Late-spring increase of trans-Pacific pollution transport in the upper troposphere

Yuhang Wang,[1] Yunsoo Choi,[1] Tao Zeng,[1] Brian Ridley,[2] Nicola Blake,[3] Donald Blake,[3] and Frank Flocke[2]

Received 17 October 2005; revised 10 November 2005; accepted 29 November 2005; published 7 January 2006.

[1] The observations during the Tropospheric Ozone Production about the Spring Equinox (TOPSE) experiment show large enhancements of NO_x, PAN, O_3, CO, CFCs, and Halon-1211 in the upper troposphere over North America in late spring. Analysis of these observations and model results indicate that the enhancements are most likely driven by a surge of trans-Pacific pollutant transport in late spring. The rapid seasonal transition is particularly striking for upper tropospheric NO_x, resulting in large increases in photochemical oxidation and O_3 production during the period. The transition is later in season than that of low-altitude trans-Pacific transport, which peaks in March and April. The current generation of global chemical transport models clearly underestimates this long-range transport of pollutants, implying an underestimation in the model-projected impact on regional air quality over North America (through subsidence). **Citation:** Wang, Y., Y. Choi, T. Zeng, B. Ridley, N. Blake, D. Blake, and F. Flocke (2006), Late-spring increase of trans-Pacific pollution transport in the upper troposphere, *Geophys. Res. Lett.*, *33*, L01811, doi:10.1029/2005GL024975.

1. Introduction

[2] Trans-Pacific transport of pollutants to North America has long been recognized [e.g., *Andreae et al.*, 1988; *Merrill et al.*, 1989; *Kritz et al.*, 1990; *Parrish et al.*, 1992]. A particular concern is how increasing pollution from Asia driven by rapid regional economic growth affects O_3 concentrations in the United States [e.g., *Berntsen et al.*, 1999; *Jacob et al.*, 1999]. For example, the subsidence of trans-Pacific transported high O_3, produced catalytically by NO_x ($NO + NO_2$) during the oxidation of CO and volatile organic compounds (VOCs), could significantly contribute to exceedances of the National Ambient Air Quality Standard at California mountain sites [*Hudman et al.*, 2004].

[3] Measurements aimed at exploring the effects of trans-Pacific transport have focused previously on low-altitude O_3, CO, and peroxyacetyl nitrate (PAN) [*Jaffe et al.*, 1999; *Lin et al.*, 2000; *Jaffe et al.*, 2003]. In this work, we focus on two aspects that have not been explored in the previous analyses of trans-Pacific transport and evaluate our current capability to simulate these observed features. The first aspect is whether the characteristics of upper tropospheric trans-Pacific transport differ from those at lower altitudes. The second is whether we can deduce the effects of trans-Pacific transport on O_3 and the most critical precursor for its production, NO_x, over North America. To our knowledge, no previous attempt has been made to examine the impact of trans-Pacific transport on North American NO_x.

[4] We focus our analysis on the measurements made during the Tropospheric Ozone Production about the Spring Equinox (TOPSE) experiment during February–May, 2000 [*Atlas et al.*, 2003]. Thirty eight science flights were conducted in 7 deployments (1–2 weeks apart), covering the region from Colorado to north of Thule, Greenland. A comprehensive suite of chemical species related to tropospheric O_3 chemistry was measured from the surface up to 8 km.

[5] To analyze these measurements, we make use of a 3-D regional chemical transport model (RCTM) [*Choi et al.*, 2005] and the global GEOS-CHEM model [*Bey et al.*, 2001]. The RCTM model domain covers the continental United States and Canada with a horizontal resolution of 70×70 km^2 and 21 layers up to 100 hpa in the vertical [*Choi et al.*, 2005]. The National Center for Atmospheric Research/Penn State MM5 was used to simulate the meteorological fields using four dimensional data assimilation with the National Center for Environmental Prediction reanalysis, surface, and rawinsonde observations. The spring 2000 simulations using the global GEOS-CHEM model (version 7.2.4 with a horizontal resolution of $2^\circ \times 2.5^\circ$ and 30 layers up to 0.01 hpa, GEOS-3 meteorological fields) provide the initial and hourly boundary conditions for trace gases. The RCTM shares the chemistry and deposition modules of GEOS-CHEM. Particular attention was paid to the implementation of convective transport and lightning NO_x production schemes in the RCTM [*Choi et al.*, 2005].

2. Results and Discussion

[6] During TOPSE, the largest increases in upper tropospheric reactive nitrogen NO_x and PAN were observed during late spring [*Wang et al.*, 2003a]. We first investigate the potential impact of trans-Pacific transport on NO_x concentrations. Figure 1 shows the observed and simulated NO_x mixing ratios from March to May during TOPSE. The aircraft observations clearly show large increases of NO_x concentrations above 5 km from March to May. The RCTM is in reasonable agreement with the observed low concentrations in the upper troposphere in February (not shown)

[1]School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia, USA.
[2]Atmospheric Chemistry Division, National Center for Atmospheric Research, Boulder, Colorado, USA.
[3]Department of Chemistry, University of California, Irvine, California, USA.

0094-8276/06/2005GL024975$05.00

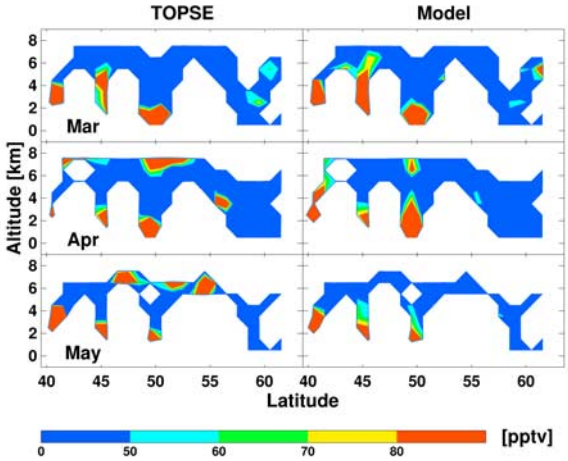

Figure 1. Observed and RCTM simulated monthly mean distributions of NO_x from March to May, 2000. The RCTM data were sampled along the TOPSE flight tracks.

and March. The model simulates some enhancements in April but none in May, and hence greatly underestimates NO_x concentrations. The April enhancements in the RCTM are due to localized convective transport and lightning NO_x production. Those enhancements were not simulated in the global GEOS-CHEM model.

[7] Both models show a lack of significant lightning and convective activity over the region in May due to the presence of a high-pressure ridge system residing over the western United States. Inspection of measurements in each flight during May (not shown) finds 4 occasions with NO_x mixing ratios > 50 pptv at altitude > 6 km. These enhancements are up to 200 km horizontally and 2 km vertically. The measured dimensions are often limited by sampling. The corresponding model simulations show discernable but much underestimated enhancements for two occasions (not shown). Previous NO_x simulations using different regional (HANK [*Hess et al.*, 2000]) and global (MOZART-2 [*Horowitz et al.*, 2003]) CTMs have also shown model underestimations of 50–60% with few data points of simulated NO_x mixing ratios > 50 pptv above 5 km [*Emmons et al.*, 2003]. The previous researchers did not speculate on the causes for the large model underestimation.

[8] Overall, four different models with largely independent model formulations of convective transport and lightning parameterization and often drastically different meteorological fields and chemical formulations show that the models greatly underestimate upper tropospheric NO_x concentrations in April and May. The cause does not appear to be a poor representation of convection or lightning NO production. Model simulated NO_x enhancements due to local convection and associated lightning NO_x production are low due to the prevailing high-pressure ridge system over the western United States. In addition, previous comparisons of RCTM simulations with satellite NO_x and CO observations indicate that the model captures reasonably well the observed day-to-day variations in lightning NO emissions and convective activity [*Choi et al.*, 2005]. We therefore hypothesize that trans-Pacific transport of pollutants in the upper troposphere into the region was underestimated in the models. The hypothesis can be better tested by examining the observations and simulations of other chemical tracers. We focus on the comparison in May when the pollutant enhancements are most significant.

[9] We compare in Figure 2 the observed and simulated CO, PAN, and O_3 concentrations in May. The RCTM has distributions similar to GEOS-CHEM but with more localized enhancements. Hence only the former is shown. Carbon monoxide is a good tracer for anthropogenic emissions. Peroxyacetyl nitrate is the reaction product of NO_2 and peroxyacetyl radicals formed during the oxidation of VOCs. It is therefore a good tracer for tropospheric chemical activity of O_3 precursors. While in reasonable agreement below 6 km, the simulated CO, PAN, and O_3 concentrations are much lower than the observations at higher altitudes. The observed upper tropospheric enhancements of CO, PAN, and O_3 tend to be collocated with those of NO_x (Figure 1). A close inspection of the simulated O_3 concentrations shows slight enhancements in the upper tropospheric regions where high O_3 was observed. The enhancements correspond to those in the GEOS-CHEM simulated western boundary conditions and are not caused by photochemical production in the regional model, suggesting that the global model does have some skill in simulating trans-Pacific transport [e.g., *Hudman et al.*, 2004] but the simulated magnitudes are too small.

[10] The discrepancies between simulated and observed CO and PAN concentrations are much larger in May than the three previous months (not shown). At lower altitudes (<6 km), the model reproduces well the observed rapid decrease of CO from April to May. The decrease reflects more active photochemical oxidation toward summer. While the observations show a large increase of CO at higher altitudes (>6 km), the simulated concentrations are less in May than April. The simulated PAN concentrations in May are similar to April at high altitudes, while the observations also show a large increase. The observed O_3 mixing ratios at high altitudes show a clear increase from

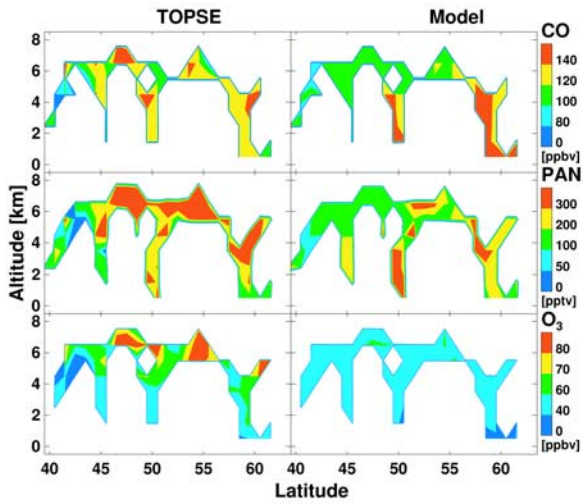

Figure 2. Same as Figure 1 but for CO, PAN, and O_3 in May. When constructing the observed O_3 distribution, we did not include measurements with mixing ratios >110 ppbv to filter out the effect of stratospheric O_3.

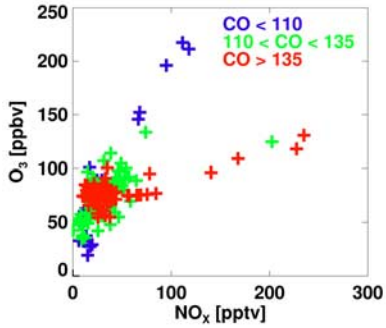

Figure 3. Observed correlations between O_3 and NO_x grouped by CO mixing ratios (ppbv) in May. Only coincidental measurements of all three species above 4 km are included.

50–60 ppbv in February to >80 ppbv in May (Figure 2) [*Browell et al.*, 2003]; the model does not reproduce the large increase.

[11] We attributed previously 60 and 80% of the observed springtime O_3 increase to photochemical production at mid and high latitudes, respectively [*Wang et al.*, 2003b]. The upper tropospheric O_3 problem in the model may therefore be attributed to the large underestimation of NO_x. There is also direct observational evidence for the importance of photochemical O_3 production catalyzed by NO_x. Figure 3 shows the observed correlation between NO_x and O_3 above 4 km in May. By examining the deviation from a normal mode in the CO cumulative probability distribution in May, we find two distinct data groups, CO < 110 ppbv (lower 10th percentile) and CO > 135 ppbv (upper 30th percentile). Low CO mixing ratios reflect strong influence by either the stratospheric or clean marine boundary layer air, while high CO mixing ratios represent polluted air masses. The low CO data points show high O_3 mixing ratios of 150–220 ppbv with NO_x of 80–110 pptv reflecting the influence of stratospheric air, since O_3 mixing ratios in the clean marine boundary layer are low.

[12] The high CO data points show O_3 mixing ratios increasing to 120 ppbv while NO_x mixing ratios reaching 250 pptv. These high O_3 concentrations mainly reflect photochemical production of O_3 in polluted tropospheric air masses. Lightning affects negligibly the concentrations of CO or O_3. Fresh local convection tends to produce higher CO and NO_x concentrations through transport, but relatively low O_3 concentrations and PAN/NO_x ratios due in part to the time required for the photochemical processing. Both the high PAN/NO_x ratios of 5–40 (not shown) and >80 ppbv of O_3 with moderate amount of NO_x (~150 pptv) suggests that the air masses are photochemically aged and not significantly affected by local lightning or convective transport. Furthermore, inspection of backtrajectories [*Wang et al.*, 2003b] for data points with NO_x > 50 pptv in Figure 3 indicates that they are driven by trans-Pacific transport not Pacific recirculation of pollutants emitted from the West Coast.

[13] Our hypothesis that the observed large enhancements of upper tropospheric NO_x, CO, PAN, and O_3 are due to trans-Pacific transport is also supported by the measurements of CFCs and Halon-1211. The production of CFCs and Halon-121 was phased out in developed counties in 1995 and will be phased out in developing countries by 2010. Therefore they are good tracers for air masses from East Asia. Observed CFCs and Halon-1211 exhibit similar features. We show the distribution of CFC-12 in May in Figure 4. The large enhancements at high altitudes (>6 km) tend to be consistent with those of NO_x, CO, PAN, and O_3. A close inspection of the measurements, which correspond to the enhancements of NO_x and CFC-12 observed at 45–50°N at high altitudes, reveals a general association of high NO_x concentrations with high CFC-12. However, the point-to-point correspondence is poor possibly for two reasons. First, CFC-12 was sampled at a much lower frequency than NO_x. Secondly, the surface sources of NO_x and CFCs are not necessarily collocated and NO_x concentrations are also affected by lightning production.

[14] A major limitation of this work is that we do not know the exact origins for the observed trace gas enhancements. While TOPSE measurements are useful to examine the impact of trans-Pacific transport, the effects of specific distant sources become difficult to diagnose. Previous studies indicate that emissions of NO_x and CO are too low in China by ~50% [*Heald et al.*, 2004; *Wang et al.*, 2004]. In a sensitivity study (not shown), we doubled the Chinese surface emissions of these two gases. The large underestimation of upper tropospheric NO_x in TOPSE regions persists, likely reflecting the low export efficiency from the boundary layer and short chemical lifetime of NO_x. Observed upper tropospheric CO enhancements are simulated well north of 50° N but still underestimated at lower latitudes. However, GEOS-CHEM now overestimates CO in February and March. TOPSE measurements do not show a strong increase of CH_3Cl in May implying that the contribution from biomass burning to the seasonal increase is limited. It is possible that trans-Pacific pollutant transport surges in May due to a significant increase of convection and lightning over East Asia or the western Pacific (not simulated in the models). Detailed analysis of other measurements will be necessary to explore that possibility.

3. Conclusions

[15] TOPSE observations show large enhancements of NO_x, PAN, CO, O_3, and CFCs at altitude > 6 km in May. We hypothesize that these enhancements are due to trans-Pacific transport. The hypothesis is supported by our analysis of the observations and model results. First, we find that these chemical tracers show consistent enhance-

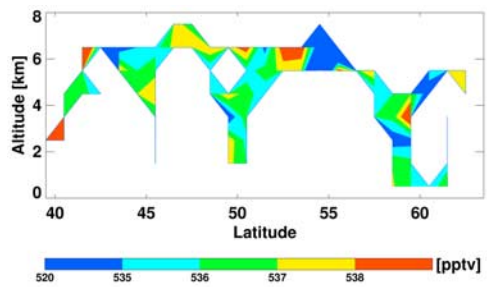

Figure 4. Observed monthly mean distribution of CFC-12 in May.

ment patterns at high altitudes. Both CFC enhancements and backtrajectory calculations imply trans-Pacific transport from East Asia. Secondly, the observed NO_x-O_3 correlation for high CO data points indicates significant tropospheric photochemical production. Thirdly, the relatively high PAN/NO_x ratios of >5 indicate photochemically aged air masses. Lastly, separate regional/global chemical transport models using different meteorological fields and chemical formulations consistently underestimate the enhancements of NO_x, PAN, and CO. The contribution by North American surface emissions is limited in these simulations because the high-pressure ridge system over the western United States suppresses convection and lightning in May.

[16] Our results indicate that the rapid late-spring increase of reactive nitrogen NO_x and PAN at northern mid-latitude upper troposphere observed during TOPSE is most likely due to the enhancements of these species by trans-Pacific transport. These enhancements result in significant increases of photochemical oxidation and O_3 production. The trace gas enhancements including that of CO are still increasing in May. It is very different from trans-Pacific transport driven CO enhancements at low altitudes, which peak in March and April [e.g., *Weiss-Penzias et al.*, 2004]. The current global CTMs do not capture this rapid seasonal transition, which results in a large underestimation of photochemical production of O_3 in the models. The problem raises concerns on our capability to assess the effects of intercontinental transport on regional air quality.

[17] **Acknowledgments.** This work was supported by the National Science Foundation Atmospheric Chemistry Program. The GEOS-CHEM model is managed at Harvard University with support from the NASA Atmospheric Chemistry Modeling and Analysis Program; we thank Robert Yantosca and Daniel Jacob for providing us the model and data. NCAR is operated by the University Corporation for Atmospheric Research under sponsorship of the National Science Foundation.

References

Andreae, M. O., H. Berresheim, T. W. Andreae, M. A. Kritz, T. S. Bates, and J. T. Merrill (1988), Vertical distribution of dimethylsul?de, sulfur dioxide, aerosol ions, and radon over the northeast Paci?c Ocean, *J. Atmos. Chem.*, *6*, 149–173.

Atlas, E. L., B. A. Ridley, and C. Cantrell (2003), The Tropospheric Ozone Production about the Spring Equinox (TOPSE) experiment: Introduction, *J. Geophys. Res.*, *108*(D4), 8353, doi:10.1029/2002JD003172.

Berntsen, T. K., S. Karlsdottir, and D. A. Jaffe (1999), Influence of Asian emissions on the composition of air reaching the northwestern United States, *Geophys. Res. Lett.*, *26*, 2171–2174.

Bey, I., D. J. Jacob, R. M. Yantosca, J. A. Logan, B. D. Field, A. M. Fiore, Q. Li, H. Y. Liu, L. J. Mickley, and M. G. Schultz (2001), Global modeling of tropospheric chemistry with assimilated meteorology: Model description and evaluation, *J. Geophys. Res.*, *106*, 23,073–23,096.

Browell, E. V., et al. (2003), Ozone, aerosol, potential vorticity, and trace gas trends observed at high-latitudes over North America from February to May 2000, *J. Geophys. Res.*, *108*(D4), 8369, doi:10.1029/2001JD001390.

Choi, Y., Y. Wang, T. Zeng, R. Martin, T. Kurosu, and K. Chance (2005), Evidence of lightning NO_x and convective transport of pollutants in satellite observations over North America, *Geophys. Res. Lett.*, *32*, L02805, doi:10.1029/2004GL021436.

Emmons, L., et al. (2003), Budget of tropospheric ozone during TOPSE from two chemical transport models, *J. Geophys. Res.*, *108*(D8), 8372, doi:10.1029/2002JD002665.

Heald, C. L., D. J. Jacob, D. B. A. Jones, P. I. Palmer, J. A. Logan, D. G. Streets, G. W. Sachse, J. C. Gille, R. N. Hoffman, and T. Nehrkorn (2004), Comparative inverse analysis of satellite (MOPITT) and aircraft (TRACE-P) observations to estimate Asian sources of carbon monoxide, *J. Geophys. Res.*, *109*, D23306, doi:10.1029/2004JD005185.

Hess, P. G., S. Flocke, J.-F. Lamarque, M. C. Barth, and S. Madronich (2000), Episodic modeling of the chemical structure of the troposphere as revealed during the spring MLOPEX 2 intensive, *J. Geophys. Res.*, *105*, 26,809–26,840.

Horowitz, L. W., et al. (2003), A global simulation of tropospheric ozone and related tracers: Description and evaluation of MOZART, version 2, *J. Geophys. Res.*, *108*(D24), 4784, doi:10.1029/2002JD002853.

Hudman, R. C., et al. (2004), Ozone production in transpacific Asian pollution plumes and implications for ozone air quality in California, *J. Geophys. Res.*, *109*, D23S10, doi:10.1029/2004JD004974.

Jacob, D. J., J. A. Logan, and P. P. Murti (1999), Effect of rising Asian emissions on surface ozone in the United States, *Geophys. Res. Lett.*, *26*, 2175–2178.

Jaffe, D., et al. (1999), Transport of Asian air pollution to North America, *Geophys. Res. Lett.*, *26*, 711–714.

Jaffe, D. A., I. McKendry, T. Anderson, and H. Price (2003), Six 'new' episodes of trans-Pacific transport of air pollutants, *Atmos. Environ.*, *37*, 391–404.

Kritz, M. A., J.-C. Le Roulley, and E. F. Danielsen (1990), The China Clipper—Fast advective transport of radon-rich air from the Asian boundary layer to the upper troposphere near California, *Tellus, Ser. B*, *42*, 46–61.

Lin, C., D. J. Jacob, W. Munger, and A. Fiore (2000), Increasing background ozone in surface air over the United States, *Geophys. Res. Lett.*, *27*, 3465–3468.

Merrill, J. T., M. Uematsu, and R. Bleck (1989), Meteorological analysis of long range transport of mineral aerosols over the North Pacific, *J. Geophys. Res.*, *94*, 8584–8598.

Parrish, D. D., C. J. Hahn, E. J. Williams, R. B. Norton, F. C. Fehsenfeld, H. B. Singh, J. D. Shetter, B. W. Gandrud, and B. A. Ridley (1992), Indications of photochemical histories of Pacific air masses from measurements of atmospheric trace species at Point Arena, California, *J. Geophys. Res.*, *97*, 15,883–15,901.

Wang, Y., et al. (2003a), Springtime photochemistry at northern mid and high latitudes, *J. Geophys. Res.*, *108*(D4), 8358, doi:10.1029/2002JD002227.

Wang, Y., et al. (2003b), Intercontinental transport of pollution manifested in the variability and seasonal trend of springtime O_3 at northern middle and high latitudes, *J. Geophys. Res.*, *108*(D21), 4683, doi:10.1029/2003JD003592.

Wang, Y. X., M. B. McElroy, T. Wang, and P. I. Palmer (2004), Asian emissions of CO and NO_x: Constraints from aircraft and Chinese station data, *J. Geophys. Res.*, *109*, D24304, doi:10.1029/2004JD005250.

Weiss-Penzias, P., D. A. Jaffe, L. Jaeglé, and Q. Liang (2004), Influence of long-range-transported pollution on the annual and diurnal cycles of carbon monoxide and ozone at Cheeka Peak Observatory, *J. Geophys. Res.*, *109*, D23S14, doi:10.1029/2004JD004505.

D. Blake and N. Blake, Department of Chemistry, University of California, Irvine, Irvine, CA 92697, USA.

Y. Choi, Y. Wang, and T. Zeng, School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA 30332, USA. (ywang@eas. gatech.edu)

F. Flocke and B. Ridley, Atmospheric Chemistry Division, National Center for Atmospheric Research, Boulder, CO 80307, USA.