sky conditions to enable MOPITT retrievals. Results presented by Jacob et al. [2003] show that MOPITT captures the variability in the observed aircraft columns, with a high bias of 6 ± 2%, but provides no apparent information on vertical structure for Asian plumes over the Pacific [Jacob et al., 2003]. One of the validation profiles (DC-8 flight 5) sampled a trans-Pacific pollution transport layer event with CO in excess of 250 ppbv, as discussed in section 3. The 6% MOPITT bias observed during TRACe-P is consistent with MOPITT validation results for a suite of aircraft campaigns and profiles (L. Emmons et al., Validation of MOPITT CO retrievals with aircraft in situ profiles, submitted to Journal of Geophysical Research, 2003).

2.3. Model Description

We use the GEOS-CHEM v. 4.33 global 3-D model of tropospheric chemistry (http://www-as.harvard.edu/chemistry/trop/geos) with $2^\circ \times 2.5^\circ$ horizontal resolution and 48 vertical levels. The model is driven by assimilated meteorology from the GEOS-3 of the NASA Data Assimilation Office and was initially described by Bey et al. [2001a]. The GEOS-3 data have a temporal resolution of 6 hours (3 hours for surface variables and mixing depths). Other TRACe-P studies using the GEOS-CHEM model have demonstrated the ability of the model to simulate the meteorological and chemical signatures of Asian outflow over the Pacific [Jaegle et al., 2003; Kiley...
We conducted a simulation for February–April 2001 with full O3-NOx-hydrocarbon chemistry. We also conducted CO-only simulations with tagged sources and monthly mean OH concentration fields archived from the full chemistry simulation. Initial conditions were taken from a 1-year spin-up simulation and model output was sampled every 3 hours. Anthropogenic sources of CO and its precursor hydrocarbons are as described by B. N. Duncan et al. (Model study of the variability and trends of carbon monoxide (1988–1997): 1. Model formulation, evaluation, and sensitivity, submitted to Journal of Geophysical Research, 2003, hereinafter referred to as Duncan et al., submitted manuscript, 2003). Our anthropogenic source of CO from China (181 Tg CO yr\(^{-1}\)) is 66% higher than in the inventory of Streets et al. [2003] and 8% higher than the a posteriori estimate from the inverse model by Palmer et al. [2003] constrained with TRACE-P observations. Biomass burning emissions are from a bottom-up inventory constrained with daily satellite fire counts for the TRACE-P period [Heald et al., 2003]. Most of the global biomass burning for this period takes place in Southeast Asia and the corresponding regional source for February–April 2001 is 69 Tg CO. The inverse model analysis of Palmer et al. [2003] suggests that this regional biomass burning source is too high by a factor of 3; as we will see, simulation of the MOPITT data leads to a similar conclusion.

Comparisons between full-year model results for 2001 and ground station CO measurements by the National Ocean and Atmospheric Administration (NOAA) Climate Monitoring and Diagnostics Laboratory (CMDL) Carbon Cycle Group for representative Northern Hemispheric sites are shown in Figure 2. Several recent changes to the GEOSCHEM chemical mechanism, including a faster N\(_2\) + O\((^1\Delta)\) rate constant [Ravishankara et al., 2002] have decreased the global mean OH concentration by 10–15%. The most recent global model evaluation of CO by Duncan et al. (submitted manuscript, 2003) which does not include this change in rate constant [Ravishankara et al., 2002] have decreased the global mean OH concentration by 10–15%. The most recent global model evaluation of CO by Duncan et al. (submitted manuscript, 2003) which does not include this change in rate constant, shows a model underestimate in the northern tropics and midlatitudes by 10–40 ppbv, with better agreement achieved in the arctic latitudes. The model simulation reported here is generally unbiased in its simulation of the CMDL Northern Hemispheric sites; however high-latitude sites are overestimated by 10–30 ppbv in summer-fall. Our 10–30 ppbv spring underestimate at Midway (MID) does not appear to be driven by an underestimate in Asian sources.

Figure 2. Comparisons of observed (solid lines) and simulated (dotted lines) monthly mean CO concentrations for 2001 at selected Northern Hemispheric Climate Monitoring and Diagnostics Laboratory surface stations.
3. Interpretation of MOPITT Observations for the TRACE-P Period

3.1. Global Distributions

[16] Figure 3 shows the mean CO column observed by MOPITT during TRACE-P (20 February to 10 April 2001) and the corresponding GEOS-CHEM model column with MOPITT averaging kernels applied (according to equation (1)). Here the MOPITT data for each day have been averaged over the $2^\circ \times 2.5^\circ$ GEOS-CHEM model grid and the resulting gridded product is then averaged over the 49-day TRACE-P period. MOPITT retrievals are not performed for cloudy scenes and are limited by the orbital coverage, but the effective coverage is increased here because of averaging over the $2^\circ \times 2.5^\circ$ grid. Temporal coverage of the gridded MOPITT product over the North Pacific is 20–70% (Figure 4). The GEOS-CHEM model results in Figure 3 were constructed by binning the model on the MOPITT pressure levels for each retrieval scene, weighting by the MOPITT averaging kernels (such as shown in Figure 1), and integrating the column.

[17] Both model and satellite observations show high CO levels over continental source and outflow regions, as well as a general latitudinal gradient. Columns are low over high terrain (e.g., the Himalayas, the Rocky Mountains). A difference plot (Figure 3, bottom panel) shows no mean global bias between the model and measured CO. Mean MOPITT and GEOS-CHEM columns for the TRACE-P period are highly correlated ($R^2 = 0.97$, slope = 0.97); and the correlation also holds for data points on individual days ($R^2 = 0.87$, slope = 0.95; Figure 5). The slope indicates that the model underestimates MOPITT observations by 5%. As pointed out in section 2.2, the MOPITT observations appear to be biased high by 6% relative to the TRACE-P aircraft data.

3.2. Constraints on Asian Emissions

[18] The pattern of model bias relative to MOPITT matches the distribution of biomass burning, notably over Southeast Asia [Heald et al., 2003]. MOPITT column observations over Southeast Asia ($10^\circ$–$25^\circ$N, $80^\circ$–$110^\circ$E), where biomass burning dominates anthropogenic emissions by a factor of two in the model, are on average 18% lower than the model column. The bias extends to southern China, where biomass burning effluents from Southeast Asia are lifted to the middle troposphere during transport in WCBs [Liu et al., 2003]. The discrepancy suggests that biomass burning emissions in the model for Southeast Asia are too high, consistent with the inverse model analysis of the TRACE-P CO data by Palmer et al. [2003]. In order to estimate how the overestimate of MOPITT observations translates to an overestimate of biomass burning emissions, we reduced the mean simulated CO profile over Southeast Asia by a fraction of the mean biomass burning contribution (determined from a sensitivity simulation). We then passed the resulting profile through the averaging kernels for 1 sample day (16 March 2001). We thus estimate in the model that reducing the biomass burning source over Southeast Asia by 60% (to 39 Tg yr$^{-1}$ CO over the $70^\circ$–$140^\circ$E, $0^\circ$–$50^\circ$N region) would

Figure 3. Mean CO columns measured by MOPITT during the Transport and Chemical Evolution Over the Pacific (TRACE-P) campaign (20 February to 10 April 2001) and corresponding GEOS-CHEM model columns sampled along the MOPITT observational track and transformed with the MOPITT averaging kernels. Both the MOPITT data and the transformed GEOS-CHEM fields have been averaged over the GEOS-CHEM $2^\circ \times 2.5^\circ$ model grid. The bottom panel shows the difference between GEOS-CHEM and MOPITT. The color scales for the top two panels are saturated at $3.5 \times 10^{18}$ molecules/cm$^2$, and the bottom panel scale is saturated at $1.0 \times 10^{18}$ molecules/cm$^2$. See color version of this figure at back of this issue.
correct the MOPITT overestimate, consistent with the previous inverse analysis of TRACE-P data by Palmer et al. [2003]. An important caveat in the interpretation of model vs. MOPITT discrepancies in terms of errors on CO sources is the possibility of model bias in the vertical structure of CO. This could arise, in particular, as a result of excessive convection transporting CO to the upper troposphere where MOPITT is most sensitive. Comparison of GEOS-CHEM and MOPITT vertical profiles over Southeast Asia shows no significant difference in shape (Figure 6), but this reflects the lack of MOPITT information on vertical structure as previously discussed. The model vertical profiles over Southeast Asia show an enhancement in the upper troposphere due to deep convection. If we were to change the shape of the vertical profile in the model while conserving the total CO column, such that we reduce upper tropospheric CO to tropical background concentrations (55–70 ppbv) and correspondingly increase lower-tropospheric CO, we would match the MOPITT observations (Figure 6). Cloud data show that frequent deep convection did in fact occur over Southeast Asia during TRACE-P [Fuelberg et al., 2003], and an intercomparison of model simulations of CO for the TRACE-P period reveals no systematic bias in the GEOS-CHEM vertical distribution [Kiley et al., 2003], but in the absence of measured vertical profiles over Southeast Asia some ambiguity remains.

The MOPITT observations reveal no evident model bias in the anthropogenic source of CO from China. This is consistent with the TRACE-P aircraft observations, since the source used here is only 8% higher than the a posteriori
estimate derived by Palmer et al. [2003] by inverse modeling of the TRACE-P data. Previous inverse model studies by Kasibhatla et al. [2002] and Pe´tron et al. [2003] required high anthropogenic emissions from eastern Asia (350–380 Tg yr
21 and >500 Tg yr
21, respectively, compared to our 323 Tg yr
21) to achieve agreement with global CMDL ground station observations in 1994 and 1990–1996, respectively. The constraints from TRACE-P and MOPITT observations imply a weaker Asian source.

3.3. Asian Outflow and Trans-Pacific Transport

We now turn to the variability of Asian outflow to the Pacific and subsequent trans-Pacific transport, as observed by MOPITT and simulated by GEOS-CHEM. Figure 7 shows MOPITT and GEOS-CHEM time series for the TRACE-P period over the northwest, central and northeast Pacific. As before, the GEOS-CHEM model results are sampled for each MOPITT scene and are processed through the MOPITT averaging kernels. The MOPITT observations over the northwest Pacific show outflow events every 5–8 days associated with the passage of cold fronts across the Asian Pacific Rim, as also observed during TRACE-P [Fuelberg et al., 2003; Liu et al., 2003]. GEOS-CHEM and MOPITT are correlated ($R^2 = 0.61$) in this region, reflecting the ability of the model to capture the WCBs driving the Asian outflow ahead of the frontal passages.

Figure 7. Spring 2001 time series of the average 2° × 2.5° gridded CO column observed by MOPITT (solid line) and simulated by GEOS-CHEM with the averaging kernel applied (dotted line) over the western, central, and eastern North Pacific. Plumes transported across the Pacific are identified and numbered. Event 4 was observed from aircraft during the Photochemical Ozone Budget of the Eastern North Pacific Atmosphere (PHOBEA) II campaign and was characterized as an air mass that had descended from high latitudes but had originated from east Asian sources [Jaffe et al., submitted manuscript, 2002]. We were unable to associate this event in the NE Pacific with any specific outflow event in the NW.

4. Ozone Production During Trans-Pacific Transport: A Case Study

4.1. Trans-Pacific Transport Event on 22–27 February

Layers with elevated CO from rapid trans-Pacific transport of Asian pollution were observed on the two outbound transit flights of the DC-8 during TRACE-P (flight tracks shown in Figure 8). In flight 4 from California to Hawaii (26 February 2001), vertical profiles indicated CO concentrations in excess of 200 ppbv in midtropospheric layers at 600–250 hPa (Figure 9, profiles A, B, and C; locations shown in Figure 8). The southern layers (B and C) were also enhanced in O$_3$, whereas the northern layer (A) at 40°N off the coast of California was not. In flight 5 from Hawaii to Guam conducted the following day (27 February 2001), strong CO and O$_3$ enhancement layers were observed in the lower free troposphere at 800–600 hPa (Figure 9, profiles D and E). CO concentrations [Liu et al., 2003]. Farther downwind across the Pacific the agreement between model and observations degrades ($R^2 = 0.35$ over the northeast Pacific), possibly due to accumulation of model transport errors or to vertical displacement of the Asian pollution layers [J. H. Crawford et al., Exploring the relationship between MOPITT and in situ observations of CO based on a large-scale feature sampled during TRACE-P, submitted to Journal of Geophysical Research, 2003]. Column concentrations are most sensitive to CO enhancements in the midtroposphere (5–6 km) due to the application of the MOPITT averaging kernels (Figure 1). The MOPITT data over the northeast Pacific identify four major events of trans-Pacific transport of Asian pollution during the TRACE-P period, and these are indicated by arrows in Figure 7. These events are all captured by the GEOS-CHEM model but with a dampened magnitude. The four trans-Pacific transport events identified by MOPITT during the TRACE-P period were also seen by in situ observations. Event 1 was observed on the outbound TRACE-P transit flights, as discussed further in section 4. Events 2 and 3 were observed at the Cheeka Peak Observatory (CPO, 48.30°N 124.62°W) on the coast of Washington state on 11 and 20 March, respectively [Jaegle et al., 2003]. There were no observations at CPO during events 1 and 4. Event 4 was observed from aircraft during the PHOBEA II experiment and was characterized as an air mass that had descended from high latitudes but originated from east Asian sources [Jaffe et al., 2003].
were greater than 200 ppbv, and were accompanied by O₃ in excess of 70 ppbv.

[23] We find that the pollution layers observed in flights 4 and 5 all originated from one single Asian outflow plume on 22 February 2001 associated with a WCB lifting Chinese pollution ahead of a cold front. Back trajectories (Figure 8) offer evidence for this common origin; further evidence from chemical tracer observations and the GEOS-CHEM model simulation will be presented below. The Asian plume was rapidly transported across the northwest Pacific and encountered a blocking high-pressure system near Hawaii on 25 February (Figure 10). It then split into northern and

Figure 8. Five-day kinematic back trajectories based on European Centre for Medium-Range Weather Forecasts meteorological fields [Fuelberg et al., 2003] for the enhanced CO layers observed in TRACE-P DC-8 flight 4 from California to Hawaii (26 February) and flight 5 from Hawaii to Guam (27 February). The flight tracks are shown in black, and arrival points in profiles A-E of Figure 9 are shown in red, green, purple, blue, and cyan, respectively. See color version of this figure at back of this issue.

Figure 9. Vertical concentration profiles of CO (black lines) and O₃ (red lines) measured from the DC-8 aircraft during the TRACE-P transit flight 4 from California to Hawaii and flight 5 from Hawaii to Guam on 25 and 26 February 2001. Profile locations and the flight tracks for flight 4 and flight 5 are shown in Figure 8. Profile A was a double spiral (ascending and then descending) conducted for MOPITT validation to check the consistency of the vertical structure of CO; data from both spirals are shown (there were no observations between 500 and 400 hPa during the ascent). CO measurements between 550 and 300 hPa in profile B are not available. Profiles D and E include descents and ascents separated by 86 km and 275 km, respectively. See color version of this figure at back of this issue.

Figure 10. Streamlines at 500 hPa for 25 February, 1800 UTC, indicating the blocking high-pressure system over the north-central Pacific that led to splitting of the Asian pollution plume sampled on TRACE-P DC-8 flights 4 and 5. (NCEP reanalysis data was provided by the NOAA-CIRES Climate Diagnostics Center, Boulder, Colorado, USA, from their Web site at http://www.cdc.noaa.gov). The arrows illustrate the transport and splitting of the Asian pollution plume.

22 February 2001 associated with a WCB lifting Chinese pollution ahead of a cold front. Back trajectories (Figure 8) offer evidence for this common origin; further evidence from chemical tracer observations and the GEOS-CHEM model simulation will be presented below. The Asian plume was rapidly transported across the northwest Pacific and encountered a blocking high-pressure system near Hawaii on 25 February (Figure 10). It then split into northern and
Table 1. Average Species Concentrations and Ratios Observed in the Trans-Pacific Asian Plume of 26–27 February 2001

<table>
<thead>
<tr>
<th></th>
<th>Profile A (^{ab})</th>
<th>Profile D (^{ab})</th>
<th>Profile E (^{ac})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, °K</td>
<td>253 ± 9</td>
<td>286 ± 1</td>
<td>286 ± 2</td>
</tr>
<tr>
<td>CO, ppbv</td>
<td>224 ± 28</td>
<td>198 ± 20</td>
<td>205 ± 29</td>
</tr>
</tbody>
</table>
| O

\(^3\)S, ppbv | 57 ± 1              | 65 ± 5              | 74 ± 9              |
| C\(_2\)H\(_2\)/CO, pptv/ppbv | 3.6 ± 0.2          | 2.7 ± 0.5           | 2.9 ± 0.3           |
| C\(_2\)H\(_4\)/C\(_2\)H\(_6\), pptv/ppbv | 0.27 ± 0.05        | 0.15 ± 0.02         | 0.14 ± 0.01         |
| C\(_2\)Cl\(_4\)/CO, pptv/ppbv | 0.041 ± 0.008      | 0.038 ± 0.013       | 0.025 ± 0.013       |
| CH\(_3\)Cl/CO, pptv/ppbv | 2.8 ± 0.3          | 3.1 ± 0.4           | 3.2 ± 0.3           |
| CH\(_3\)CN/HCN, pptv/ppbv | 0.67 ± 0.04        | 0.73 ± 0.03         | 0.63 ± 0.03         |

\(^a\)Sampled between California and Hawaii on 26 February (average for 600–370 hPa and standard deviation).
\(^b\)Sampled between Hawaii and Guam on 27 February (average for 800–600 hPa and standard deviation).
\(^c\)Less than three coincident observations.

4.2. Source Characteristics of Trans-Pacific Asian Plume

[24] Both the northern and southern plumes sampled in TRACE-P exhibit the characteristics of recently emitted pollution, as indicated in Table 1. The high C\(_2\)H\(_2\)/CO concentration ratios (2.7–3.6 pptv/ppbv) are characteristic of fresh Asian outflow [Russo et al., 2003]. The C\(_2\)H\(_6\)/C\(_2\)H\(_4\) ratio for the northern plume is also characteristic of fresh pollution [Russo et al., 2003], but the values for the southern plume are lower and indicate some photochemical aging.

[25] Perchloroethene (C\(_2\)Cl\(_4\)), a chemical used in dry cleaning, is a tracer of urban pollution whereas methyl chloride (CH\(_3\)Cl) is often viewed as a tracer of biomass burning [Blake et al., 2003]. Blake et al. [2003] examined the chemical tracer signatures for the high-CO layers in flight 5. They find correlated enhancements of CH\(_3\)Cl, C\(_2\)Cl\(_4\), ethyne and halocarbons, implying a mixture of fossil fuel and biomass burning (or biofuel) sources. We further examined the CH\(_3\)CN/HCN enhancement ratio in an attempt to separate biomass burning from biofuel influence, as this ratio in TRACE-P was much higher in biomass burning plumes (0.46) than in anthropogenic Chinese plumes including biofuel but no biomass burning influence (0.23) [Li et al., 2003; Singh et al., 2003]. We find CH\(_3\)CN/HCN ratios > 0.6 in the pollution layers of flights 4 and 5 (Table 1), implying a biomass burning contribution to the Asian outflow. Blake et al. [2003] suggest that lower levels of halocarbons and C\(_2\)Cl\(_4\) in profile E vs. profile D are indicative of somewhat different origins. We find here that the CH\(_3\)Cl/CO ratios were similar in profiles A, D and E, and the C\(_2\)Cl\(_4\)/CO ratio was consistent within a factor of 2 (Table 1). This together with the back trajectories supports a common origin, however there is clearly some heterogeneity present in the plume, which is not inconsistent with WCB lifting air masses from different sources over east Asia.

4.3. Model Simulation and MOPITT Observations

[26] The simulation of this trans-Pacific transport event by GEOS-CHEM is shown in Figure 11. The pollution transport in the model is consistent with the back trajectories shown in Figure 8. The model plume is transported across the Pacific in the midtroposphere (~6 km) and encounters the blocking high-pressure system near the dateline where it splits into southern and northern branches. The southern branch subsides (to 4–5 km altitude) while the northern branch is forced upward (to 7–8 km altitude). The northern enhancement is displaced upward in the model relative to the observed aircraft profiles (Figure 9), which would reduce its sensitivity to observation by MOPITT as discussed in section 3. The tagged tracer simulations indicate that the model enhancement was 70–80% anthropogenic and 20–30% from biomass burning. Such mixing of anthropogenic and biomass burning effluents in the WCBs driving Asian outflow to the Pacific was frequently observed in TRACE-P [Carmichael et al., 2003; Liu et al., 2003; Ma et al., 2003].

[27] Although the model successfully describes the pathways for trans-Pacific transport of the 26–27 February plume, it greatly underestimates (by 50–100 ppbv) the CO maxima observed by the aircraft. Numerical diffusion in the model may be responsible. Such an underestimate was noted previously in the simulation of MOPITT observations of trans-Pacific transport events over the northeast Pacific (Figure 7) and is seen in particular in comparison to the MOPITT column observations for 23–27 February 2001. The daily MOPITT data are relatively sparse, because of incomplete orbit coverage and clouds over the Pacific, but comparison to the model results with averaging kernels applied (Figure 11, center panels) allows one to visualize the Asian outflow plume as it progresses across the Pacific. MOPITT observations indicate high levels of CO reaching North America on 27 February.

4.4. Photochemical Evolution and Ozone Production

[28] Although the pollution layers sampled by the TRACE-P aircraft on flights 4 and 5 originated from the same outflow event from Asia, as confirmed by the back trajectories and the chemical tracer signatures, they show evidence of very different photochemical evolution. We previously commented on the lower C\(_3\)H\(_8\)/C\(_2\)H\(_4\) relationship observed in flight 5. The northern plume sampled in flight 4 exhibited no significant O\(_3\) enhancement (Figure 9, profile A). Conversely, the subsiding southern plume sampled on flight 5 contained large O\(_3\) enhancements (Figure 9, profiles D and E). Differential absorption lidar (DIAL) observations of O\(_3\) vertical cross sections along the tracks of flights 4 and 5 (Figure 12) show no O\(_3\) pollution enhancement at high latitudes (>35°N) consistent with the in situ observations in the northern Asian plume. The DIAL observations show a pronounced high-O\(_3\) layer between 2 and 4 km on flight 5, with levels exceeding 80 ppbv, consistent with the in situ observations of Figure 9 and demonstrating the broad horizontal extent (at least 2500 km) of this subsiding pollution layer. A positive correlation between O\(_3\) and aerosols was also found in these pollution plumes by Browell et al. [2003].
who attributed the enhancement to biomass burning sources in southeast Asia. The differences in O₃ enhancements between the northern and southern plumes reflects not only the effect of solar radiation but also, and more importantly, the effect of subsidence driving PAN decomposition to NOₓ and hence O₃ production. Figure 13 shows the concentrations of NOₓ species observed in the northern plume (profile A, flight 4) and in the southern plume (profiles D and E, flight 5). The total NOₓ concentration in both plumes is about the same (470–530 pptv), consistent with their common origin as NOₓ is conserved. Mean NOₓ levels are 18 pptv in the northern plume (4% of total NOₓ) and 163 pptv in the southern plume (30% of total NOₓ). Total NOₓ also includes 13% HNO₃+nitrate aerosol and 74% PAN in the northern plume, vs. 51% HNO₃+nitrate aerosol and 14% PAN in the southern plume (Figure 13). The dominant PAN contribution in the northern plume is consistent with the mean PAN/NOₓ molar ratio (0.75 ± 0.10) observed in the warm conveyor belt outflow in the free troposphere during TRACE-P [Miyazaki et al., 2003]. The difference in speciation between the northern and southern plumes can be explained by PAN decomposition to NOₓ during subsidence following the split of the original plume on 25 February. From the temperature measurements in the layers sampled in TRACE-P (Table 1), we find that the PAN lifetime drops from 105 days in profile A to 5–6 hours in profiles D and E.

[29] We can relate the observed PAN decomposition and O₃ production in the southern plume. From Figure 8, O₃ in the southern plume appears to be enhanced by 40 ppbv above the local tropical background. However, considering the midlatitude origin of this plume, a background O₃ concentration of 57 ppbv (such as seen in profile A, Table 1) is more appropriate as a baseline for quantifying the O₃ enhancement in the southern plume (65–74 ppbv, Table 1). We deduce a net ozone production of 8–17 ppbv in the southern plume in the 2 days following the splitting of the plume. Photochemical model calculations by A. J. Hamlin et al. (manuscript in preparation, 2003) initialized with the conditions observed in the northern plume yield an O₃ production of only 2–5 ppbv in 2 days over the subsiding trajectory of the southern plume and do not reproduce the observed PAN loss. Increasing the rate of
PAN decomposition by a factor of 2.1–2.3 in that calculation, within the range of the uncertainty in the rate constant [Sander et al., 2003] can match the observed PAN decomposition and produces an additional 2–3 ppbv of O₃. This O₃ increment matches the O₃ enhancement observed in profile D but still underestimates that in profile E. Interpretation of this discrepancy is difficult as a result of uncertainty in the initial conditions. Heterogeneity within the plume, which was not captured in the model calculations, is a factor of uncertainty in the analysis.

5. Conclusions

[30] We have presented an integrated analysis of continental outflow and trans-Pacific transport of Asian pollution by using aircraft observations from the TRACE-P mission (February–April 2001), concurrent satellite observations of CO columns from the MOPITT instrument, and a global 3-D simulation with the GEOS-CHEM model. We used this analysis to determine the utility of the MOPITT observations to quantify Asian outflow and trans-Pacific transport, and to examine in more detail the sources and photochemical evolution (in particular O₃ production) in a major trans-Pacific event observed during TRACE-P.

[31] The GEOS-CHEM model, previously evaluated with TRACE-P observations of Asian outflow of CO over the northwest Pacific, is found to be highly correlated and globally unbiased with respect to the MOPITT observations during TRACE-P ($R^2 = 0.87$, slope = 0.95). The agreement between MOPITT observations and the GEOS-CHEM model simulation over China suggests no obvious bias in anthropogenic sources in this region. There are some regional biases, the largest of which is an 18% model overestimate of MOPITT CO columns over Southeast Asia. We estimate that a 60% decrease in seasonal biomass

---

**Figure 12.** Cross section of O₃ concentrations measured by the differential absorption laser (DIAL) along the tracks of TRACE-P (left) flight 4 between California and Hawaii and (right) flight 5 between Hawaii and Guam. See Figure 8 for details of flight tracks. Extensive Asian pollution layers characterized by elevated CO were sampled by the aircraft between 5 and 10 km altitude on flight 4 and between 2 and 4 km altitude on flight 5. These layers contained elevated O₃ only south of 35°N, as shown. See color version of this figure at back of this issue.

---

**Figure 13.** Concentrations of NOₓ species in the northern and southern branches of the Asian trans-Pacific plume observed by the TRACE-P DC-8 aircraft on 26 February 2001 during flight 4 between California and Hawaii (profile A between 600–370 hPa) and on 27 February 2001 during flight 5 between Hawaii and Guam (profiles D and E between 800–600 hPa). The concentrations are averages of 8 and 21 observations, respectively.
burning from that region would resolve this discrepancy, and such a correction would be consistent with an inverse model analysis of the TRACE-P CO observations using GEOS-CHEM [Palmer et al., 2003]. An important caveat is that model simulation of the MOPITT column CO is sensitive (through the instrument averaging kernel) to the shape of the CO vertical profile. As an extreme case, suppression of deep convection over Southeast Asia in the model would resolve the regional discrepancy with MOPITT without any change to the biomass burning source. This result highlights the importance of in situ measurements of vertical profiles from aircraft to assist the interpretation of satellite observations.

[32] The MOPITT observations for February-April 2001 identify four major events of trans-Pacific transport of Asian pollution to North America. The GEOS-CHEM model reproduces these events and shows high correlation with the corresponding MOPITT data, degrading however from the northwest to the northeast Pacific. Both numerical diffusion and vertical bias in the model may contribute to the underestimate over the northeast Pacific. All four events observed by MOPITT were also sampled in situ over the northeast Pacific by either the TRACE-P or the PHOBEA-II aircraft missions, or by the Cheeka Peak Observatory in Washington State.

[33] A series of major Asian pollution layers sampled in TRACE-P transit flights from California to Hawaii (26 February) and Hawaii to Guam (27 February) provided an opportunity for a more detailed investigation of the trans-Pacific transport and chemical evolution of these layers, including in particular O₃ production. Concentrations of CO in the layers approached 300 ppbv. Elevated O₃, approaching 80 ppbv, was observed in the low-latitude layers only. Back trajectories and chemical tracers reveal that these layers all originated from a single Asian outflow event on 22 February when a warm conveyor belt ahead of a cold front lifted Asian anthropogenic and biomass burning pollution to the free troposphere. The plume split into southern and northern branches upon encountering a blocking high-pressure system over the mid-Pacific. The MOPITT observations and the GEOS-CHEM model simulation allow a reconstruction of the evolution of this Asian outflow plume during trans-Pacific transport, although GEOS-CHEM does not reproduce the magnitude of the enhancements, perhaps because of numerical diffusion. Elevated O₃ (ΔO₃ = 8–17 ppbv) was observed in the southern but not in the northern plume. Reactive nitrogen in the northern plume was present mostly as PAN, but subsidence in the southern plume was found to drive PAN decomposition and from there O₃ formation. The ΔO₃ observed in the southern plume was high relative to values obtained from a photochemical model calculation initialized with the conditions of the northern plume. This represents the first field observation of PAN decomposition driving O₃ production in polluted plumes transported to the remote troposphere.

[34] Acknowledgments. This work was supported by the Global Tropospheric Chemistry Program (GTCP), the NASA Atmospheric Chemistry Modeling and Analysis Program (ACMAP), and by NASA Headquarters under the Earth System Science Fellowship Grant NGS-30460. CLH was also supported by the Natural Science and Engineering Research Council of Canada. We gratefully acknowledge Daniel Ziskin and Jarmei Chen for accelerating the data processing for TRACE-P and Bob Yantosca for HDF programming assistance. We would also like to acknowledge useful discussions with Paul Palmer and Jennifer Logan as well as the comments from two anonymous reviewers.

References


Figure 3. Mean CO columns measured by MOPITT during the Transport and Chemical Evolution Over the Pacific (TRACE-P) campaign (20 February to 10 April 2001) and corresponding GEOS-CHEM model columns sampled along the MOPITT observational track and transformed with the MOPITT averaging kernels. Both the MOPITT data and the transformed GEOS-CHEM fields have been averaged over the GEOS-CHEM 2° × 2.5° model grid. The bottom panel shows the difference between GEOS-CHEM and MOPITT. The color scales for the top two panels are saturated at 3.5 × 10^{18} molecules/cm^2, and the bottom panel scale is saturated at 1.0 × 10^{18} molecules/cm^2.

Figure 4. Percentage of days with MOPITT observations in each 2° × 2.5° GEOS-CHEM model grid square during the TRACE-P period (20 February to 10 April 2001).
Figure 8. Five-day kinematic back trajectories based on European Centre for Medium-Range Weather Forecasts meteorological fields [Fuelberg et al., 2003] for the enhanced CO layers observed in TRACE-P DC-8 flight 4 from California to Hawaii (26 February) and flight 5 from Hawaii to Guam (27 February). The flight tracks are shown in black, and arrival points in profiles A-E of Figure 9 are shown in red, green, purple, blue, and cyan, respectively.

Figure 9. Vertical concentration profiles of CO (black lines) and O$_3$ (red lines) measured from the DC-8 aircraft during the TRACE-P transit flight 4 from California to Hawaii and flight 5 from Hawaii to Guam on 25 and 26 February 2001. Profile locations and the flight tracks for flight 4 and flight 5 are shown in Figure 8. Profile A was a double spiral (ascending and then descending) conducted for MOPITT validation to check the consistency of the vertical structure of CO; data from both spirals are shown (there were no observations between 500 and 400 hPa during the ascent). CO measurements between 550 and 300 hPa in profile B are not available. Profiles D and E include descents and ascents separated by 86 km and 275 km, respectively.
Figure 11. CO columns during the trans-Pacific Asian pollution event on 23–27 February. (left) MOPITT observations. (middle) GEOS-CHEM model results sampled along MOPITT orbit tracks and with averaging kernel applied. (right) Original GEOS-CHEM model results sampled at 1200 UT. The color bar is saturated at $3.5 \times 10^{18}$ molecules/cm$^2$.
Figure 12. Cross section of O₃ concentrations measured by the differential absorption laser (DIAL) along the tracks of TRACE-P (left) flight 4 between California and Hawaii and (right) flight 5 between Hawaii and Guam. See Figure 8 for details of flight tracks. Extensive Asian pollution layers characterized by elevated CO were sampled by the aircraft between 5 and 10 km altitude on flight 4 and between 2 and 4 km altitude on flight 5. These layers contained elevated O₃ only south of 35°N, as shown.