Intercontinental Transport of Anthropogenic and Biomass Burning Pollution

A thesis presented

by

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Abstract

I apply a global 3-dimensional model of tropospheric ozone- NO_x -hydrocarbon chemistry to investigate intercontinental transport of anthropogenic and biomass burning pollution, and its impact on global atmospheric chemistry and regional air quality.

Model simulation of tropospheric ozone shows a summer maximum over the Middle East which is supported by observations. The maximum results from anticyclonic circulation in the middle-upper troposphere over the region funneling northern midlatitude pollution transported in the westerly midlatitude jet and lightning outflow from the Indian monsoon and pollution from China transported in an easterly tropical jet. This ozone maximum is a major diagnostic feature for intercontinental transport.

An important diagnostic site for transatlantic transport of North American pollution is Bermuda, where surface ozone shows a spring maximum. Boundary layer transport of North American pollution behind cold fronts is responsible for springtime high-ozone events at Bermuda. Model reproduces positive ozone correlations with ⁷Be and ²¹⁰Pb; the ozone-⁷Be correlation reflects subsidence behind cold fronts, resulting in mixing of middle-tropospheric air with boundary layer outflow (an obfuscating factor in past interpretations of subsiding back-trajectories as evidence for a stratospheric origin for ozone).

Export efficiency of NO_y from continental boundary layer has important implication for intercontinental transport. Lagrangian analyses of the NO_y -CO correlations observed from aircraft downwind of North America indicated significantly lower NO_y export efficiency and NO_x fraction in exported NO_y than 3-dimensional model Eulerian budget analyses. Model reproduces observed NO_y -CO correlations. Previous Lagrangian analyses of NO_y export efficiency were biased low due to underestimate of CO background. Correcting for this bias results in similar NO_y export efficiencies in the model and observations from Lagrangian analysis that are consistent with Eulerian analysis. Different NO_x fractions in exported NO_y from Lagrangian and Eulerian analyses reflect fast oxidation of NO_x . Eventual ozone production due to exported NO_y is comparable to direct ozone export.

I examined transatlantic transport of ozone pollution and its effects on surface ozone in Europe and North America. Surface ozone and CO observations at Sable Island and Mace Head were used for model evaluation. North American emissions contribute 5 ppbv to Mace Head ozone (10-20 ppb during transatlantic events). This North American influence is strongly correlated with the North Atlantic Oscillation index, implying that this index could be used to forecast transatlantic transport. European emissions contribute < 2 ppb to Sable Island ozone (5-10 ppb during transatlantic events). North American emissions enhance surface ozone in Europe by 2-4 ppb (5-10 ppb during transatlantic events).

I evaluated atmospheric budgets of biomass burning tracers HCN and CH₃CN. Observations imply a much shorter lifetime for HCN than previously thought. I proposed ocean uptake as the missing HCN sink, and found that model can reproduce observations with biomass burning and ocean uptake as the main source and sink. Aircraft observations of HCN and CH₃CN confirm dominant ocean sink and biomass burning source for both. HCN enhancements in Chinese urban plumes are attributed to residential coal burning. Exclusive biomass burning source for CH₃CN implies that it is a sensitive biomass burning tracer.

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Chapter 1

Overview

There is presently much interest in intercontinental transport of anthropogenic and biomass burning ozone pollution as a factor to be considered in the design of regional air quality control strategies [*NAS*, 2001; *CENR*, 2001]. In this study, I use the GEOS-CHEM global 3-D model of tropospheric chemistry driven by assimilated meteorology [*Bey et al.*, 2001a] to investigate intercontinental transport of anthropogenic ozone pollution and to evaluate the atmospheric budgets of the biomass burning tracers hydrogen cyanide (HCN) and methyl cyanide (CH₃CN).

I begin in chapter 2 by examining the origin of the prominent summer maximum in the tropospheric concentrations and columns of ozone simulated by GEOS-CHEM over the Middle East [*Li et al.*, 2001]. The Middle East is a largely unexplored region for ozone observations, but vertical profiles from the MOZAIC program on commercial aircraft [*Marenco et al.*, 1998; *Stohl et al.*, 2001] indicate high summer mixing ratios that are comparable to model values. Tropospheric observations of ozone from SAGE II have since supported the presence of this summer ozone maximum [*Kar et al.*, 2002]. The Middle East ozone maximum in the model appears in May and disappears in September, consistent with the available observations. It is due in large part to upper-level east-erly transport of pollution and lightning outflow from India and China, followed by subsidence over the Middle East. This represents an important case of transcontinental transport of pollution, and

a somewhat counter-intuitive one as it involves fast easterly transport in the subtropical free troposphere. Further investigation of the Middle East ozone maximum by more detailed observations in the future should provide an important test of our understanding of tropospheric chemistry. An anthropogenic origin for this maximum would have important implications for radiative forcing of climate [*Mickley et al.*, 1999].

An important diagnostic site for the transatlantic transport of North American pollution is Bermuda. Surface ozone at that site and other remote sites in northern midlatitudes shows a strong spring maximum [Oltmans, 1981; Logan, 1985; Oltmans and Levy II, 1992, 1994; Logan, 1999; Monks, 2000]. This springtime ozone maximum has been the focal point in the debate of the relative importance of tropospheric production versus stratospheric influx as sources of tropospheric ozone. There are conflicting interpretations of the spring ozone maximum observed at Bermuda. Oltmans and Levy II [1992,1994] and Moody et al. [1995] argued for a stratospheric origin based on isentropic back-trajectories indicating strong subsidence. Dickerson et al., [1995] argued that boundary layer transport of North American pollution behind cold fronts is responsible based on observed correlation between ozone and CO. I show in chapter 3 [Li et al., 2002b] that past interpretations of the origin of ozone at Bermuda can be reconciled through a concerted GEOS-CHEM analysis of observed fields of ozone, CO, and radionuclides, including Lagrangian examination of isentropic back-trajectories. The model reproduces the observed seasonal cycle of surface ozone at Bermuda and captures the springtime day-to-day variability. I find that boundary layer transport of North American pollution behind cold fronts is the principal contributor to springtime surface ozone at Bermuda and is responsible for all the high-ozone events. The model reproduces the observed positive correlations of surface ozone with ⁷Be and ²¹⁰Pb at Bermuda; the correlation with ⁷Be reflects the strong subsidence behind cold fronts, resulting in the mixing of middle-tropospheric air with continental boundary layer outflow. This mixing appears to have been an obfuscating factor in past interpretations of subsiding back-trajectories at Bermuda as evidence for a stratospheric or upper-tropospheric origin for ozone.

The export efficiency of NO_x from the continental boundary layer has important implication on intercontinental transport of ozone pollution. Most of the global production of tropospheric ozone takes place in the free troposphere [Wang et al., 1998], where the limiting factor is the availability of nitrogen oxides ($NO_x = NO + NO_2$) [*Chameides et al.*, 1992]. About half of the global emission of NO_x is from fossil fuel combustion in the continental boundary layer [IPCC, 2001]. Much of the fossil fuel NO_x is oxidized to nitric acid (HNO₃) in less than a day and removed within the boundary layer by deposition. The fraction of fossil fuel NO_x exported out of the continental boundary layer as NO_v provides an important NO_x source in the remote troposphere [Moxim et al., 1996; Horowitz and Jacob, 1999; Kasibhatla et al., 1993]. A recent Lagrangian analysis [Parrish et al., 2003] of the NO_v-CO correlations observed from aircraft in the North Atlantic Regional Experiment (September 1997, NARE'97) downwind of eastern North America indicated a NO_v export efficiency of < 10%, with < 10% of the exported NO_v present as NO_x. However, previous 3-D model Eulerian budget analyses [Kasibhatla et al., 1993, Horowitz et al., 1998, Liang et al., 1998] for the North American boundary layer indicated NO_v export efficiencies of 25-30% with 30-35% of the exported NO_y present as NO_x. I investigate this apparent discrepancy in chapter 4 [Li et al., 2003b] by simulating the NARE'97 aircraft observations with GEOS-CHEM and using the model to calculate the NO_v export efficiency both through a Lagrangian analysis of the NO_v-CO correlations along the aircraft flight tracks and through a Eulerian budget analysis for the North American boundary layer. The model reproduces the variability and NO_{y} -CO correlations observed in the aircraft data and also at the Harvard Forest surface site in the northeastern United States. I show that the previous Lagrangian analyses [Stohl et al., 2002, Parrish et al., 2003] of the NO_{ν} export efficiency during NARE'97 were probably biased low due to underestimate of the CO background. Correcting for this bias I find a NO_y export efficiency of $17\pm7\%$ in the model and $15\pm11\%$ in the observations. A similar NO_v export efficiency (20%) in the model is obtained from the Eulerian budget analysis, demonstrating that the Lagrangian and Eulerian approaches are in fact consistent. Export efficiencies of NO_y in previous 3-D model Eulerian budget analyses [*Kasibhatla et al.*, 1993, *Horowitz et al.*, 1998, *Liang et al.*, 1998] were probably too high because of insufficient scavenging out of the continental boundary layer. Model results indicate that only 6% of the exported NO_y is present as NO_x along the aircraft flight tracks, in agreement with the observations [*Parrish et al.*, 2003], but that 40% of the NO_y export flux is as NO_x, in agreement with the previous 3-D model analyses [*Kasibhatla et al.*, 1993, *Horowitz et al.*, 1998, *Liang et al.*, 1998]. This result reflects the fast oxidation of NO_x during transport downwind of North America. The eventual ozone production in the global troposphere due to the exported NO_x and PAN is estimated to be comparable to the direct export of ozone pollution from the North American boundary layer.

I examine in chapter 5 [*Li et al.*, 2002a] the transatlantic transport of ozone pollution and its effect on surface ozone in Europe and North America by using a 5-year (1993-1997) GEOS-CHEM simulation evaluated with coastal observations on both sides of the North Atlantic. Recent studies have indicated that transpacific transport of Asian pollution affects North America [*Jacob et al.*, 1999; *Jaffe et al.*, 1999; *Wilkening et al.*, 2000; *Yienger et al.*, 2000; *Fiore et al.*, 2002], transatlantic transport of North American pollution affects Europe [*Derwent et al.*, 1998; *Ryall et al.*, 1998; *Stohl and Trickl*, 1999; *Forster et al.*, 2001], and transeurasian transport of European pollution affects Asia [*Liu et al.*, 2001]. The magnitudes of these effects and the need to include them in air quality control strategies are still highly uncertain. I focus the model evaluation on observed time series of ozone and CO in 1993-1997 at Mace Head (53°N, 10°W) in western Ireland and Sable Island (44°N, 60°W) in Atlantic Canada. I find that North American anthropogenic emissions contribute on average 5 ppbv to surface ozone at Mace Head, and up to 10-20 ppbv during transatlantic transport events which are forerunners of broader events in Europe. North American influence on ozone at Mace Head is strongly correlated with the North Atlantic Oscillation (NAO), implying that the NAO index could be used to forecast transatlantic transport of North American pollution on long time scales. European anthropogenic emissions contribute on average less than 2 ppbv to surface ozone at Sable Island but up to 5-10 ppbv during transatlantic transport events. North American anthropogenic emissions enhance surface ozone in continental Europe by 2-4 ppbv on average in summer, and by 5-10 ppbv during transatlantic transport events; transport in the boundary layer and subsidence from the free troposphere are both important mechanisms. I find in the model that 20% of the violations of the European Council ozone standard (55 ppbv, 8-hour average) in the summer of 1997 over Europe would not have occurred in the absence of anthropogenic emissions from North America. North American influence on surface ozone in Europe is particularly strong at the thresholds used for the European standards (55-65 ppbv).

In parallel to my work on the intercontinental transport of anthropogenic ozone pollution, I have been interested in biomass burning as another major factor influencing global tropospheric ozone. Intercontinental transport of biomass burning ozone has been observed extensively in the tropics [*Thompson et al.*, 1996a,b; *Schultz et al.*, 1999], but overlap of anthropogenic and biomass burning sources can make interpretation confusing [*Bey et al.*, 2001b]. I have focused on the development of nitriles (HCN and CH₃CN) as biomass burning tracers to improve source attribution of gases including ozone. Previous work suggests the utility of these compounds as biomass burning tracers [*Lobert et al.*, 1990; *Hamm and Warneck*, 1990], but no 3-D model analysis of atmospheric observations had been attempted prior to my work.

My initial work examined the global budget of HCN. Spectroscopic measurements of the atmospheric column of HCN at northern midlatitudes indicate factors of 2-3 seasonal variation with maxima in spring-summer [*Mahieu et al.*, 1995, 1997; *Zhao et al.*, 2000]. Mixing ratio of HCN retrieved from spectroscopic measurements of HCN column on board a space shuttle in the tropical upper troposphere indicate a range from 200 to 900 pptv [*Rinsland et al.*, 1998]. Such large variations are inconsistent with the conventional view prior to my work that HCN has an atmospheric lifetime of a few years with oxidation by OH providing the main sink [*Cicerone and*]

Zellner, 1983]. I propose in chapter 6 [*Li et al.*, 2000] that ocean uptake could provide the missing sink for atmospheric HCN, and show with the GEOS-CHEM model that the available observations of atmospheric HCN are consistent with a scenario where biomass burning provides the main source and ocean uptake provides the main sink. The Henry's law constant of HCN is sufficiently high (12 M atm⁻¹ at 298 K; *Edwards et al.* [1978]) for ocean uptake to impose an atmospheric lifetime of a few months if HCN(aq)/CN⁻ (*pKa* = 9.2) is consumed chemically or biologically in the ocean on a time scale of a few months or less. From the constraint offered by the relative seasonal amplitude in the column observations, I predicted a saturation of less than 5/6 (0.83) for HCN in the ocean.

In chapter 7, I use GEOS-CHEM model analysis of HCN and CH₃CN observations in Asian outflow from the TRACE-P aircraft mission over the NW Pacific [Li et al., 2003a] to further improve the constraints on the budgets of these two gases. The TRACE-P data represented the first in situ measurements for HCN in the troposphere, and one of the first for CH₃CN. Observed background vertical gradients of HCN and CH₃CN confirmed that the ocean is a sink for both gases, with deposition velocity of 0.13 cm s^{-1} for both and saturation ratios of 0.79 for HCN and 0.88 for CH₃CN. The resulting tropospheric lifetimes are 5.3 months for HCN and 5.8 months for CH₃CN. Observations for both gases in the free troposphere confirmed a dominant source from biomass burning. Enhancements of HCN were also observed in Chinese urban plumes, which I attributed tentatively to residential coal burning. My GEOS-CHEM model analysis of the HCN-CH₃-CO system in TRACE-P indicates that biomass burning and residential coal burning emission ratios relative to CO of 0.27% and 1.6% respectively for HCN, and of 0.20% and 0.25% respectively for CH₃CN, are consistent with observations in biomass burning and Chinese urban plumes, and provide the best fit in the model for simulation of observed TRACE-P vertical profiles, HCN-CH₃CN-CO correlations, as well as long-term records of HCN columns and CH₃CN observations over the northern Indian Ocean. The lack of a significant urban source for CH₃CN suggests that it is a better biomass burning tracer than HCN. The model predicts very low HCN and CH₃CN concentrations at high southern latitudes, reflecting the assumption of uniform saturation ratio; observations in that region are needed.

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Chapter 2

A Tropospheric Ozone Maximum Over the Middle East

[Li, Q., D. J. Jacob, J. A. Logan, I. Bey, R. M. Yantosca, H. Liu, R. V. Martin, A. M. Fiore, B. D. Field, B. N. Duncan, and V. Thouret, A tropospheric ozone maximum over the Middle East, *Geophys. Res. Lett.*, 28, 3235-3238, 2001.]

Abstract

The GEOS-CHEM global 3-D model of tropospheric chemistry predicts a summertime ozone maximum over the Middle East, with mean mixing ratios in the middle and upper troposphere in excess of 80 ppby. This model feature is consistent with the few observations from commercial aircraft in the region. Its origin in the model reflects a complex interplay of dynamical and chemical factors, and of anthropogenic and natural influences. The anticyclonic circulation in the middle and upper troposphere over the Middle East funnels northern midlatitude pollution transported in the westerly subtropical jet as well as lightning outflow from the Indian monsoon and pollution from eastern Asia transported in an easterly tropical jet. Large-scale subsidence over the region takes place with continued net production of ozone and little mid-level outflow. Transport from the stratosphere does not contribute significantly to the ozone maximum. Sensitivity simulations with anthropogenic or lightning emissions shut off indicate decreases of 20-30% and 10-15% respectively in the tropospheric ozone column over the Middle East. More observations in this region are needed to confirm the presence of the ozone maximum.

2.1 Introduction

The GEOS-CHEM global 3-D model of tropospheric chemistry [*Bey et al.*, 2001] predicts a summer ozone maximum in the middle troposphere over the Middle East (Figure 2.1, left panel). This maximum is also seen in the simulated tropospheric ozone column (Figure 2.1, right panel). The Middle East is a largely unexplored region for ozone observations, but vertical profiles from the MOZAIC program on commercial aircraft [*Marenco et al.*, 1998; *Stohl et al.*, 2001] indicate high summer mixing ratios that are comparable to model values (Figure 2.1 and Figure 2.2). Tropospheric ozone columns in July simulated with GEOS-CHEM are usually within 10% of values observed in the MOZAIC and ozonesonde data. The Middle East maximum in the model appears in May and disappears in September, consistent with the MOZAIC data (Figure 2.2).



Figure 2.1: Simulated monthly mean ozone in July 1997. Left panel: 400 hPa mixing ratios (ppbv). Right panel: tropospheric columns in Dobson units (1 DU = 2.69×10^{16} molecules cm⁻²). Colored circles in the left panel show measured monthly mean ozone mixing ratios at 400 hPa in July including climatological ozonesonde data [*Logan*, 1999], and values from commercial aircraft over Tel-Aviv (32°N, 35°E), Dubai (25°N, 55°E), and Teheran (36°N, 51°E) during 1995-2000 as part of the MOZAIC program.



Figure 2.2: Monthly mean January (blue) and July (red) ozone vertical profiles over Tel-Aviv, Dubai, and Teheran. Solid lines are model results. Observations during 1995-2000 from the MOZAIC program are shown as dotted lines with standard deviations indicated. The number of observed profiles are indicated by the two numbers with the first one for July and the second one for January. The elevated ozone at 2-4 km over Tel-Aviv in the observations is due to European influence.

Several global 3-D models of tropospheric chemistry have been described in the recent literature, but only a few have published documentations on their global ozone distributions in the free troposphere in summer. *Hauglustaine et al.* [1998] find a maximum in the tropospheric ozone column over the Middle East in September-October. *Wang et al.* [1998b] and *Mickley et al.* [1999] show a broad Eurasian maximum in summer. *Jonson et al.* [2001] show high values (> 90 ppbv) at 500 hPa over the Middle East in July, but even higher values at northern midlatitudes. *Horowitz et al.* [2001] show a 500 hPa ozone maximum over the Middle East in July.

We examine here the origin of the Middle East ozone maximum simulated by the GEOS-CHEM model. This origin is not obvious, and its confirmation or rejection by more detailed observations of ozone in the future will provide an important test of our understanding of tropospheric chemistry. An anthropogenic origin for this maximum would have important implications for radiative forcing of climate [*Mickley et al.*, 1999].

2.2 Model Description and Simulation of the Middle East Ozone Maximum

The GEOS-CHEM model is driven by assimilated meteorological data from the Goddard Earth Observing System (GEOS) of the NASA Data Assimilation Office (DAO) [*Schubert et al.*, 1993]. We use meteorological fields for 1993-1997 provided at 3- and 6-hour frequencies with horizontal resolution of 4° latitude by 5° longitude and with 20 (1993-1995) or 26 (1996-1997) σ layers in the vertical between the Earth's surface and 10 hPa (1993-1995) or 0.1 hPa (1996-1997). Simulation of ozone in the model uses a chemical mechanism with 120 species to describe tropospheric ozone-NO_x-hydrocarbon chemistry. A detailed description and evaluation of the model is given by *Bey et al.* [2001].

Anthropogenic emissions are specified using a base emission inventory for 1985 scaled to 1993-1995 following *Bey et al.* [2001]. The base inventory includes NO_x emissions from *Benkovitz*



Figure 2.3: Simulated horizontal ozone fluxes (arrows) and net chemical ozone production rates (contours, $> 4 \text{ ppb} \text{ day}^{-1}$) at 250 hPa (left panel) and horizontal ozone fluxes at 500 hPa (right panel). Values are model monthly means for July 1997. The rectangle in the right panel indicates the Middle East region used for budget analysis.

et al. [1996], nonmethane hydrocarbon (NMHC) emissions from *Piccot et al.* [1992] and CO emissions as summarized in *Wang et al.* [1998a]. Lightning NO_x emissions are linked to deep convection following the parameterization of *Price and Rind* [1992]. The resulting anthropogenic and lightning sources of NO_x are 22.8 TgNyr⁻¹ and 3.4 TgNyr⁻¹, respectively. The cross-tropopause transport of ozone is simulated by the Synoz method of *McLinden et al.* [2000] with a global cross-tropopause flux of 475 TgO₃ yr⁻¹.

We conducted a five-year simulation for 1993-1997. The interannual variations in the 400 hPa ozone mixing ratios and tropospheric ozone columns averaged over the Middle East in July are less than 5%. All five years feature the Middle East maximum. Our analysis focuses on July 1997. Sensitivity simulations are initialized in March 1997; earlier initialization has little effect on results.

Figure 2.3 shows the ozone fluxes and production rates at 250 hPa (left panel) and the ozone fluxes at 500 hPa (right panel). In summer, the meteorological setting over the Middle East is dominated by a heat low at the surface and an anticyclonic circulation in the middle and upper troposphere with large-scale subsidence [*Takahashi and Arakawa*, 1981; *Ye and Wu*, 1998]. In the north of the region, circumpolar transport of ozone takes place in the westerly subtropical jet cen-

tered at 40°N (Figure 2.3). Much of the ozone at northern midlatitudes is of anthropogenic origin. Entrainment of this midlatitude pollution into the anticyclonic circulation over the Middle East is apparent below 400 hPa (Figure 2.3, right panel). In the lower troposphere, the prevailing summer northwesterlies over the eastern Mediterranean [*Dayan*, 1986] transport anthropogenic ozone from Europe into the Middle East and northern Africa.

The left panel of Figure 2.3 indicates easterly transport at high altitudes of ozone produced in the upper troposphere over southern and eastern Asia. Intense lightning associated with the summer monsoon produces large amounts of NO_x in the upper troposphere over the Indian subcontinent [*Christian and Latham*, 1998; *Nesbitt et al.*, 2000], while strong convection over eastern Asia transports large amounts of anthropogenic NO_x to the upper troposphere. The model simulates 0.20-0.24 ppbv NO_x in the upper troposphere over the Indian subcontinent, similar to the levels of NO_x observed by commercial aircraft over that region [*Brunner et al.*, 1998]. Simulated ozone production rates in the upper troposphere over southern and eastern Asia exceed 5 ppb day⁻¹ (Figure 2.3, left panel), an unusually high value [*Jaeglé et al.*, 2001]. The resulting ozone is transported to the Middle East by the tropical easterly jet as part of the anticyclonic circulation over South Asia (Figure 2.3, left panel). The easterly flow in the upper troposphere at 20°N-30°N is a wellknown feature of the summertime South Asia circulation [*Takahashi and Arakawa*, 1981; *Ye and Wu*, 1998].

We analyzed the model budget of tropospheric ozone for the Middle East region defined as the rectangle in the right panel of Figure 2.3. Net inflow through the eastern boundary of the region accounts for 65% of the regional ozone supply to the upper troposphere (< 300 hPa) while *in situ* chemical production provides another 30%. Downward transport from the stratosphere is unimportant. Net ozone production takes place above 500 hPa (\sim 6 km) and in the boundary layer up to 700 hPa (2-3 km). In the upper troposphere, the production is driven primarily by lightning NO_x advected into the region from the Indian monsoon, while in the boundary layer it is driven



Figure 2.4: Decreases in simulated monthly mean tropospheric ozone columns (left panels, in DU) and 400 hPa ozone mixing ratios (right panels, in ppbv) over the Middle East in July 1997 when (a, b) lightning (c, d) anthropogenic (e, f) Asian anthropogenic (g, h) North American and European anthropogenic emissions are suppressed, relative to the standard simulation.

by local anthropogenic NO_x . Subsidence from the upper troposphere provides 80% of the ozone supply to the middle troposphere in the region, sustaining the ozone maximum. Upward transport takes place in the lower troposphere due to convection and convergence associated with the surface heat low. Removal of ozone from the region is mostly by outflow to the Indian Ocean and to the Sahara at about 700 hPa.

2.3 Sources Contributing to the Ozone Maximum

We used tagged ozone (odd oxygen) tracers [*Wang et al.*, 1998c] and sensitivity simulations to further understand the geographical source regions and precursor emissions contributing to the Middle East maximum. The tagged tracer simulation transports as separate tracers ozone originating in the stratosphere, upper troposphere (< 300 hPa), middle troposphere (300-600 hPa) and the lower troposphere (> 600 hPa). We find that production in the upper and middle troposphere accounts for 30-40 ppbv (35-50%) and 10-20 ppbv (15-25%) respectively of the 400 hPa ozone over the Middle East, while production in the lower troposphere and transport from the stratosphere account for 15-20 ppbv (20-25%) and less than 10 ppbv (15%), respectively. The particularly high contribution of upper tropospheric production to ozone over the Middle East, relative to other regions in the northern subtropical band, reflects the large-scale subsidence over the region. Although the overall contribution from the stratosphere is relatively small, it is higher over the Middle East than over other northern subtropical regions.

To determine the relative contributions to the ozone maximum from anthropogenic versus lightning emissions, we conducted sensitivity simulations with either anthropogenic or lightning emissions or both omitted. We also conducted simulations in which anthropogenic emissions from the Middle East, Asia (not including the Middle East), Europe, and North America were omitted separately. Figure 2.4 shows the differences in the simulated tropospheric ozone columns and 400 hPa ozone mixing ratios relative to the standard simulation. Suppressing lightning emissions decreases the ozone column over the Middle East in July by 5-7 DU (10-15%), while suppressing anthropogenic emissions leads to a 8-12 DU (20-30%) decrease (Figures 2.4a, c). The effects of lightning and anthropogenic emissions on the tropospheric ozone column both show maxima in the Middle East, because of the strong subsidence over the region as discussed previously. Lightning and anthropogenic emissions each contribute 10-20 ppbv to the 400 hPa ozone over the Middle East (Figures 2.4b,d). The effect of suppressing both lightning and anthropogenic emissions is found to

be nearly additive; even with these two sources suppressed there remains a Middle East maximum (peaking at 47 ppbv at 400 hPa) because of subsidence.

Further investigation of the anthropogenic influence on the Middle East maximum indicates that Asian influence dominates in the southern part of the region, while European and North American influences dominate in the north, reflecting the flow patterns described previously (Figures 2.4e-h). European and North American influences are found to be of comparable magnitudes. The column maximum in Figure 2.4e is mainly due to local emissions, while the mixing ratio maximum at 400 hPa in Figure 2.4f is due largely to emissions from southern and eastern Asia.

The summertime troposphere ozone maximum simulated by the GEOS-CHEM model over the Middle East thus reflects a complex interplay of transport and chemistry as well as a superimposition of anthropogenic and natural (lightning) influences. More observations are needed to confirm the presence and intensity of this maximum, and would provide an important test for the current understanding of tropospheric ozone chemistry. Satellite observations would be particularly valuable.

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Chapter 3

Stratospheric Versus Pollution Influences on Ozone at Bermuda: Reconciling Past Analyses

[Li, Q., D. J. Jacob, T. D. Fairlie, H. Liu, R. M. Yantosca, and R. V. Martin, Stratospheric versus pollution influences on ozone at Bermuda: Reconciling past analyses, *J. Geophys. Res.*, *107*(D22), 4611, doi:10.1029/2002JD002138, 2002.]

Abstract

Conflicting interpretations of the spring ozone maximum observed at Bermuda (32°N, 65° W) have fueled the debate on stratospheric influence versus tropospheric production as sources of tropospheric ozone. We use a global 3-D model of tropospheric ozone-NO_x-hydrocarbon chemistry driven by assimilated meteorological observations to reconcile these past interpretations. The model reproduces the observed seasonal cycle of surface ozone at Bermuda and captures the springtime day-to-day variability (r = 0.82). We find that boundary layer transport of North American pollution behind cold fronts is the principal contributor to springtime surface ozone at Bermuda and is responsible for all the high-ozone events. The model reproduces the observed positive correlations of surface ozone with ⁷Be and ²¹⁰Pb at Bermuda; the correlation with ⁷Be reflects the strong subsidence behind cold fronts, resulting in the mixing of middle-tropospheric air with continental boundary layer outflow. This mixing appears to have been an obfuscating factor in past interpretations of subsiding back-trajectories at Bermuda as evidence for a stratospheric or upper-tropospheric origin for ozone. Even in the free troposphere we find that the stratosphere contributes less than 5 ppbv (< 10%) to spring ozone over Bermuda. Positive O_3 -⁷Be and negative O_3 -²¹⁰Pb correlations observed at Tenerife (28°N, 16°W, 2.4 km) in summer are reproduced by the model and are consistent with a middle-tropospheric source of ozone, not an upper-tropospheric or stratospheric source as previously suggested. A regional budget for the North Atlantic in spring indicates that the stratosphere contributes less than 10 ppbv ozone (< 5%) below 500 hPa, while the lower troposphere contributes 20-40 ppbv ozone throughout the troposphere.

3.1 Introduction

There is a continuing debate surrounding the relative importance of tropospheric production versus stratospheric influx as sources of tropospheric ozone. A focal point of the debate is the spring ozone maximum observed at remote sites in northern midlatitudes [*Oltmans*, 1981; *Logan*, 1985; *Oltmans and Levy II*, 1992, 1994; *Monks*, 2000]. A number of hypotheses have been proposed to explain this spring maximum, including stratospheric injection [*Logan*, 1985; *Levy II et al.*, 1985], intensifying photochemistry in spring [*Penkett and Brice*, 1986], wintertime accumulation of ozone and its precursors at high latitudes [*Liu et al.*, 1987; *Honrath et al.*, 1996], and phase overlap between transport from the stratosphere and production in the troposphere [*Wang et al.*, 1998b; *Yienger et al.*, 1999]. Recent observations support photochemical production as the cause of the spring ozone maximum [*Kajii et al.*, 1998; *Pochanart et al.*, 1999; *Zanis et al.*, 2000]. In particular, O₃-⁷Be correlations measured from aircraft over North America argue against a stratospheric cause [*Allen et al.*, 2003; *Dibb et al.*, 2003].

Resolving stratospheric and anthropogenic influences on tropospheric ozone over the North Atlantic has been a central objective of the North Atlantic Regional Experiment (NARE) [*Fehsenfeld et al.*, 1996a,b]. Positive correlation between ozone and CO over the region in summer implies a major anthropogenic influence [*Parrish et al.*, 1993, 1998]. In spring, however, ozonesonde measurements and isentropic back-trajectories have been used to suggest a dominant stratospheric influence [*Oltmans et al.*, 1996]. Summer observations of ozone at Tenerife (28°N, 16°W, 2.4 km altitude) show a positive correlation with cosmogenic ⁷Be, and a negative correlation with terrigenic ²¹⁰Pb, which have been interpreted as implying a stratospheric or at least a high-altitude ozone source [*Prospero et al.*, 1995].

Ozone observations at Bermuda (32°N, 66°W) have received particular attention. Surface ozone at that site shows a strong spring maximum and summer minimum [*Oltmans and Levy II*, 1992, 1994; *Logan*, 1999]. The summer minimum is due to a combination of photochemical loss and inflow of tropical marine air around the Bermuda-Azores high [*NRC*, 1991; *Oltmans and Levy II*, 1992, 1994; *Moody et al.*, 1995]. *Oltmans and Levy II* [1992,1994] and *Moody et al.* [1995] argued for a stratospheric origin for the spring maximum based on isentropic back-trajectories indicating strong subsidence, while *Dickerson et al.*, [1995] argued that boundary layer transport of North American pollution behind cold fronts is responsible based on observed correlation between ozone and CO. Chemical observations show that transport of North American pollution to Bermuda peaks in spring [*Van Valin et al.*, 1988; *Huang et al.*, 1999; *Milne et al.*, 2000], reflecting the frequency of frontal passages. However, *Moody et al.* [1995] found a positive correlation between ozone and ⁷Be in spring, supporting a high-altitude origin for ozone. *Arimoto et al.* [1999] and *Huang et al.* [1999] reported correlated maxima of ²¹⁰Pb, ⁷Be and ozone at Bermuda when airflow is from the northwest, further complicating the interpretation.

We use the GEOS-CHEM global 3-D model of tropospheric ozone-NO_x-hydrocarbon chemistry driven by assimilated meteorological observations to determine the relative influences of transport from the stratosphere and photochemical production on ozone at Bermuda in particular and over the North Atlantic in general. This paper is the second of a series applying the GEOS-CHEM model to simulate tropospheric ozone chemistry over the North Atlantic. In the first companion paper, the model was used to examine transatlantic transport of pollution [*Li et al.*, 2002]. We show here that we can reconcile past interpretations of the origin of ozone at Bermuda through analysis of simulated and observed fields of ozone, CO, and radionuclides, as well as through Lagrangian examination of isentropic back-trajectories in the meteorological fields used to drive the model.

3.2 Model Description

The original description of the GEOS-CHEM model is given by *Bey et al.* [2001a]. We use here GEOS-CHEM version 4.16 (see http://www-as.harvard.edu/chemistry/trop/geos). The model is driven by assimilated meteorological fields from the Goddard Earth Observing System (GEOS) of the NASA Data Assimilation Office (DAO) [*Schubert et al.*, 1993]. We use meteorological fields for 1996 (GEOS-STRAT) which are provided with 6-hour temporal resolution (3-hour for surface variables), $2^{\circ} \times 2.5^{\circ}$ horizontal resolution, and 46 vertical sigma levels with the lowest 3 levels centered at 50 m, 300 m, and 500 m above the surface for a column based at sea level. For the

work presented here, we regrid the meteorological fields to $4^{\circ} \times 5^{\circ}$ horizontal resolution for computational expediency and merge the vertical levels above the lower stratosphere. A 1-year simulation with the 1995 (GEOS-1) meteorological fields is conducted to provide proper initialization for the 1996 simulation.

The model includes 80 chemical species and transports 24 tracers to describe tropospheric ozone- NO_x -hydrocarbon chemistry. Anthropogenic emissions in the model are specified using a base emission inventory for 1985 described by *Wang et al.* [1998a], scaled to 1996 using national emission inventories and economic data [*Bey et al.*, 2001a]. The current model version includes updated anthropogenic CO emissions and an improved biomass burning emission inventory that includes interannual variability determined from satellite observations [*Duncan et al.*, 2003].

Transport of ozone from the stratosphere is simulated with the Synoz (synthetic ozone) method of *McLinden et al.* [2000]. In this method, stratospheric ozone is represented by a passive tracer that is released uniformly in the tropical lower troposphere (between 30°S to 30°S and 70 hPa to 10 hPa) at a rate constrained to match a prescribed global mean cross-tropopause ozone flux.Cross-tropopause flux used in recent modeling studies ranges from 400 to 850 TgO₃ yr⁻¹ [*Lelieveld et al.*, 1999], and satellite observations imply a narrower range of 450-590 TgO₃ yr⁻¹ [*Gettelman et al.*, 1997]. We adopt a global cross-tropopause flux of 475 TgO₃ yr⁻¹ recommended by *McLinden et al.* [2000], which results in a satisfactory simulation of vertical ozone profiles at northern middle and high latitudes [*Bey et al.*, 2001a,b; *Liu et al.*, 2002]. Global tropospheric production and loss rates of ozone (actually odd oxygen $O_x = O_3 + NO_2 + 2 \times NO_3 + HNO_3 + peroxyacyl nitrates + HNO_4 + 3 \times N_2O_5$) in the model are 4900 TgO₃ yr⁻¹ and 4300 TgO₃ yr⁻¹, respectively. Previous global 3-D models indicate photochemical production ranging from 3425 to 4550 TgO₃ yr⁻¹ and photochemical loss from 3350 to 4065 TgO₃ yr⁻¹ [*Lelieveld et al.*, 1999]. As discussed in *Bey et al.* [2001a], we believe that the higher values in our model reflect an improved treatment of radiative transfer through clouds with the Fast-J algorithm of *Wild et al.* [2000].

A global evaluation of the model including general analysis of the seasonal and latitudinal variations of tropospheric ozone is presented by *Bey et al.* [2001a] using the 1994 GEOS-1 meteorological fields. Additional evaluations of the simulation of tropospheric ozone chemistry for different regions of the world and for different years have been presented in a number of papers [*Bey et al.*, 2001b; *Li et al.*, 2001a,b, 2002; *Chandra et al.*, 2002; *Fiore et al.*, 2002; *Martin et al.*, 2002a,b; *Liu et al.*, 2002]. *Fiore et al.* [2002] showed detailed comparisons with observational statistics for ozone and its precursors in the United States. In a companion paper, *Li et al.* [2002] evaluate transatlantic transport in the model with long-term ozone and CO measurements at coastal sites on both sides of the North Atlantic. The model reproduces well the day-to-day variabilities of surface ozone and CO, including the magnitudes and frequencies of pollution episodes. *Allen et al.* [1996a,b] previously showed in a 3-D model similarly driven by GEOS meteorological data that the transport of North American ²²²Rn and CO to Bermuda behind cold fronts is well simulated throughout the year.

To investigate the contributions to tropospheric ozone concentrations over the North Atlantic from different source regions, we include tagged ozone tracers [*Wang et al.*, 1998b; *Li et al.*, 2001b, 2002] in our simulation. The tagged ozone tracer simulation uses archived daily 3-D fields of O_x production rates and loss frequencies from the standard full-chemistry simulation to transport eight separate O_x tracers originating from different regions: the stratosphere (ST), the upper troposphere (UT: 400h Pa-tropopause), the middle troposphere (MT: 400-700 hPa), the continental lower troposphere (LT: 700 hPa-surface; separately North America, Europe, Asia, and other continents), and the marine lower troposphere. Here we define North America as the domain extending over 25°N-75°N and 50°W-160°W, including part of the western North Atlantic. The tracers are removed by chemical loss and dry deposition at the same frequencies as those for total O_x in the standard simulation. By summing the concentrations of all eight tracers, we reproduce closely the total O_x concentrations in the standard full-chemistry simulation. Since ozone typically accounts



Figure 3.1: Observed and simulated monthly mean surface ozone concentrations at Bermuda for 1996. The vertical lines show the standard deviations for the observations. The observations are from the Climate Monitoring and Diagnostics Laboratory (CMDL) network [*Oltmans and Levy II*, 1992, 1994] and were provided by Samuel J. Oltmans.

for over 95% of O_x , we will refer to the tagged O_x as tagged ozone in what follows.

3.3 Ozone Over Bermuda

3.3.1 Seasonal Variation of Surface Ozone

The observed and simulated monthly mean surface ozone concentrations at Bermuda for 1996 show a distinct spring maximum and a summer minimum (Figure 3.1). The observed and simulated ozone concentrations agree within 2-5 ppbv except for July, when the model overestimates the ozone concentration by 7 ppbv. The observations show a maximum of 52 ppbv in April and a minimum of 26 ppbv in July-August, while the corresponding model results are 50 ppbv and 32 ppbv.

The overestimate of summertime surface ozone at Bermuda in the model is caused by ex-

cessive deep convection in the GEOS-STRAT data over the Caribbean and western North Atlantic during that season, resulting in excessive ozone being entrained from aloft. *Allen et al.* [1997] previously identified this problem in the 1990-1992 GEOS-1 data by comparison with satellite observations of deep convective clouds [*Schiffer et al.*, 1983; *Rossow et al.*, 1996]. We find the same problem in the July 1996 data. Observed surface ozone at Bermuda in summer shows a diurnal variation with a maximum in early morning and a minimum in the afternoon, reflecting photochemical ozone destruction during daylight hours in a regime with very low NO_x concentrations [*Oltmans*, 1981; *Oltmans and Levy II*, 1992, 1994]. The model shows a similar diurnal cycle and net photochemical loss of surface ozone at Bermuda in summer (not shown), indicating that it is not photochemistry but rather transport that causes the overestimate.

3.3.2 Day-to-day Variations of Surface Ozone

The March-June 1996 observations (Figure 3.2) show large day-to-day variations typical of springtime surface ozone at Bermuda [*Oltmans and Levy II*, 1992, 1994]. The model results are superimposed on Figure 3.2. The simulated contributions from different source regions are also shown using tagged ozone tracers.

Both the observations and model results in Figure 3.2 show an ozone background of 30-40 ppbv, with events in excess of 60 ppbv. The high-ozone events, for example on March 15-16, April 13, and May 26, are associated with the passage of cold fronts, as diagnosed by abrupt increases in pressure and decreases in temperature. The simulated ozone closely matches the observations during periods of frontal passage. Figure 3.3 shows statistics of comparison between the observed and simulated time series. The model captures the background concentrations, the probability distribution, the frequencies and magnitudes of the pollution events, and the day-to-day variations (r = 0.82, n = 122, p < 0.001). The model evidently has a good predictive capability for surface ozone at Bermuda. The simulated ozone and CO concentrations at Bermuda for March-June are positively



Figure 3.2: Daily mean surface ozone concentrations at Bermuda in March-June 1996. The contributions from different source regions are shown using the tagged ozone tracers. "LT N. America" refers to ozone produced in the lower troposphere (700 hPa-surface) over North America and the western North Atlantic ($25^{\circ}N-75^{\circ}N$, $50^{\circ}W-160^{\circ}W$). "MT" refers to ozone produced in the middle troposphere (400-700 hPa). "UT/ST" refers to ozone produced in the upper troposphere (400 hPa-tropopause) and the stratosphere. "Other" refers to ozone produced in the lower troposphere outside of North America and the western North Atlantic ($25^{\circ}N-75^{\circ}N$ and $50^{\circ}W-160^{\circ}W$).



Figure 3.3: Statistics of comparison between simulated and observed time series of surface ozone at Bermuda in March-June 1996: cumulative probability distributions (left panel) and scatterplot of simulated versus measured values (right panel). Values are daily averages for both the observations and the model. Also shown in the scatterplot are the correlation coefficient (r), the number of data points (n), and the p-value indicating the significance level of the correlation.

correlated with a slope of 0.32 mol mol⁻¹ and a correlation coefficient of 0.82 (n = 122, p < 0.001) (Figure 3.4), consistent with observations where the corresponding values are 0.27 mol mol⁻¹ and 0.81 [*Dickerson et al.*, 1995]. The positive correlations are a clear indication of anthropogenic influence [*Parrish et al.*, 1993, 1998].

Decomposition of the model time series into tagged ozone tracers (Figure 3.2) shows that transport of ozone produced in the lower troposphere (below 700 hPa) over North America and the western North Atlantic accounts for on average 70% of surface ozone at Bermuda, and singly determines the occurrence of the high-ozone events. Ozone produced in the upper troposphere and the stratosphere contributes only about 5 ppbv, and production in the middle troposphere contributes 5-10 ppbv. Our model results agree with the previous estimate by *Dickerson et al.* [1995] that half or more of the excess surface ozone in Bermuda in spring originates from pollution over eastern North America. They do not support a stratospheric or upper-tropospheric origin for this excess ozone [*Oltmans et al.*, 1992, 1994; *Moody et al.*, 1995]. We find in the model mean net ozone



Figure 3.4: Scatterplot of simulated ozone versus CO at Bermuda for March-June 1996. Values are daily averages. Also shown are the correlation coefficient (r), the number of data points (n), and the *p*-value indicating the significance level of the correlation.



Figure 3.5: GEOS-CHEM monthly mean net ozone production (ppbv day⁻¹) at 915 hPa (left panel) and as a function of altitude over the eastern U.S. (30°N-50°N, 70°W-90°W) (right panel) for April 1996. The solid circle indicates the location of Bermuda.

production below 800 hPa from the eastern U.S. all the way to Bermuda (Figure 3.5). The highest surface ozone concentrations are between the east coast and Bermuda (not shown), downwind of the highest production region.

3.3.3 Vertical Distribution

Figure 3.6 shows the monthly mean vertical profile of ozone over Bermuda for April 1996 from 28 ozonesonde soundings [*Oltmans et al.*, 1996]. The simulated monthly mean vertical profile for April 1996 is superimposed, along with contributions from different source regions. The observed and simulated ozone concentrations agree within 5 ppbv throughout the troposphere. We find that ozone produced in the lower troposphere over North America and the western North Atlantic contributes 40 ppbv (70-80%) to the total ozone below the 800 hPa pressure level but drops rapidly above. Transport of ozone from the stratosphere contributes less than 5 ppbv (< 10%) to



Figure 3.6: Monthly mean vertical profile of ozone at Bermuda in April 1996. The solid circles are averages of 28 ozonesonde soundings during the month, provided by Samuel J. Oltmans. The horizontal lines show the standard deviations for the observations. The open circles show the model results. The contributions from different source regions in the model are shown using the tagged ozone tracers. "LT N. America" refers to ozone produced in the lower troposphere (700 hPa-surface) over North America and the western North Atlantic (25°N-75°N, 50°W-160°W). "MT", "UT", and "ST" refer to ozone produced in the middle troposphere (400-700 hPa), the upper troposphere (400 hPa-tropopause), and the stratosphere, respectively. "Other" refers to ozone produced in the lower troposphere over regions outside of 25°N-75°N and 50°W-160°W.

ozone below 400 hPa; local production is the principal source of ozone in the middle and upper troposphere.

Arguments for a stratospheric or upper-tropospheric origin of ozone at Bermuda in spring, both at the surface and in the free troposphere, have largely been founded on correlation with subsiding back-trajectories originating over North America [*Oltmans and Levy II*, 1992, 1994; *Moody et al.*, 1995]. Back-trajectories generated from our model will be discussed in section 3.5. To further evaluate our model results we compared the simulated vertical ozone distributions in spring over North America with ozonesonde measurements obtained from the World Ozone and Ultraviolet Data Center (WOUDC), Environment Canada, Ontario (http://www.msc-smc.ec.gc.ca/woudc) [*Logan*, 1999]. The results are shown in Figure 3.7. The simulated and observed ozone concentrations agree within 5 ppbv (< 10%) throughout the troposphere below 400 hPa. The model underestimates ozone concentrations above 400 hPa, a problem that we attribute to the coarse vertical resolution near the tropopause; this underestimate does not affect the overall cross-tropopause flux of ozone in the model, which is prescribed as a boundary condition using the Synoz algorithm (see section 3.2).

3.4 Ozone Correlations With ⁷Be and ²¹⁰Pb

Observations at Bermuda in spring indicate positive correlations of ozone with both ⁷Be and ²¹⁰Pb [*Moody et al.*, 1995; *Arimoto et al.*, 1999; *Huang et al.*, 1999], while observations at the Tenerife free-tropospheric site (28°N, 16°W, 2.4 km altitude) in the eastern North Atlantic in summer show that ozone is positively correlated with ⁷Be but negatively correlated with ²¹⁰Pb [*Prospero et al.*, 1995]. The combination of ⁷Be and ²¹⁰Pb provides a sensitive test of vertical transport in global 3-D models [*Koch et al.*, 1996; *Liu et al.*, 2001]. We examine in this section the ability of our model to reproduce these correlations using the ²¹⁰Pb and ⁷Be GEOS-CHEM simulation for 1996 previously reported by *Liu et al.* [2001]. Comparisons presented in that paper with worldwide



Figure 3.7: Observed (solid lines, solid circles) and simulated (dashed lines, open circles) monthly mean vertical profiles of ozone at Alert, Churchill, Edmonton, Boulder, Goose Bay, and Wallops Island for April. The measurements are averages of ozonesonde soundings for 1988-2001, obtained from the World Ozone and Ultraviolet Data Center (WOUDC) at http://www.msc-smc.ec.gc.ca/woudc. The horizontal lines show the standard deviations for the observations (the number of observations is given as inset on each panel). The model results are monthly averages for April 1996.



Figure 3.8: Scatterplots of simulated ozone versus ⁷Be and ²¹⁰Pb at Bermuda for March-May 1996 (upper panels) and at Tenerife (28° N, 16° W, 2.4 km altitude) for June-August 1996 (bottom panels). Values are daily averages. Also shown in each scatterplot are the correlation coefficient (*r*), the number of data points (n), and the *p*-value indicating the significance level of the correlation.



Figure 3.9: Time series of simulated (a) ⁷Be and ozone, and (b) ²¹⁰Pb and ozone at Bermuda for March-May 1996. Values are daily averages.

observations of ²¹⁰Pb and ⁷Be concentrations and deposition fluxes indicate no significant global bias, and significant success in reproducing the observed latitudinal and seasonal distributions.

Our model results show positive ozone correlations with ²¹⁰Pb (r = 0.71, n = 92, p < 0.001) and with ⁷Be (r = 0.36, n = 92, p < 0.001) for March-May 1996 at Bermuda (upper panels, Figure 3.8), consistent with observations [*Moody et al.*, 1995; *Arimoto et al.*, 1999; *Huang et al.*, 1999]. Our simulated correlation coefficient of 0.36 between ozone and ⁷Be is consistent with that observed by *Moody et al.* [1995] (r = 0.34). At Tenerife in summer, we find a positive correlation between ozone and ⁷Be (r = 0.52, n = 92, p < 0.001) and a negative correlation between ozone and ²¹⁰Pb (r = -0.59, n = 92, p < 0.001) (bottom panels, Figure 3.8), consistent with the observations of *Prospero et al.* [1995]. The simulated ⁷Be and ²¹⁰Pb concentrations at Tenerife are higher than those at Bermuda, consistent with observations [*Arimoto et al.*, 1999] and reflecting both higher altitude (for ⁷Be) and greater aridity (less aerosol scavenging).

The simulated time series of ⁷Be, ²¹⁰Pb, and ozone at Bermuda for March-May 1996



Figure 3.10: Scatterplot of simulated ⁷Be versus ²¹⁰Pb at Bermuda for March-May 1996. Values are daily averages. Also shown are the correlation coefficient (r), the number of data points (n), and the *p*-value indicating the significance level of the correlation.



Figure 3.11: Time series of simulated (a) ⁷Be and ozone, (b) ²¹⁰Pb and ozone, and (c) tagged ozone tracers at Tenerife (28°N, 16°W, 2.4 km altitude) in the Canary Islands for June-August 1996. Values are daily averages. "LT", "MT", "UT", and "ST" refer to ozone produced in the lower troposphere (surface-700hPa), the middle troposphere (400-700 hPa), the upper troposphere (400 hPa-tropopause), and the stratosphere, respectively.

are shown in Figure 3.9. High ²¹⁰Pb and ⁷Be are associated with high-ozone events originating from the lower troposphere (below 700 hPa) over North America as previously discussed. Since there is no significant latitudinal gradient in ⁷Be in the lower troposphere at northern midlatitudes [*Liu et al.*, 2001], the positive ozone correlation with ⁷Be at Bermuda must reflect subsidence. This point will be discussed further in section 3.5. The positive ozone correlation with ²¹⁰Pb at Bermuda is consistent with the lower-tropospheric source for ozone. We find in the model a positive correlation (r = 0.52, n = 92, p < 0.001) between ⁷Be and ²¹⁰Pb at Bermuda in spring (Figure 3.10), consistent with observations [*Arimoto et al.*, 1999; *Huang et al.*, 1999] and reflecting the mixing of subsiding air and continental outflow behind cold fronts.

The simulated time series of ozone, ²¹⁰Pb, and ⁷Be at Tenerife for June-August 1996 are shown in Figure 3.11. [Prospero et al., 1995] suggested that the positive ozone correlation with ⁷Be and the negative ozone correlation with ²¹⁰Pb observed at Tenerife are evidence for a high-altitude source of ozone, possibly from the stratosphere, but we find that they simply reflect the common vertical trends of ⁷Be and ozone, and the opposite vertical trend of ²¹⁰Pb. We see from Figure 3.11 that the positive ozone correlation with ⁷Be and the negative ozone correlation with ²¹⁰Pb are mostly driven by ozone produced in the middle troposphere (400-700 hPa). Sources of ozone in the lower, middle, and upper troposphere contribute on average 15 ppbv (32%), 24 ppbv (49%), and 7 ppbv (14%), respectively, to the total ozone at Tenerife, while ozone transported from the stratosphere contributes 2 ppbv (5%) (bottom panel, Figure 3.11). Our model results are consistent with the analysis by Graustein et al. [1996], who found that a stratospheric source could not explain the observed ozone correlation at Tenerife with the normalized fraction of ⁷Be with respect to ²¹⁰Pb. They suggested that the elevated ozone observed at Tenerife is due to the lifting of continental boundary layer air to the middle and upper troposphere followed by net ozone production. Even though episodic stratosphere-troposphere-exchange events may make a large occasional contribution to ozone at Tenerife [Kentarchos et al., 2000], our model results suggest that the overall ozone levels are controlled by photochemical formation in the middle and lower troposphere.

3.5 Reconciling Past Analyses of Ozone at Bermuda

In this section we reconcile our results with past inferences of a high-altitude source of ozone at Bermuda based on isentropic back-trajectory analyses and correlation with ⁷Be [*Oltmans and Levy II*, 1992, 1994; *Moody et al.*, 1995]. We compute isentropic back-trajectories for the spring of 1996 with the GEOS meteorological fields interpolated from the native sigma grid to potential temperature (θ) surfaces. We apply for this purpose the NASA Langley 3-D trajectory model [*Pierce et al.*, 1993, 1994], which uses fourth-order Runge-Kutta time stepping and a 20-minute timestep. Air parcels are initialized at a 1°×1° horizontal resolution; the winds are interpolated to the position of each parcel.

The most thorough trajectory analysis of transport patterns for Bermuda was given by *Moody et al.* [1995], who examined the major transport patterns for Bermuda by applying cluster analysis to isentropic trajectories for a two-year period (1988-1991). They found that the back-trajectories associated with springtime high-ozone events originate from an average altitude of 700 hPa over northwest North America (see their Plate 2).

We computed 10-day isentropic back-trajectories using the GEOS fields for each highozone event at Bermuda during the spring of 1996. All show strong subsidence from around the 700 hPa pressure level to the surface, consistent with the results of *Moody et al.* [1995]. We examined further the particularly strong episodes on March 16, April 13, and May 26 (see Figure 3.2). Figure 3.12 shows a mean isentropic back-trajectory at $\theta = 290$ K for a cluster of air parcels arriving at Bermuda on March 16, 1996. The mean back-trajectory originates from the northwest over North American continent, and exhibits strong subsidence from 600-700 hPa to the surface during the final 5 days of approach to Bermuda. Also shown in Figure 3.12 are the GEOS-CHEM daily mean net ozone production rates sampled every 6 hours along the back-trajectory. The model indicates net



Figure 3.12: Isentropic back-trajectory computed from the GEOS meteorological fields at $\theta = 290$ K for air arriving at Bermuda at 0000 UTC, March 16, 1996. Shown is the average trajectory for 25 parcels ending within the area of 30°N-34°N and 64°W-68°W. The parcels are initialized at a horizontal resolution of 1° longitude by 1° latitude. The error bars show the standard deviations for longitude, latitude, and pressure at each 24-hour interval. The color contours show the GEOS-CHEM daily mean net ozone production (ppbv day⁻¹) sampled every 6 hours along the trajectory.



Figure 3.13: Same as Figure 3.12, except for April 13, 1996 and $\theta = 295$ K.



Figure 3.14: Same as Figure 3.12, except for May 23, 1996 and $\theta = 290$ K. The color scale is different from that in Figure 3.12 and Figure 3.13.

ozone production of 4-8 ppbv day⁻¹ along the back-trajectory during the final two days of approach to Bermuda. The March 16 high-ozone event is associated with high ⁷Be (Figure 3.9), clearly reflecting the subsidence suggested by the back-trajectory shown in Figure 3.12. Nevertheless, the dominant contribution to ozone at Bermuda is from production below 700 hPa over North America and the western North Atlantic during transit, not transport from the stratosphere (Figure 3.2). The concurrent positive ozone correlation with ²¹⁰Pb during this event and more generally in the Bermuda data (Figure 3.9) implies mixing between the subsiding airmass and continental boundary layer outflow behind the cold fronts delivering high ozone to the site.

Figure 3.13 shows the mean isentropic back-trajectory at $\theta = 295$ K for a cluster of air parcels arriving at Bermuda on April 13, 1996. Again, it indicates subsiding flow from 700 hPa over northwest North America. We find daily mean net ozone production of 4-10 ppbv day⁻¹ along the trajectory during the final two days of approach to Bermuda, larger than for the March 16 event because of stronger solar radiation. However, despite the higher net ozone production, the ozone peak for the April 13 event is less than that for the March 16 event (Figure 3.2). This can be explained by the shorter transport time from the east coast to Bermuda.

For the May 26 high-ozone event (not shown), we find that the mean isentropic backtrajectory at $\theta = 295$ K shows direct boundary layer transport off the eastern U.S., while that at $\theta = 300$ K shows strong subsidence, illustrating the concurrence of the two patterns during high-ozone episodes. One might expect higher ozone levels during the May 26 events than the earlier events because of higher ozone production. However, in addition to a shorter lifetime of ozone in May, the core of the North American outflow shifts northward from beginning to late spring, and Bermuda then receives only the southern edge of the continental plume [*Li et al.*, 2002]. The May 26 event is also associated with high ²¹⁰Pb and ⁷Be, but ⁷Be is much lower than during March 16 and April 13 (Figure 3.9), reflecting the seasonal weakening of subsidence.

We find that back-trajectories during periods of low ozone at Bermuda originate from the



Figure 3.15: Contributions (in ppbv) from sources at different altitudes to simulated ozone concentrations averaged between 70°W and 10°W over the North Atlantic for April 1996.

marine boundary layer over the tropical North Atlantic, also consistent with previous back-trajectory analyses [*Oltmans and Levy II*, 1992, 1994; *Moody et al.*, 1995]. For example, Figure 3.14 shows a typical case for May 23, when surface ozone dipped to below 20 ppbv (Figure 3.2). Net ozone destruction of 2-6 ppbv day⁻¹ takes place during the transport to Bermuda.

3.6 Sources of Tropospheric Ozone Over the North Atlantic in Spring

Our source attribution for ozone over Bermuda can be generalized to the North Atlantic troposphere. Figure 3.15 shows the contributions from each source region (see section 3.2) to simulated ozone concentrations between 70°W and 10°W over the North Atlantic for April 1996. Transport from the stratosphere and production in the upper troposphere both contribute on average less than 5 ppbv (5%) to ozone in the lower troposphere. Examination of other seasons (not shown) indicates that stratospheric influence on the lower troposphere peaks in winter but is then only 10-15%. In comparison, Follows et al. [1992] obtained in a two-dimensional model study a stratospheric contribution of less than 5% to surface ozone in all seasons, while Wang et al. [1998b] obtained in a 3-D model study a zonal mean stratospheric influence of 5% in summer and 10-20% in winter at northern midlatitudes. The stratospheric contribution increases above 500 hPa to reach about 40 ppbv (50%) just below the tropopause (Figure 3.15; also see Figure 3.6). Our results are not inconsistent with those of Oltmans et al. [1996], who suggested based on ozonesonde measurements and back-trajectories that stratospheric ozone plays an important role in loading the middle and upper troposphere over the North Atlantic with ozone in spring. However, we find that most of the ozone in the middle and upper troposphere in spring originates from the troposphere, with all altitudes contributing (Figure 3.15).

A remarkable result from Figure 3.15 is the pervasive influence of lower-tropospheric production on ozone concentrations at all levels in the troposphere. This result reflects the rapid production of ozone in the continental boundary layer and the long lifetime of ozone in spring, particularly at higher latitudes. We find that throughout the troposphere the lower-tropospheric influence is largest in summer and smallest in winter, consistent with the results of *Wang et al.* [1998b].

3.7 Summary and Conclusions

Conflicting interpretations in the literature of stratospheric versus anthropogenic influences on the springtime ozone maximum at Bermuda have confused assessments of the sources of tropospheric ozone over the North Atlantic and more generally have fueled the debate on the stratospheric contribution to the tropospheric ozone budget. We have used here the GEOS-CHEM global 3-D model of tropospheric ozone-NO_x-hydrocarbon chemistry driven by assimilated meteorological observations for 1996 to reconcile past interpretations. The model reproduces the observed seasonal cycle of surface ozone at Bermuda to within 2-5 ppbv. It captures the day-to-day variation of springtime ozone at the site (r = 0.82), including the occurrence of events with concentrations in excess of 70 ppbv. We find that this variability is singly driven by ozone produced in the lower troposphere over North America and advected to Bermuda in the boundary layer behind cold fronts. This result agrees with some previous analyses of observations [*Van Valin et al.*, 1988; *Dickerson et al.*, 1995; *Huang et al.*, 1999; *Milne et al.*, 2000]. Ozone in the model correlates with CO and ²¹⁰Pb similarly to the observations, further supporting this interpretation.

Other past analyses based on isentropic back-trajectories pointed out that high-ozone at Bermuda occurs when airflow is from the middle troposphere over North America, and argued that the associated strong subsidence and observed correlation with ⁷Be imply a stratospheric or uppertropospheric origin for ozone [*Oltmans and Levy II*, 1992; *Moody et al.*, 1995]. We computed isentropic back-trajectories with the GEOS meteorological fields and find that they are consistent with these past analyses, i.e., back-trajectories associated with high-ozone events originate typically from the 700 hPa pressure level over the northwest of North America. Ozone and ⁷Be are correlated in the model similarly to observations. However, contrary to past interpretations, we find that the subsidence does not imply a dominant transport of ozone from the stratosphere or even the free troposphere to Bermuda. Instead, ozone originates from continental boundary layer outflow and mixes with the subsiding air during the transport to Bermuda behind cold fronts. Positive correlation between ⁷Be and ²¹⁰Pb during the high-ozone events provides evidence for this mixing, which was not accounted for in the past isentropic back-trajectory analyses, but is readily apparent in our Eulerian model.

The model also reproduces the observed positive and negative correlations of summertime ozone at Tenerife (Canary Islands, 2.4 km altitude) with ⁷Be and ²¹⁰Pb, respectively. We find that the positive correlation with ⁷Be is driven by ozone produced in the middle troposphere (400-700 hPa), rather than from the stratosphere or even upper troposphere as previously proposed on the basis of this correlation [*Prospero et al.*, 1995]. The average stratospheric contributions at the site is less than 10 ppbv.

We examined the sources of ozone at Bermuda at different altitudes in the troposphere. The model reproduces the observed vertical ozone distributions there and over North America to within 5 ppbv throughout the troposphere. We find that the stratospheric contribution to ozone in the free troposphere over Bermuda is less than 5 ppbv (10%) below the 400 hPa pressure level and increases to 50% just below the tropopause.

We generalized our results for Bermuda to the North Atlantic troposphere using regional budgets computed from the model. We find that the stratosphere contributes less than 5% on average to ozone below 500 hPa, and that production in the lower troposphere has a pervasive influence at all tropospheric altitudes.

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Chapter 4

Export of NO_y From the North American Boundary Layer: Reconciling Aircraft Observations and Global Model Budgets

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Abstract

Fossil fuel combustion accounts for > 50% of the global atmospheric emission of NO_x, but this source is concentrated in the polluted continental boundary layer (CBL) and only a small fraction is exported to the global troposphere. Better quantification is needed of the export efficiency of NO_y (NO_x and its oxidation products) out of the CBL. A recent Lagrangian analysis of the NO_y-CO correlations observed from aircraft in the North Atlantic Regional Experiment (September 1997, NARE'97) downwind of eastern North America indicated a NO_{y} export efficiency of 3-9%, with < 10% of the exported NO_y present as NO_x. Previous 3-D model Eulerian budget analyses for the North American boundary layer indicated NO_v export efficiencies of 25-30% with 30-35% of the exported NO_y present as NO_x. We investigated this discrepancy by simulating the NARE'97 observations with a global 3-D model of tropospheric chemistry (GEOS-CHEM), and using the model to calculate the NO_v export efficiency both through a Lagrangian analysis of the NO_v-CO correlations along the aircraft flight tracks and through an Eulerian budget analysis for the North American boundary layer. The model reproduces the NO_{v} -CO correlations in the aircraft data and at the Harvard Forest surface site in the northeastern United States. We show that the previous Lagrangian analyses of the NO_{ν} export efficiency during NARE'97 were probably biased low due to underestimate of the CO background. Correcting for this bias we find a NO_v export efficiency of $17\pm7\%$ in the model and $15\pm11\%$ in the observations. A similar NO_y export efficiency (20%) in the model is obtained from the Eulerian budget analysis. Export efficiencies of NO_v in previous 3-D model Eulerian budget analyses were probably biased high because of insufficient scavenging out of the CBL. Only 6% of the exported NO_v in the model is present as NO_x along the NARE'97 flight tracks, in agreement with the observations, but 40% of the NO_v export flux is as NO_x, in agreement with the previous 3-D model analyses. This result reflects the fast oxidation of NO_x during transport downwind of North America. The eventual ozone production in the global troposphere due to the exported NO_x and PAN, with comparable contributions from each, is estimated to be similar in magnitude to the direct export of ozone pollution from the North American boundary layer.

4.1 Introduction

Most of the global production of tropospheric ozone takes place in the free troposphere [*Wang et al.*, 1998b]. This production is primarily limited by the availability of nitrogen oxides $(NO_x = NO + NO_2)$ [*Chameides et al.*, 1992]. More than half of the global emission of NO_x is from fossil fuel combustion [*IPCC*, 2001], but this source is concentrated in the continental boundary layer (CBL). Most of the NO_x emitted from fossil fuel combustion (hereafter referred to as anthropogenic NO_x) is oxidized to nitric acid (HNO₃) in less than a day and lost within the CBL through deposition. The fraction of anthropogenic NO_x and its oxidation products), particularly NO_x and peroxyacetyl nitrate (PAN), provides an important NO_x source in the remote atmosphere that needs to be quantified [*Moxim et al.*, 1996, *Lamarque et al.*, 1996, *Horowitz and Jacob*, 1999].

Simulations with 3-D Eulerian models of atmospheric chemistry have suggested that 25-35% of NO_x emitted in the United States is exported out of the CBL as some form of NO_y, and that the rest is deposited within the CBL mainly as HNO₃ [*Kasibhatla et al.*, 1993, *Horowitz et al.*, 1998, *Liang et al.*, 1998]. The detailed study by *Liang et al.* [1998] finds little seasonal variation in this export efficiency. It finds more seasonal variation in the composition of the exported NO_y, with the fraction exported as NO_x varying from 30-35% in summer and fall to 40% in spring and 60% in winter.

Aircraft measurements from the North Atlantic Regional Experiment in September 1997 (NARE'97) offer an opportunity to test these model results. Measurements of NO_y , NO_x , PAN, and CO were made aboard an aircraft based in Newfoundland and sampling North American outflow. By viewing CO as an inert tracer in the outflow, one can use the NO_y -CO correlation in the aircraft observations as a measure of the export efficiency of NO_y from a Lagrangian perspective. *Stohl et al.* [2002] thus estimate that only 3% of surface NO_x emissions was exported to the free troposphere above 3 km during NARE'97. A more detailed study by *Parrish et al.* [2003] of the data from NARE'97 and from four other North American aircraft missions estimates a NO_y export efficiency of about 10% in early fall and spring and 20% in summer. These values are much lower than the 3-D model Eulerian budget estimates. The analysis by *Parrish et al.* [2003] further indicates that NO_x represented only 8% of the NO_y exported to the free troposphere during NARE'97, with PAN contributing 34% and HNO₃ contributing presumably the remainder. This NO_x fraction is considerably lower than the 3-D model estimate of *Liang et al.* [1998].

Similar discrepancies between 3-D model and observation-based estimates of the export efficiency of NO_y have been found for East Asia. A global 3-D model simulation by *Bey et al.* [2001b] indicates that 20-30% of the NO_x emitted in East Asia in spring is exported to the free troposphere as NO_y, and that the major component of the exported NO_y is PAN (45%) with NO_x and HNO₃ each contributing 25-30%. However, a recent study by *Koike et al.* [2003], using observed NO_y-CO correlations in Asian outflow from the TRACE-P aircraft mission in February-April 2001 [*Jacob et al.*, 2003], estimates that only 15% of the NO_x emitted in China is exported to the free troposphere (2-7 km) as NO_y. *Koike et al.* [2003] find that PAN was the dominant form of the exported NO_y, while only 0.5% remained as NO_x in the free troposphere. A study by *Miyazaki et al.* [2003] using meteorological (back-trajectory) and chemical (tracer correlation) analyses of the TRACE-P observations, estimates similarly that only 10-20% of NO_y emitted from East Asia was exported to the free troposphere.

Such large discrepancies between estimates of the export efficiency of NO_y and the speciation of the exported NO_y have major implications for assessing the effect of anthropogenic NO_x emissions on the global ozone budget. *Liang et al.* [1998] estimated that the eventual ozone production in the free troposphere due to the exported NO_x + PAN is twice as large as the direct export of ozone pollution from the U.S. boundary layer. In contrast, *Parrish et al.* [2003] argued that anthropogenic production of ozone in the free troposphere must be of little importance due to the small fraction of NO_v exported to the free troposphere and its prevailing form as HNO_3 .

We attempt here to understand these apparent discrepancies by using a global 3-D model simulation of the in situ aircraft measurements from NARE'97. We evaluate the model with aircraft and ozonesonde observations from the mission, as well as with surface observations from the eastern United States. By using the model to replicate both the observation-based analysis of the NO_y export efficiency by *Parrish et al.* [2003] and the CBL NO_y budget analysis of *Liang et al.* [1998], we can shed light on the difference between the two studies. Results have important general implications for the ability of models to describe properly the export of soluble gases and aerosols out of the CBL.

4.2 The NARE'97 Aircraft Mission

The NARE'97 aircraft mission was conducted from September 6 to October 2, 1997 over the Canadian maritime provinces and the western North Atlantic Ocean (Figure 4.1). It used a WP-3D aircraft (ceiling 8 km) based out of St John's, Newfoundland. A total of 13 flights were conducted, with principal focus on sampling of North American outflow. Daily ozonesondes were launched from Sable Island, Nova Scotia (44°N, 60°W) from September 5 to October 5.

Ozone was measured aboard the aircraft by a fast-response NO-ozone chemiluminescence instrument [*Ryerson et al.*, 1998]. CO was measured by vacuum UV fluorescence [*Holloway et al.*, 2000]. NO was detected by ozone-induced chemiluminescence and NO_x was inferred from NO-NO₂-O₃ photostationary steady state using radiometer data for the NO₂ photolysis frequency. Total gasphase NO_y was measured by Au-tube conversion to NO with added CO followed by ozone chemiluminescence. Measurement accuracy was estimated at 5% for the NO data and +5% to -25%for the NO_y data [*Ryerson et al.*, 1999]. PAN and peroxyacyl nitrate (PPN) were measured at 5 minute or shorter intervals by an onboard gas chromatograph with electron capture detection, and



Figure 4.1: Flight tracks of the NOAA WP-3D aircraft during the North Atlantic Regional Experiment in September 1997 (NARE'97). The rectange (dashed line) defines the North American domain (130°W-65°W, 25°N-55°N) used in our budget analysis.

the uncertainty in the measurements is estimated to be $\pm 25\%$ at mixing ratios of 50 pptv or above [*Williams et al.*, 2000]. The original CO, ozone, NO, and NO_y data were reported as 1-second averages; we use here 1-minute averages.

Cooper et al., [2001, 2002a,b] presented comprehensive analyses of the in situ aircraft observations from the NARE'97. They found that the export of pollution from North America to the free troposphere was largely controlled by midlatitude cyclones and the associated warm conveyor belts (WCB)s. They further found that NO_y was efficiently removed from the airstreams that transported polluted boundary layer air to the free troposphere, consistent with the analyses of *Stohl et al.* [2002] and *Parrish et al.* [2003].

4.3 Model Description

We use the GEOS-CHEM global 3-D model of tropospheric chemistry driven by assimilated meteorological observations from the Goddard Earth Observing System (GEOS) of the NASA Data Assimilation Office (DAO). The first description of the model as applied to simulation of tropospheric ozone- NO_x -hydrocarbon chemistry was presented by *Bey et al.* [2001a]. We use here GEOS-CHEM version 4.26 (http://www-as.harvard.edu/chemistry/

trop/geos), which includes a number of updates from *Bey et al.* [2001a] as described in particular by *Martin et al.* [2002]. Meteorological fields for 1997 (GEOS-STRAT) are provided at 6-hour frequencies (3-hour frequencies for surface fields and mixing depths) with horizontal resolution of 2° latitude by 2.5° longitude (degraded here to 4° latitude by 5° longitude) and 26 σ levels in the vertical between the Earth's surface and 0.1 hPa. The boundary layer up to 2 km altitude is resolved with five σ levels. All simulations presented here were conducted for four months (June-September 1997) using standard GEOS-CHEM model output as initial conditions. The first three months were used for initialization and we focus our attention on results for September.

The model includes 80 chemical species and over 300 reactions to describe tropospheric ozone-NO_x-hydrocarbon chemistry. Detailed photooxidation schemes are used for major hydrocarbons including isoprene [*Horowitz et al.*, 1998]. The NO_y chemistry is mainly from *DeMore et al.* [1997] and *Horowitz et al.* [1998]. Rate constants for NO_x-HNO₃ cycling have been updated following *Brown et al.* [1999a,b]. Hydroxy organic nitrates produced by isoprene oxidation appear to decompose quickly to HNO₃ on surfaces [*Chen et al.*, 1998], and we assume in the model that this decomposition is instantaneous [*Fiore et al.*, 2002]. No consideration of phase partitioning between gas-phase HNO₃ and aerosol nitrate is included in the model. Reactions of N₂O₅, NO₃, and NO₂ in aerosols are included using reaction probabilities from *Jacob* [2000] applied to global 3-D sulfate aerosol fields from *Chin et al.* [1996], as described by *Bey et al.* [2001a].

Dry deposition of oxidants and water soluble species is computed using a resistance-inseries model based on the original formulation of *Wesely* [1989] with a number of modifications [*Wang et al.*, 1998a]. The dry deposition velocities are calculated locally using GEOS data for surface momentum and sensible heat fluxes, temperature, and solar radiation. Wet deposition (applied to HNO_3 and H_2O_2 only) includes scavenging by convective updrafts, anvils, and large-scale precipitation as described by *Liu et al.* [2001].

Global anthropogenic and natural emissions are specified for 1997 following the procedure described by *Bey et al.* [2001a]. The current model includes updated CO emissions from *Duncan et al.* [2003]. Total anthropogenic emissions of CO and NO_x in the United States for 1997 are 97 TgCOyr⁻¹ and 6.7 TgNyr⁻¹, respectively. For comparison, the corresponding values for 1997 are 107 TgCOyr⁻¹ and 6.8 TgNyr⁻¹ in the most recent EPA report available (February 2003, see http://www.epa.gov/ttn/chief/trends/index.html). Transport of ozone from the stratosphere is simulated with the Synoz (synthetic ozone) method of *McLinden et al.* [2000] by imposing a global cross-tropopause flux of 475 TgO₃ yr⁻¹, which provides for a satisfactory simulation of vertical ozone profiles at northern middle and high latitudes [*Bey et al.*, 2001a,b; *Liu et al.*, 2002; *Li et al.*, 2002b]. The cross-tropopause flux of NO_y is 0.65 TgNyr⁻¹, including 0.17 TgNyr⁻¹ as NO_x and 0.48 TgNyr⁻¹ as HNO₃.

A global evaluation of the GEOS-CHEM simulation of tropospheric ozone-NO_x-hydrocarbon chemistry using assimilated meteorological data for 1994 (GEOS-1) was presented by *Bey et al.* [2001a]. That simulation underestimated CO concentrations at northern midlatitudes by 10-20 ppbv. *Duncan et al.* [2003] have since corrected this flaw with additional sources of CO from biogenic methanol and acetone, and updated estimates of nonmethane hydrocarbon (NMHC) emissions from biofuels, fossil fuels, and biomass burning. *Bey et al.* [2001a] found that simulated monthly mean concentrations of NO and PAN at northern midlatitudes were generally within a factor of 2 of aircraft observations with no systematic biases. HNO₃ was generally overestimated by a factor of 2-3, possibly due to a combination of insufficient scavenging in the free troposphere and the absence of gas-aerosol partitioning of HNO₃ in the model. Recent evaluation of the present model version simulation for 2001 using GEOS-3 assimilated meteorological data shows much less discrepancy between simulated and observed HNO₃ (Arlene Fiore, personal communication, 2003), due possibly to improved precipitation fields in the GEOS-3 meteorological product (as compared to GEOS-STRAT available for 1997). Overestimate of HNO₃ is a frequent problem in global models [*Wang et al.*, 1998b, *Lawrence et al.*, 1999, *Tie et al.*, 2003]. *Liu et al.* [2001] evaluated wet deposition in the model by simulation of the aerosol tracers ²¹⁰Pb and ⁷Be and found negligible simulation bias for both.

More specific evaluations of the GEOS-CHEM simulation of tropospheric ozone-NO_xhydrocarbon chemistry over North America and in North American outflow have been presented in a number of studies. *Fiore et al.* [2002] showed detailed comparisons with observational statistics for ozone and its precursors in the United States for the summer of 1995. They found that the model reproduces the principal features in the observed distributions of ozone and its precursors. Simulated NO_x and NO_y concentrations were typically within 50% of the observations, with no systematic bias. *Martin et al.* [2002] compared GEOS-CHEM results to tropospheric NO₂ columns retrieved from the GOME satellite instrument over the United States; they found strong spatial correlation (r = 0.78) and a 18% low bias in the model. *Li et al.* [2002a,b] found strong correlations and no systematic biases in comparisons of model results to time series of observations of surface ozone and CO at coastal and North Atlantic sites.

The focus of model application in this paper is to quantify the export of anthropogenic NO_x from the North American boundary layer and its implications for global ozone production. The North American boundary layer is defined as the horizontal domain (130°W-65°W, 25°N-55°N; see Figure 4.1) extending vertically up to 3 km or 730 hPa. This definition is similar to that used by *Liang et al.* [1998] in their model budget analysis. We will compare results from the standard simulation as described above to those from a sensitivity simulation with no anthropogenic NO_x , CO, or NMHC emissions from North America, and diagnose anthropogenic NO_y by difference. Although this attribution is not exact because of nonlinearity in NO_x chemistry, the perturbing effect is relatively small. We also conducted a sensitivity simulation in which only anthropogenic emissions



Figure 4.2: Simulated (blue) and observed (red) mean vertical profiles of CO, ozone, NO_y , NO, and PAN concentrations during NARE'97. Horizontal bars represent standard deviations. Model results are sampled along the flight tracks.

of NO_x from North America were suppressed (CO and NMHC emissions were kept at their values from the standard simulation) and found little difference with the results presented here.

4.4 Model Evaluation With NARE'97 Data

Simulated and observed vertical distributions of CO, ozone, NO_y, NO, and PAN are shown in Figure 4.2 for the ensemble of NARE'97 flights in Figure 4.1. Scatter plots for the 1-minute data are shown in Figure 4.3. Model results were sampled along the flight tracks, at the time of the flights. Concentrations of CO, NO, and NO_y are elevated in the boundary layer relative to the free troposphere, both in the model and in the observations, reflecting post-frontal continental outflow [*Cooper et al.*, 2001]. Simulated CO concentrations show no bias in the free troposphere but are 10-20 ppbv too high in the boundary layer. Our previous GEOS-CHEM simulation of surface CO concentrations at Sable Island off the coast of Nova Scotia [*Li et al.*, 2002a] shows that the model reproduces the North American boundary layer outflow with usually no bias except in September 1997 where the outflow events are too large. We thus believe that the overestimate of boundary layer CO during NARE'97 is due to a transport anomaly rather than an overestimate of North American sources.

The model reproduces the observed increase of ozone concentration with altitude, which is a well-known feature of observations over the North Atlantic [*Oltmans et al.*, 1996] and reflects efficient production and the long lifetime of ozone in the free troposphere. Boundary layer outflow from North America is not enhanced in ozone in September because of the relatively weak photochemical production and the competing effect of boundary layer sinks from chemistry and deposition [*Parrish et al.*, 1998]. A comparison of simulated and observed ozonesonde vertical profiles at Sable Island during the mission (Figure 4.4) shows that simulated ozone concentrations agree with observed values to within 5 ppbv through much of the troposphere.

There is no bias in simulated NO concentrations over the range of measurement alti-



Figure 4.3: Scatter-plots of simulated versus observed CO, ozone, NO_y, NO, and PAN concentrations during NARE'97. Observations are 1-minute averages. Model results are sampled along the flight tracks. The y = x and regression lines (RMA method) are also shown. NO_y, NO, and PAN are plotted on a logarithm scale.



Figure 4.4: Simulated (dashed line) and observed (solid line) mean vertical profile of ozone at Sable Island in September 1997. Horizontal bars represent standard deviations of the observation. A total of 30 ozone sondes were launched during September 5-October 5, 1997.

tudes, but NO_y and PAN concentrations are overestimated on average by 35% and 50% in the free troposphere, respectively, which by difference would indicate that HNO₃ concentrations are overestimated on average by 40% in the free troposphere. Understanding the cause of the model overestimate of PAN, HNO_3 , and NO_y , i.e., whether it is due to background or to excessive North American outflow, is critical in assessing the model simulation of NO_v export. Regression lines for model versus observed NO_y and PAN (Figure 4.3) indicate elevated intercepts, but the slopes (0.82-0.87) are less than unity; this implies that the model overestimate is due to the background and that there is in fact little bias in simulation of North American outflow. Comparison of model results with observed vertical profiles of PAN and HNO₃ from a number of other aircraft missions at northern midlatitudes [Bey et al., 2001a] and for several versions of the GEOS-CHEM model [Fiore 2003] confirms that the problem is one of background and is specific to GEOS-STRAT meteorology. Model versions using GEOS-3 meteorology (available from 1998 on) show much improved simulations of PAN and HNO₃ [Fiore 2003]. It is known that GEOS-STRAT underestimates precipitation along the storm track over the western North Atlantic [Allen et al., 1997] and we find this is indeed the case for September 1997 by comparison with data from the Global Precipitation Climatology Project (GPCP) [Huffman et al., 1997]. The improved simulation of HNO₃ in GEOS-3 is due to a wetter environment. We find in the model that only 39% of total NO_y in the free troposphere along the NARE'97 flight tracks is of North American anthropogenic origin, consistent with the previous estimate of Stohl et al. [2002] and further supporting the view that the model overestimate of NO_{y} must reflect a background problem.



Figure 4.5: Observed (left panel) and simulated (right panel) NO_y -CO correlations during NARE'97. Observations are 1-minute averages and include all altitudes. Model results are sampled along the flight tracks. The curves give the relationships expected from equation 4.1 for different values of the NO_y export efficiency *f* (indicated on the plots as percentages) and with values of background CO, background NO_y, and CO/NO_y emission ratio taken from *Parrish et al.* [2003]. See text for details.

4.5 Export of NO_v From the North American Boundary Layer

4.5.1 Lagrangian Approach: Mixing Model of Parrish et al. [2003]

Figure 4.5 shows the observed and simulated NO_v-CO correlations along the NARE'97

flight tracks. The curves give the relationships expected from

$$f = \frac{\Delta \text{NO}_y}{\Delta \text{CO}} R \alpha \tag{4.1}$$

following the mixing model of *Parrish et al.* [2003], where *f* is the export efficiency of NO_y from the North American boundary layer, ΔNO_y and ΔCO are the enhancements above background concentrations, *R* is the average anthropogenic emission ratio of CO to NO_x in North America, and the multiplicative coefficient α accounts for natural sources of CO within the North American boundary layer, particularly the oxidation of isoprene.

Table 4.1: Export Efficiency of NO_v From the North American Boundary Layer (NARE'97 Data)

	Stohl et al. [2002]	Parrish et al. [2003]	this work ^a
Export efficiency ^b	3%	9±5%	$\frac{11.5{\pm}3\%^{c}}{17{\pm}7\%^{d}}$
Speciation of exported NO _y			
NO _x		8%	$6\pm4\%$
PAN		34%	36±13%
HNO ₃		57%	52±14%

^{*a*}Calculations based on GEOS-CHEM global 3-D model results sampled along the NARE'97 flight tracks. ^{*b*}Derived from the relationship of NO_y with CO along the NARE'97 aircraft flight tracks, as decribed in the text. Export efficiencies in *Parrish et al.* [2003] and in this work are calculated from equation 4.1.

^{*c*}Calculated using *Parrish et al.* [2003] values for the mixing model parameters in equation 4.1 including background concentrations of CO and NO_y of 75 ppbv and 0.1 ppbv, respectively, $R = 5.67 \text{ mol mol}^{-1}$, and $\alpha = 1.18$.

^{*d*}Calculated using mixing model parameters for equation 4.1 consistent with the GEOS-CHEM model environment including background concentrations of CO and NO_y of 95 ppbv and 0.3 ppbv, respectively, R = 6.5, and $\alpha = 1$.

Derivation of the export efficiency f from the NARE'97 observations of NO_y and CO concentrations requires assumptions of the background concentrations of NO_y and CO, and of the values of R and α . *Parrish et al.* [2003] adopted 0.1 ppbv for background NO_y, 75 ppbv for background CO, $R = 5.67 \text{ mol mol}^{-1}$, and $\alpha = 1.18$ (the latter from *Chin et al.* [1994]). They applied equation 4.1 to every pair of NO_y and CO concentrations observed in anthropogenic plumes in the free troposphere above 2 km during NARE'97. The anthropogenic plumes were defined by $\Delta CO > 30$ ppbv. They thus estimated that on average 9±5% of North American anthropogenic NO_x was exported to the free troposphere above 2 km as some form of NO_y (Table 4.1).

We can estimate similarly the export efficiency of North American anthropogenic NO_y in our model by applying equation 4.1 to the simulated NO_y and CO concentrations sampled along the NARE'97 flight tracks above 2 km, with the same values of mixing model parameters (background concentrations of CO and NO_y, *R*, α) as used by *Parrish et al.* [2003], and the same criteria (Δ CO > 30 ppbv) for selection of anthropogenic plumes (26% of the model data). We obtain an average export efficiency of 11.5±3%, similar to the *Parrish et al.* [2003] value.

The above comparison of simulated and observed values of f, using the same values of



Figure 4.6: Correlation of background CO and NO_y concentrations with North American outflow in the model sampled along the NARE'97 flight tracks above 2 km altitude. The plots show background CO and NO_y, as determined from the sensitivity simulation with North American anthropogenic emissions shut off, versus CO in the standard simulation. The regression lines (RMA method) are also shown.

mixing model parameters for equation 4.1, tests the similarity in the NO_v -CO relationships between model and observations. However, we find that the mixing model parameter values of Parrish et al. [2003] are inconsistent with the model environment, so that the above value of f (at least in the model) should not be viewed as an export efficiency. Figure 4.6 shows correlations along the NARE'97 flight tracks between CO concentrations from the standard simulation and CO and NO_{y} concentrations from the sensitivity simulation with no North American anthropogenic emissions. The latter represent the background concentrations in the model as appropriate for application of equation 4.1. The CO concentrations from the standard simulation are used as an indicator of North American outflow. We find that the background CO concentration increases in the outflow, reflecting natural sources of CO in the North American boundary layer in particular from oxidation of isoprene. In contrast the background NO_y concentration is lower in the outflow than in free tropospheric air, reflecting the loss of NO_{y} in the boundary layer by deposition. If we define North American outflow following *Parrish et al.* [2003] by $\Delta CO = 30$ ppbv above background, then we find from Figure 4.6 that appropriate CO and NO_{ν} background concentrations in the model environment for application of equation 4.1 are 95 ppbv for CO and 0.3 ppbv for NO_v . We then also need to use $\alpha = 1$ since the model CO background accounts for biogenic source enhancements in the boundary layer. This biogenic enhancement is about 10 ppby, on the basis of the range in the CO background in Figure 4.6.

As seen in Figure 4.6, background CO in the model never drops below 80 ppbv. There is independent evidence that the 75 ppbv value used by *Parrish et al.* [2003] may be too low, resulting in their underestimating of the NO_y export efficiency. Table 4.2 shows monthly mean concentrations of CO at several northern midlatitude NOAA CMDL sites in September 1997. These concentrations are filtered based on wind direction such that they represent background conditions at those sites [*Novelli et al.*, 2003]. The sites represent locations both upwind and downwind of North America. The background concentrations of CO at these sites range from 83 ppbv to 96 ppbv. Previous

Site code	Location	Latitude	Longitude	Elevation (m)	CO (ppbv)
MID	Sand Island, Midway	28.2°N	177.4°W	4	94
SHM	Shemya Island, Alaska	52.7°N	$174.1^{\circ}W$	40	94
CBA	Cold Bay, Alaska	55.2°N	162.7°W	25	87
MLO	Mauna Loa, Hawaii	19.5°N	155.6°W	3397	86
CMO	Cape Meares, Oregon	45.5°N	124.0°W	30	96
NWR	Niwot Ridge, Colorado	40.1°N	105.6°W	3475	94
BMW	Tudor Hill, Bermuda	32.3°N	64.9°W	30	85
AZR	Azores, Portugal	38.8°N	27.4°W	40	83
MHD	Mace Head, Ireland	53.3°N	9.9°W	25	87

Table 4.2: Monthly Mean CO Concentrations at Northern Midlatitude Sites for September 1997

Data are from the NOAA Climate Monitoring and Diagnostics Laboratory (CMDL) network (http://www.cmdl.noaa.gov/info/ftpdata.html). Observations are filtered based on wind direction such that the concentrations represent background conditions [*Novelli et al.*, 2003].

estimates of the background CO cocentration at Sable Island (just upstream of the NARE'97 region), taken as the 17th percentile of observed CO concentrations, are 90 ppbv on average for September 1991-1994 [*Parrish et al.*, 1998] and 84 ppbv for September 1997 [*Li et al.*, 2002a].

Observations of the NO_y-CO correlation at Harvard Forest (42.5°N, 72.2°W, 340 m altitude), a rural site in central Massachusetts, offer a measure of the CO background typical of the northeastern United States. Figure 4.7 shows a comparison of simulated (1997) and observed (1994-1996, 2001) daytime (10-16 local time) NO_y-CO correlations for September at Harvard Forest (no observations are available for September 1997). NO_y and CO concentrations are strongly correlated, both in the observations and in the model. The observed CO/NO_y slopes are 15-16 molmol⁻¹, except for 1996, which shows a slope of 11molmol⁻¹. Model results show a slope of 16 molmol⁻¹, indicating a deposition loss of NO_y in the CBL that is consistent with observations. The intercepts of the regression lines can be taken as representing the background concentrations of CO at that site [*Parrish et al.*, 1991]. The observations thus indicate a CO background of 96-112 ppbv for September 1994-1996 and 76 ppbv for September 2001. Model results indicate a CO background of 105 ppbv for September 1997, comparable to the 1994-1996 values though much higher than the 2001 value.



Figure 4.7: Simulated (1997) and observed (1994-1996, 2001) NO_y-CO correlations at Harvard Forest (42.5°N, 72.2°W, 340 m altitude) for September 1997, plotted on a logarithm scale. Data used are daytime only (10-16 local time). The regression lines (RMA method) are also shown.

The average anthropogenic emission ratios of CO/NO_y in the model are respectively 7.2 and 6.5 mol mol⁻¹ for eastern North America (east of 95°W) and all of North America (Figure 4.1) for September 1997. These values are higher than the 5.67 mol mol⁻¹ value used by *Parrish et al.* [2003] but lower than the 1997 value of 7.8 mol mol⁻¹ for the United States estimated by EPA (see section 4.3). *Stohl et al.* [2002] used $R = 6.3 \text{ mol mol}^{-1}$ in their analysis of the NARE'97 data. We use $R = 6.5 \text{ mol mol}^{-1}$ (taken as the CO/NO_y source ratio for eastern North America) in our calculations hereafter. As discussed above, the CO background of 95 ppbv determined from our sensitivity simulation includes natural sources of CO, so it is appropriate for us to use $\alpha = 1$ in our application of equation 4.1. *Parrish et al.* [2003] used $\alpha = 1.18$ in their analysis. Their value of *R* (5.67 mol mol⁻¹) multiplied by $\alpha = 1.18$ gives 6.7 mol mol⁻¹, comparable to the value used here. *Stohl et al.* [2002] used $\alpha = 1$ in their analysis.

With the model results for background concentrations of CO (95 ppbv) and NO_y (0.3

ppbv), together with $R = 6.5 \text{ mol mol}^{-1}$ and $\alpha = 1$, we calculate in the model an average NO_y export efficiency of $f = 17\pm7\%$ for North American anthropogenic NO_y during NARE'97 (Table 4.1). As discussed above, it appears at least that the background CO concentration of 75 ppbv used in the analysis of *Parrish et al.* [2003] is too low. With a CO background of 95 ppbv that includes the natural boundary layer enhancement, a NO_y background of 0.1 ppbv, R = 5.67, and $\alpha = 1$, they would have derived in addition a NO_y export efficiency of $f = 14.5\pm11\%$, 60% higher than their original value of $9\pm5\%$. With R = 6.5 (our model value) they would have obtained $f = 17\pm13\%$, same as the model.

Any general definition of background CO concentrations, in the observations or in the model, is still fairly arbitrary. A different approach for deriving ΔNO_y and ΔCO in the model for application of equation 4.1 is by the local difference of model results between the standard simulation and the sensitivity simulation with no anthropogenic North American emissions, sampled along the NARE'97 flight tracks. Any assumption of a uniform background is then avoided, and ΔNO_y and ΔCO are the true enhancements due to North American anthropogenic emissions in the model environment. In this application, we again set $\alpha = 1$ since the contribution to CO from biogenic emissions is included in the background. We obtain in this manner an average NO_y export efficiency of $f = 17\pm6\%$, consistent with the value of $17\pm7\%$ obtained in the above model analysis. Further examination of model results along the NARE'97 flight tracks indicates that NO_y exported from the North American boundary layer is mostly HNO₃ (52%), with 36% as PANs and only 6% as NO_x, in agreement with the *Parrish et al.* [2003] observations (Table 4.1).

4.5.2 Eulerian Approach: Boundary Layer Budget

Our next step is to compare the NO_y export efficiencies derived in the model from the above Lagrangian perspective along the NARE'97 flight tracks to those derived from the more standard Eulerian budget calculation for the North American boundary layer, following the approach

of *Liang et al.* [1998]. A model budget for anthropogenic NO_y in the North American boundary layer in September 1997 is shown in Table 4.3. The North American boundary layer is defined as the domain extending horizontally over the domain of Figure 4.1 and vertically up to 730 hPa (2.6 km). The budget for anthropogenic NO_y is determined by difference between the standard simulation and the sensitivity simulation in which North American anthropogenic emissions are shut off.

Table 4.3: Model Budget of Anthropogenic NO_y in the North American Boundary Layer for September 1997

	NO_x	PANs	HNO ₃	Alkyl nitrates	Total
Concentration (ppbv)	0.27	0.16	0.69	0.03	1.15
Lifetime (day)	0.50	0.31	2.0		
Emission (G mol day ⁻¹)	1.32				1.32
Net production ($Gmolday^{-1}$)	-1.11	0.09	1.00	0.02	< 0.01
Wet deposition $(G \mod day^{-1})$			0.42		0.42
Dry deposition ($G \mod day^{-1}$)	0.08	0.04	0.49	< 0.01	0.62
Export (G mol day ⁻¹)	0.11	0.05	0.10	0.01	0.27
Composition of exported NO _v	40%	19%	37%	4%	

The North American boundary layer is defined as the domain extending horizontally over the domain $(130^{\circ}W-65^{\circ}W, 25^{\circ}N-55^{\circ}N)$ in Figure 4.1 and vertically up to 730 hPa (about 3 km). The budgets are for NO_y of North American anthropogenic origin, determined by difference between the standard simulation and a sensitivity simulation with North American fossil fuel emissions shut off. PANs includes PAN, MPAN (produced by isoprene oxidation) and other peroxyacylnitrates. Lifetimes are calculated with respect to the sinks from chemical loss and deposition.

We find that the exported anthropogenic NO_y (0.27 Gmolday⁻¹) amounts to 20% of emissions (1.31 Gmolday⁻¹), consistent with the values derived from the Lagrangian model of equation 4.1 by sampling the model results along the flight tracks. This export efficiency of 20% includes 14% ventilated through the top of the domain (convection, WCBs) and 6% advected through the sides. Previous 3-D model budget analyses for a similar North American domain indicated NO_y export efficiencies of 25-30% (annual) [*Kasibhatla et al.*, 1993], and seasonal values of 25% in summer and 30% in fall [*Liang et al.*, 1998]. Our model values are significantly ower. Concentrations and lifetimes of NO_y species in the North American boundary layer in our model are similar to those of *Liang et al.* [1998] (compare our Table 4.3 to their Table 3). We attribute their higher NO_y



Figure 4.8: Simulated monthly mean (September 1997) ozone production enhancements due to exported NO_y from the North American boundary layer, integrated over the free tropospheric column. Also shown are the NARE'97 aircraft flight tracks.

export efficiency to insufficient scavenging of NO_y during export out of the boundary layer. They did not have observations in North American outflow to evaluate that component of their model.

The composition of the exported NO_y in our simulation (40% NO_x, 19% PANs, and 37% HNO₃) is similar to that of *Liang et al.* [1998] (34% NO_x, 26% PANs, and 35% HNO₃). The NO_x fraction of the exported NO_y is considerably higher than that along the NARE'97 flight tracks, either in our model or in the observations (Table 4.1). This reflects in the model the rapid oxidation of NO_x during transport from the point of exit out of the CBL to the point of sampling by the NARE'97 aircraft. Such rapid oxidation of NO_x during transport was also inferred from the TRACE-P observations of the export of NO_y from East Asia in spring [*Miyazaki et al.*, 2003].

4.5.3 Implications for Ozone

It thus appears that we can reconcile the high NO_{y}/NO_{y} ratios in the exported NO_{y} in the Liang et al. [1998] model with the low NO_x/NO_y ratios observed by Parrish et al. [2003] in NARE'97 as reflecting the fast oxidation of anthropogenic NO_x in the free troposphere during transport downwind of North America. Some ozone production would be expected during this transport. We examined this issue by difference between our standard simulation and the sensitivity simulation with North American anthropogenic sources shut off. Comparison of the gross ozone (odd oxygen) production rates in the two simulations gives the enhancements in ozone production in the North American boundary layer and in the free troposphere due to North American anthropogenic emissions. We thus find that the ozone production enhancement from North American anthropogenic emissions is 13 Gmolday^{-1} in the North American boundary layer, of which 40% (5 Gmolday^{-1}) is exported out of the North American boundary layer. This export of pollution ozone is similar to the model estimate of *Liang et al.* [1998] for fall (4 Gmolday^{-1}). We also find that the ozone production enhancement outside the North American boundary layer due to North American anthropogenic emissions (i.e., due to exported NO_v) is 5.8 Gmolday⁻¹, of which 2.8, 1.3, and 1.7 Gmolday⁻¹ are in the free troposphere over North America, in the rest of the global free troposphere, and in the global boundary layer outside North America. In the free troposphere, 70% of the eventual ozone production enhancement takes place in the near-field (i.e., over North America) due to exported NO_x . This is illustrated in Figure 4.8, which shows the ozone production enhancement integrated over the free tropospheric column. We see that the ozone production enhancement is largely realized by the time that the North American outflow is transported over the NARE'97 domain, consistent with the fast oxidation of NO_x during transport and the low NO_x/NO_y ratios observed in NARE'97. Globally, the ozone production enhancements due to exported NO_x and to exported PANs in the model are about equal. The eventual ozone production from the exported NO_x and PANs is similar to the model estimate of *Liang et al.* [1998] for fall (6 Gmol day⁻¹) and is comparable to the direct export of pollution ozone out of the North American boundary layer.

4.6 Summary and Conclusions

Recent analyses of the NO_y-CO correlation observed during the NARE'97 aircraft campaign downwind of eastern North America in September 1997 have indicated that less than 10% of the NO_x emitted in the North American boundary layer is exported as NO_y to the free troposphere above 2 km, and that HNO₃ is the dominant form of exported NO_y while less than 10% remains as NO_x [*Stohl et al.*, 2002, *Parrish et al.*, 2003]. These results are in contrast to previous 3-D model budget analyses that indicate much higher export efficiencies of anthropogenic NO_y from North America (25-30%) [*Kasibhatla et al.*, 1993, *Liang et al.*, 1998] and a much higher fraction of NO_x in the exported NO_y (> 30%) [*Liang et al.*, 1998]. Such large differences need to be understood because of their implications for the ability of models to simulate properly global anthropogenic influences on tropospheric ozone.

We investigated this problem by using the GEOS-CHEM global 3-D model of tropospheric chemistry to simulate the NARE'97 aircraft observations. We diagnosed the export of anthropogenic NO_y species from North America in the model through a Lagrangian analysis of the NO_y-CO correlation along the flight tracks (following the previous observation-based analyses) and an Eulerian NO_y budget analysis of the North American boundary layer (following the previous 3-D model analyses).

As a first step in the analysis, we replicated in the model the estimate of the export efficiency of North American anthropogenic NO_y from the NARE'97 data by using the NO_y-CO correlations along the NARE'97 flight tracks and applying the mixing model analysis of *Parrish et al.* [2003] to our model fields. Critical parameters in this mixing model analysis are the CO background, the NO_y background, and the CO/NO_y source ratio for North America. *Parrish et al.* [2003] used background concentrations of 75 ppbv for CO and 0.1 ppbv for NO_y, and a CO/NO_x molar source ratio $R = 5.67 \text{ mol mol}^{-1}$ multiplied by a factor $\alpha = 1.18$ to account for natural CO sources (i.e, an equivalent CO/NO_y source ratio of 6.7 mol mol⁻¹). They derived in this manner a NO_y export efficiency of 9±5%. By applying the same values of the mixing model parameters to our simulated NO_y-CO correlations along the NARE'97 flight tracks, we obtain an average export efficiency of 11.5±3%, just 25% higher than the *Parrish et al.* [2003] value.

The above result is important as a comparative test of the NO_{y} -CO correlation in the model versus the observations. However, we find that the values of the mixing model parameters assumed by Parrish et al. [2003] are not consistent with our model environment. The actual background concentration of CO in the model is 95 ppby, as obtained from a sensitivity simulation in which North American anthropogenic emissions are shut off. This background includes a 10 ppbv enhancement from North American natural hydrocarbon emissions, principally isoprene. It is consistent with NOAA CMDL observations at northern midlatitude stations in 1997. A low bias in the 75 ppbv CO background assumed by Parrish et al. [2003] would result in an underestimate of the NO_{ν} export efficiency in their analysis. At a CO background of 95 ppbv, their observationderived NO_v export efficiency would be 14.5 \pm 11%. The average anthropogenic CO/NO_v emission ratio in eastern North America in the model is R = 6.5. With this value of R and with background concentrations of 95 ppbv for CO and 0.3 ppbv for NO_v, and $\alpha = 1$, we calculate in the model an average NO_v export efficiency of $17\pm7\%$. The assumption of a fixed background for CO and NO_v is clearly an over-simplification, and we can jettison it in the model by defining North American anthropogenic NO_x and CO as the local difference between the standard and sensitivity simulation along the NARE'97 flight tracks. We estimate in this manner an NO_y export efficiency of $17\pm6\%$, consistent with the above analysis.

North American anthropogenic NO_y along the NARE'97 flight tracks in the model is mostly present as HNO₃ (52%), with 36% as PAN and only 6% as NO_x . This is in agreement with the observations (57% HNO₃, 34% PAN, 8% NO_x). We find in the model that 39% of the total NO_y in the free troposphere above 3 km along the NARE'97 flight tracks is from North American anthropogenic sources, consistent with the *Stohl et al.* [2002] estimate of 35%.

An Eulerian budget analysis for the North American boundary layer in the model indicates a NO_y export efficiency of 20%, in agreement with the Lagrangian analysis of the model fields along the NARE'97 flight tracks. This value is lower than the 30% value in the previous 3-D model simulation of *Liang et al.* [1998], and we believe that this reflects an underestimate of HNO₃ scavenging during export out of the CBL in that simulation. Our Eulerian budget analysis indicates a large contribution of NO_x (40%) to the exported NO_y, consistent with the previous 3-D model budget analysis of *Liang et al.* [1998] simulation (35%). This high NO_x/NO_y ratio in the exported NO_y versus the low NO_x/NO_y ratio along the NARE'97 flight tracks can be explained by fast oxidation of free tropospheric NO_x between the point of ventilation out of the CBL and the point of sampling by the NARE'97 aircraft.

The flux and speciation of exported NO_y from the North American boundary layer has important implications for global ozone production from North American anthropogenic emissions. We estimated the enhancements of ozone production in the North American boundary layer versus in the free troposphere due to North American anthropogenic emissions by difference between the standard simulation and the sensitivity simulation with North American anthropogenic emissions shut off. We find that this ozone production enhancement is 13 Gmol day⁻¹ in the North American boundary layer, of which 40% (5 Gmol day⁻¹) is exported out of the North American boundary layer, and 5.8 Gmol day⁻¹ in the global troposphere excluding the North American boundary layer. This production in the global troposphere is driven by exported NO_x and PANs, with comparable contributions from each and is similar in magnitude to the direct export of pollution ozone out of the North American boundary layer.

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Chapter 5

Transatlantic Transport of Pollution and its Effects on Surface Ozone in Europe and North America

[Li, Q., D. J. Jacob, I. Bey, P. I. Palmer, B. N. Duncan, B. D. Field, R. V. Martin, A. M. Fiore, R. M. Yantosca, D. D. Parrish, P. G. Simmonds, and S. J. Oltmans, Transatlantic transport of pollution and its effects on surface ozone in Europe and North America, *J. Geophys. Res.*, *107*(D13), doi:10.1029/2001JD001422, 2002.]

Abstract

We examine the transatlantic transport of anthropogenic ozone and its impact on surface ozone in Europe and North America by using a 5-year (1993-1997) simulation with the GEOS-CHEM global 3-D model of tropospheric chemistry. Long-term time series of ozone and CO at Mace Head (Ireland) and Sable Island (Canada) are used to evaluate transatlantic transport in the model. North American anthropogenic emissions contribute on average 5 ppbv to surface ozone at Mace Head, and up to 10-20 ppbv during transatlantic transport events which are forerunners of broader events in Europe. These events are associated with low-level westerly flow driven by an intense Icelandic low between Iceland and the British Isles. North American influence on ozone at Mace Head is strongly correlated with the North Atlantic Oscillation (NAO), implying that the NAO index can be used to forecast transatlantic transport of North American pollution to Europe. European anthropogenic emissions contribute on average less than 2 ppbv to surface ozone at Sable Island but up to 5-10 ppby during transatlantic transport events. These events are associated with low-level easterly flow established by anomalous low pressure at 45°N over the North Atlantic. North American anthropogenic emissions enhance surface ozone in continental Europe by 2-4 ppbv on average in summer, and by 5-10 ppbv during transatlantic transport events; transport in the boundary layer and subsidence from the free troposphere are both important mechanisms. We find in the model that 20% of the violations of the European Council ozone standard (55 ppby, 8-hour average) in the summer of 1997 over Europe would not have occurred in the absence of anthropogenic emissions from North America. North American influence on surface ozone in Europe is particularly strong at the thresholds used for the European standards (55-65 ppbv).

5.1 Introduction

There is presently much interest in intercontinental transport of ozone and aerosol pollution as a factor to be considered in the design of regional air quality control strategies [*NAS*, 2001; *CENR*, 2001]. Recent studies have indicated that transpacific transport of Asian pollution affects North America [*Jacob et al.*, 1999; *Jaffe et al.*, 1999; *Wilkening et al.*, 2000; *Yienger et al.*, 2000], transatlantic transport of North American pollution affects Europe [*Derwent et al.*, 1998; *Ryall et al.*, 1998; *Stohl and Trickl*, 1999], and transeurasian transport of European pollution affects Asia [*Liu et al.*, 2002]. The magnitudes of these effects and the need to include them in air quality control strategies are still highly uncertain. In a global 3-D model study, *Fiore et al.* [2002] found that anthropogenic sources in Asia and Europe enhance surface ozone in the United States by 3-7 ppbv in summer, with maximum effect under moderately polluted conditions (50-70 ppbv).

In this work, we quantify the transatlantic transport of ozone pollution and its effect on surface ozone in Europe and North America by using a 5-year (1993-1997) global 3-D model simulation evaluated with coastal observations on both sides of the North Atlantic. The Mace Head site (53°N, 10°W) on the west coast of Ireland is of particular interest. It receives westerly flow from the North Atlantic and is not impacted by local pollution sources [*Jennings et al.*, 1991]. Long-term measurements of ozone, carbon monoxide (CO), black carbon, and chlorofluorocarbons (CFCs) at Mace Head have been used to estimate transatlantic North American influence [*Jennings et al.*, 1996; *Derwent et al.*, 1998; *Ryall et al.*, 1998; *Forster et al.*, 2001]. Carbon monoxide is directly emitted by combustion sources and has a lifetime of 1-3 months in the atmosphere, therefore it is a sensitive tracer for long-range transport of pollution. *Jennings et al.* [1996] used air back-trajectories to indicate a North American origin for an event of weakly enhanced CO (30 ppbv above background)observed in the spring of 1992 at Mace Head.

In the case of ozone, the complexity of sources and the short lifetime (days to weeks) make it difficult to quantify, or even identify, a transatlantic transport influence at the surface from simple analysis of observations [*Fehsenfeld et al.*, 1996a; *Derwent et al.*, 1998]. *Stohl and Trickl* [1999] identified by trajectory analysis an episode of long-range transport of North American ozone pollution in the upper troposphere over Europe following uplift by a warm conveyor belt (WCB)

[*Browning*, 1999, *Cooper et al.*, 2001] over the western North Atlantic. As pointed out by *Stohl* [2001] and *Stohl et al.* [2002], such long-range transport of ozone pollution is far more efficient in the free troposphere than near the surface because of stronger winds and a longer ozone lifetime.

Even though the influence of transatlantic pollution transport on surface ozone in Europe or North America may be too weak to be easily detected from observations, it is still highly relevant for regional air pollution. A transatlantic pollution enhancement of only a few ppbv would make the achievement of ozone air quality standards in Europe significantly more difficult [*Jonson et al.*, 2001]. Global 3-D models of tropospheric ozone-NO_x-hydrocarbon chemistry offer a tool for quantifying such enhancements, provided that they are carefully evaluated for the purpose.

We use the GEOS-CHEM global model [*Bey et al.*, 2001a] for our 5-year simulation. The model is driven by assimilated meteorological observations from the Goddard Earth Observing System (GEOS) of the NASA Data Assimilation Office (DAO) [*Schubert et al.*, 1993]. Evaluations of the GEOS-CHEM simulation of tropospheric O₃-NO_x-hydrocarbon chemistry for different regions of the world have been presented in a number of papers [*Bey et al.*, 2001a,b; *Fiore et al.*, 2002; *Li et al.*, 2001a,b; *Palmer et al.*, 2001; *Chandra et al.*, 2002; *Liu et al.*, 2002; *Martin et al.*, 2002a,b]. *Fiore et al.* [2002] reported detailed comparisons with observations for ozone and its precursors in the United States. Here we focus our model evaluation on observed time series of ozone and CO in 1993-1997 at Mace Head and Sable Island (44°N, 60°W), off the east coast of Canada. Measurements of ozone and CO at Mace Head are part of the Global Atmospheric Gases Experiment (GAGE) and later the Advanced GAGE (AGAGE) program [*Simmonds et al.*, 1997; *Prinn et al.*, 2000]. Measurements of ozone and CO at Sable Island are part of the North Atlantic Regional Experiment (NARE) and have been used to monitor North American continental outflow to the North Atlantic [*Fehsenfeld et al.*, 1996a,b; *Parrish et al.*, 1993, 1998].

We briefly describe the model simulation in section 5.2, including the tagged tracer and sensitivity analyses used to diagnose transatlantic transport of pollution. Transatlantic transport

pathways are examined in section 5.3. In section 5.4 we analyze and interpret the model simulation of the observed time series of ozone and CO at the three North Atlantic sites. We quantify the impact of transatlantic pollution transport on surface ozone in Europe and North America in section 5.5. Summary and conclusions are given in section 5.6.

5.2 Model Simulation

A detailed description of the GEOS-CHEM model for tropospheric O_3 -NO_x-hydro-carbon chemistry is given by *Bey et al.* [2001a]. We use here model version 4.16 (http://www-as.harvard.edu/chemistry/tr applied to a continuous 5-year record (1993-1997) of GEOS assimilated meteorological observations with 3- or 6-hour temporal resolution depending on the variable and 2° latitude by 2.5° longitude horizontal resolution. The GEOS assimilation system is GEOS-1 for 1993-1995 and GEOS-STRAT for 1996-1997. Meteorological fields are provided on a sigma coordinate with 20 vertical levels up to 10 hPa in GEOS-1 and 46 up to 0.1 hPa in GEOS-STRAT. For computational expediency we degrade the horizontal resolution to $4^{\circ} \times 5^{\circ}$ and merge the vertical layers above the lower stratosphere in the 1996-1997 GEOS-STRAT fields. There are typically 14-17 tropospheric vertical layers in the model. The lowest 3 layers extend to 100 m, 600 m, and 1 km altitude for a column based at sea level. The 5-year simulation is initialized on January 1, 1993 after a 1-year spin-up using meteorological fields from 1993.

Anthropogenic emissions are specified using a base emission inventory for 1985 described by *Wang et al.* [1998a]. The base emission inventory is then scaled to specific years using national emission inventories and economic data [*Bey et al.*, 2001a]. The current model version includes updated anthropogenic CO emissions and an improved biomass burning emission inventory that includes interannual variability determined from satellite observations [*Duncan et al.*, 2003]. Ship emissions of NO_x are from *Benkovitz et al.* [1996]. A sensitivity simulation using the much higher ship emission estimate of *Corbett et al.* [1999] yields NO_x concentrations over the North Atlantic
that are too high compared to aircraft observations, as previously reported in the global 3-D model study of *Kasibhatla et al.* [2000].

We will present sensitivity simulations with anthropogenic emissions in North America, Europe, or Asia shut off to quantify their contributions to intercontinental transport. The sensitivity simulations are conducted from January to August 1997; the first 5 months are used for initialization and we focus our analysis on the summer of 1997. Summer is when ozone pollution is usually of greatest concern.

To gain a longer perspective on intercontinental transport, we also repeat the 5-year standard simulation using tagged CO and ozone tracers as a computationally expedient method for source attribution [*Wang et al.*, 1998b; *Bey et al.*, 2001b; *Staudt et al.*, 2001]. The tagged CO simulation separates contributions by source types [*Bey et al.*, 2001b; *Staudt et al.*, 2001] including anthropogenic emissions in North America, Europe, and Asia (Figure 5.1). Here we define Europe to include eastern Russia, but emissions in eastern Russia are very small and inconsequential for the analysis that follows. Loss of the tagged CO tracers is computed using archived daily 3-D fields of OH from the standard full-chemistry simulation.

In the case of ozone, we use archived daily 3-D fields of odd oxygen ($O_x = O_3 + NO_2 + NO_3 + HNO_3 + PAN + HNO_4 + N_2O_5$) production rates and loss frequencies from the standard fullchemistry simulation to transport separate O_x tracers originating from the lower troposphere (below 700 hPa) over different continents (Figure 5.1), the lower troposphere over the oceans, the middle troposphere (400-700 hPa), the upper troposphere (400 hPa-tropopause), and the stratosphere. The tracers are removed by chemical loss and dry deposition at the same frequencies as those for total O_x in the standard simulation. By summing the concentrations of all the tracers, we reproduce closely the total O_x concentrations in the standard full-chemistry simulation. Since ozone typically accounts for over 95% of O_x , we will refer to the tagged O_x as tagged ozone in what follows for the sake of clarity. We will further refer to the tagged ozone tracer produced in the lower troposphere over North



Figure 5.1: Source regions used for the tagged ozone and CO simulations.

America as "North American ozone", and similarly for the other source regions of Figure 5.1.

Interpretation of results for tagged ozone tracers such as "North American ozone" requires caution. First, "North American ozone" includes contributions from both anthropogenic and natural production within the continental lower troposphere, but does not include the contribution from production outside the continental lower troposphere driven by precursors emitted from North America. Second, because of the nonlinear chemistry involved in ozone production, the decrease of ozone in a simulation with North American sources shut off is less than the North American contribution to total ozone in the standard simulation. We find in practice that the contributions to surface ozone at Mace Head and Sable Island from the tagged North American and European ozone tracers replicate closely the results from the sensitivity simulations with anthropogenic sources in these regions shut off (see section 5.5). This result must reflect some compensation between nonlinear response and contributions from biogenic sources to ozone production in North America and Europe. It does imply that the tagged ozone tracer simulation offers a good measure of anthropogenic influence from different continents. Using the tagged ozone and CO tracers, we can conveniently probe the seasonal and interannual variability of transatlantic transport of pollution in the 5-year simulation.

5.3 Pathways for Transatlantic Transport

The circulation over the North Atlantic is characterized by three main features: (1) the Icelandic low, (2) the semi-permanent Bermuda-Azores high, and (3) the trade wind region south of the Bermuda-Azores high [*Tucker and Barry*, 1984]. Figure 5.2 shows monthly average GEOS sea level pressures and 925 hPa winds for January, April, July, and October 1997. The winds are strongest along the storm track off the east coast of North America over the western North Atlantic. Over eastern North America between 30°N-60°N, the westerly winds extend to the surface essentially year-round. This allows transport in the lower troposphere of North American pollution to the North Atlantic and on to Europe, as will be discussed below. Another pathway for transatlantic transport of North American pollution involves strong convection over the central and eastern United States, particularly in summer, that lifts ozone and its precursors to the middle and upper troposphere where they are exported by the westerlies [*Jacob et al.*, 1993a; *Thompson et al.*, 1994]. Yet another mechanism for transatlantic transport of North American pollution involves frontal lifting over the western North Atlantic by WCBs [*Stohl*, 2001; *Stohl et al.*, 2002].

The prevailing westerlies at northern midlatitudes generally preclude direct transatlantic transport of European pollution to North America, although we will see that such conditions can occasionally occur. A more general route for transatlantic transport of European pollution involves circulation around the southern branch of the Bermuda-Azores high, particularly in summer when the high extends far to the north and east (Figure 5.2c). Evidence for such transport of European pollution has been seen in aerosol observations in the Canary Islands [*Raes et al.*, 1997] and at Barbados [*Hamelin et al.*, 1989; *Li et al.*, 1998]. For ozone, as we will see, the short lifetime at low latitudes limits the efficiency of this transport. European pollution can also be transported to North



Figure 5.2: Monthly average GEOS sea-level pressure and 925 hPa winds for January, April, July, and October 1997.

America by circulation around the Icelandic low, and by westerly transport around the northern midlatitude band. We will quantify the importance of these different processes.

Figure 5.3 shows the simulated monthly average transport fluxes (0-3 km altitude) and surface air concentrations of North American anthropogenic CO and North American ozone in January, April, July, and October 1997. Figure 5.4 shows the same for European anthropogenic CO and European ozone. "Surface air", here and in what follows, refers to the lowest model layer (0-100 m above the surface). The model does not resolve the nighttime depletion of surface ozone often seen at continental sites because of loss by deposition and chemistry in a shallow surface layer (a few tens of meters deep). As a result, model results are expected to be representative of surface ozone concentrations over continents only in the daytime, when the mixed layer is sufficiently deep to be resolved by the model [*Jacob et al.*, 1993b]. This is not an issue for the marine sites used for model evaluation in section 5.4.

We see from Figure 5.3 that surface concentrations of North American anthropogenic CO are highest in winter and lowest in summer, due to more efficient boundary layer ventilation and chemical loss of CO in summer. Export fluxes of North American anthropogenic CO in the lower troposphere are correspondingly strongest in winter and weakest in summer (left panels, Figure 5.3). Surface concentrations of North American ozone in contrast are highest in summer and lowest in winter, due to more active photochemical ozone production in summer. Export fluxes of North American ozone are strongest in spring and summer (right panels, Figure 5.3).

We find that transatlantic transport of North American ozone and CO takes place in the lower troposphere year round, and transport in the middle and upper troposphere is also important in summer. Compared to transpacific transport of Asian pollution to North America, which takes place mainly in the free troposphere followed by subsidence [*Jacob et al.*, 1999; *Yienger et al.*, 2000; *Fiore et al.*, 2002], the relatively short distance between North America and Europe and the prevailing westerly flow extending down to the surface favor transport in the boundary layer. Over



Figure 5.3: Simulated monthly average fluxes at 0-3 km altitude of North American anthropogenic CO (left panels) and North American ozone (right panels) for January, April, July, and October 1997. Contours are concentrations in the lowest model layer (0-100 m above the surface). Solid circles indicate the locations of Mace Head and Sable Island.



Figure 5.4: Simulated monthly average fluxes at 0-3 km altitude of European anthropogenic CO (left panels) and European ozone (right panels) for January, April, July, and October 1997. Contours are concentrations in the lowest model layer (0-100 m above the surface). Solid circles indicate the locations of Mace Head and Sable Island.

eastern Asia, in contrast, westerly winds do not extend down to the surface, so that lifting to the free troposphere is necessary to enable transpacific transport [*Bey et al.*, 2001b].

Figure 5.4 illustrates the mean transatlantic flow patterns for European anthropogenic CO and European ozone. Transport of pollution from Europe to North America in winter is mainly by the general westerly circulation. In summer, that circulation is considerably weaker, and European influence on North America takes place principally by transatlantic circulation around the Bermuda-Azores high and the Icelandic low. The influence of European sources on surface ozone in North America is minimum in summer due to the weak circulation and the short lifetime of ozone.

5.4 Time Series of Ozone and CO at North Atlantic Sites

5.4.1 Mace Head

Ozone and CO measurements at Mace Head are available for 1994-1997. Time series for 1997 are shown in Figure 5.5 and Figure 5.6. The model results are superimposed. The simulated contributions from North American ozone and North American anthropogenic CO are also shown using tagged tracers. The simulated contributions from other source regions are shown and discussed in a separate report [*Li et al.*, 2001b]. Statistics of comparisons between the observed and simulated time series for 1994-1997 are shown in Figure 5.7. For ozone the model captures the background concentrations, the probability distributions, the frequencies and magnitudes of pollution events, and the day-to-day variations. Similarly, good agreement is found for CO. The simulated mean concentrations of ozone and CO for 1994-1997 are 34 ppbv and 137 ppbv, respectively, in good agreement with observed means (34 ppbv and 146 ppbv). The correlation coefficients between the model results and measurements are 0.62 for ozone and 0.71 for CO.

Figure 5.8 (left panel) shows the observed and simulated O_3 -CO correlations at Mace Head for 1997. Significant positive correlations are found in the summer months; correlation coefficients are higher in the model, as would be expected since the model has fewer factors of variability



Figure 5.5: Hourly average surface concentrations of ozone and for January to November 1997 at Mace Head ($53^{\circ}N$, $10^{\circ}W$) (green: observations; blue: model). Contributions from North American ozone in the model are shown as red lines. The arrows indicate major transatlantic transport events for ozone.



Figure 5.6: Hourly average surface concentrations of CO for January-November 1997 at Mace Head $(53^{\circ}N, 10^{\circ}W)$ (green: observations; blue: model). Contributions from North American CO in the model are shown as red lines.



Figure 5.7: Cumulative probability distributions (top panels) and scatterplots (bottom panels) of measured and simulated surface ozone and CO for 1994-1997 at Mace Head (1994-1996: light dots; 1997: dark dots). The y = x lines are also shown. Data points are 24-hour averages. The cumulative probability distribution is plotted on a probability scale such that a normal distribution would plot as a straight line.



Figure 5.8: Observed (solid lines) and simulated (dashed lines) O_3 -CO correlations at Mace Head for 1997 (left panel) and at Sable Island for 1993 (right panel). The slope of the regression line is plotted against the square of the correlation coefficient for individual months.

than the observations. The slope of the O_3 -CO correlation in the model in summer (0.3 molmol⁻¹) is consistent with observations and tests the simulation of photochemical ozone production in a manner relatively independent of model transport [*Chin et al.*, 1994; *Atherton et al.*, 1996]. Ozone and CO are anticorrelated in the winter, both in the model and in the observations, due to titration by NO_x emissions [*Derwent et al.*, 1994; *Parrish et al.*, 1998].

We find that all major high-O₃ and high-CO events at Mace Head are of European origin in our 5-year simulation [*Li et al.*, 2001b]. North American ozone contributes only 5 ppbv on average (Figure 5.5), while North American anthropogenic CO contributes on average 10-20 ppbv (Figure 5.6). Asian ozone influence is negligible (never more than 2 ppbv) over the 1993-1997 period. The 5-year monthly statistics of the simulated North American contribution to surface ozone at Mace Head are shown in Figure 5.9. There is relatively little seasonal variation in the monthly means, and about a factor of 2 interannual variability. The largest interannual variability and the largest events are in spring and fall, reflecting a combination of efficient ozone production, long ozone lifetime, and fast transport [*Wang et al.*, 1998b].



Figure 5.9: Simulated seasonal variation of the North American contribution to surface ozone at Mace Head. Values are 5-year statistics (1993-1997) of 24-hour average data. Shown are monthly averages (white bar) and standard deviations (bracket). The black bars indicate the interannual range of the monthly averages. The whiskers represent the monthly maxima over the 5-year period.

During transatlantic transport events in the model, North American ozone contributes up to 10-15 ppbv in summer and 15-25 ppbv in other seasons to surface ozone at Mace Head, while North American anthropogenic sources contribute up to 40 ppbv CO. For purpose of later discussion, we define a transatlantic transport event as a North American contribution to surface ozone at Mace Head of 10 ppbv or more. The events for 1997 are highlighted with arrows in Figure 5.5 and Figure 5.6. We find that these transatlantic transport events occur in every season of the year in the 5-year simulation (Figure 5.9).

A question to be addressed is whether the transatlantic transport events seen in the model would be detectable in the observations. We find that these events correspond to secondary peaks in the observations of ozone and CO, for example, on June 18, July 25, August 1, and August 21 (Figure 5.5 and Figure 5.6). The strongest event in our 5-year simulation (26 ppbv) is on April 10, 1994. Examination of the observations reveals an increase from 40 ppbv before April 10 to 50 ppbv on April 10. Observed CO concentrations similarly increased from 180 ppbv before April 10 to 260 ppbv on April 10. Two transatlantic transport events in March and November 1994 previously identified by *Ryall et al.* [1998] from their particle dispersion model analysis of CFCs at Mace Head are also seen in our 1994 tagged ozone and CO simulations.

We examined the meteorological pattern for each of the transatlantic transport events identified by the model simulation for 1993-1997. Figure 5.10 illustrates a typical case (June 18, 1997). An intense Icelandic low between Iceland and the British Isles channeled outflow from North America to Mace Head. In contrast, the mean summer flow patterns in Figure 5.2 and Figure 5.3 indicate that the North American outflow over the eastern North Atlantic diverges to the Arctic and to the tropics, largely missing Europe. Transport of North American pollution to Mace Head on June 18 and during other episodes is largely confined to below 3 km altitude in the model, consistent with air back-trajectories (Mathew Evans, personal communication, 2001). This particular event lasted until June 20 when the low pressure system moved eastward, channeling the flow further to



Figure 5.10: North American pollution episode at Mace Head: simulated daily average surface concentrations of North American ozone on June 18, 1997 (top panel) and GEOS sea-level pressure and 925 hPa winds on the same day (bottom panel). The solid circle indicates the location of Mace Head.

continental Europe. As will be discussed in section 5.5, transatlantic transport events in the model at Mace Head are forerunners of events over continental Europe. Such transatlantic transport in the lower troposphere is also seen in the analysis of intercontinental transport pathways by *Stohl et al.* [2002] using a Lagrangian particle dispersion model. For the entire 1993-1997 record, we find that the strength and location of the Icelandic low can be used as an indicator of the occurrence of transatlantic transport events at Mace Head and in Europe.

Long-term meteorological observations have shown that a stronger than normal Icelandic low is usually accompanied by a stronger than normal Bermuda-Azores high, a phenomenon called the North Atlantic Oscillation (NAO) [*Walker and Bliss*, 1932; *Loon et al.*, 1978]. The NAO is recognized as a major factor of interannual variability in temperature and precipitation over Europe [*Hurrell*, 1995]. It is measured by the NAO index, representing the difference of normalized sealevel pressure between a station in Iceland and one in the Azores [*Rogers et al.*, 1984, 1997], Lisbon (Portugal) [*Hurrell et al.*, 1995, 1997], or Gibraltar (UK) [*Jones et al.*, 1997]. Sea-level pressures are normalized by dividing monthly anomalies (compared to the long-term mean) by long-term monthly standard deviations. The positive phase of the NAO is characterized by a strong Icelandic low and Bermuda-Azores high and hence a strong north-south pressure gradient and, as a result, strong surface westerlies across the North Atlantic onto Europe. The pressure gradient is weak in the negative phase of the NAO.

The left panel of Figure 5.11 shows a time series of the monthly mean NAO index together with our simulated monthly mean North American ozone at Mace Head for 1993-1997. The right panel of Figure 5.11 shows the correlation between these two quantities over that record. There is a strong correlation (r = 0.57), particularly in spring (r = 0.72). The NAO index used here is from *Jones et al.* [1997], i.e., based on pressure difference between Reykjavik (Iceland) and Gibraltar. We find that NAO indices based on other definitions (see references above) show similar correlations. The high correlation implies that the NAO index can be used as a predictor for the transatlantic



Figure 5.11: Time series (left panel) and scatterplots (right panel) of the monthly average North Atlantic Oscillation (NAO) index (solid line) and simulated North American ozone at Mace Head (dashed line) for 1993-1997. The NAO index is defined as the difference of normalized sea-level pressure between Reykjavik (Iceland) and Gibraltar (U.K.) [*Jones et al.*, 1997] and was obtained from the Climatic Research Unit, University of East Anglia at http://www.cru.uea.ac.uk/cru/data/nao.htm.

transport of North American pollution to Mace Head and on to Europe.

Recent studies have shown that the NAO exhibits coherent variability on decadal time scales, both in observations [*Hurrell et al.*, 1995; *Jones et al.*, 1997; *Sutton et al.*, 1997; *Rajagopalan et al.*, 1998] and in coupled ocean-atmosphere general circulation models (GCMs) [*Delworth et al.*, 1998; *Grotzner et al.*, 1998; *Rodwell et al.*, 1999; *Mehta et al.*, 2000]. There is also considerable month-to-month variability, as is apparent in Figure 5.11. Most studies of the interannual variability of the NAO have focused on December-March, when the NAO exerts strong influence on the climate of the Northern Hemisphere and the index exhibits the strongest interdecadal variability. The December-March 1993-1997 period was in a strong positive phase of the NAO, with the exception of 1996 which shows a negative NAO index [*Hurrell et al.*, 1995; *Jones et al.*, 1997], but the monthly data show a range of positive and negative values for each year (Figure 5.11). Using GCM with anthropogenic forcing from greenhouse gases and sulphate aerosol, *Osborn et al.* [1999] predicted a significant decline in the NAO index over the 21st century. Such a decline would reduce the transatlantic transport of North American pollution to Europe. On a year-to-year time scale, the

predictability of the NAO in GCMs [*Sutton et al.*, 1997; *Griffies et al.*, 1997; *Rodwell et al.*, 1999; *Mehta et al.*, 2000; *Bretherton et al.*, 2000] suggests that one could in this manner forecast not only precipitation and temperature in Europe, but also the transatlantic transport of pollution.

5.4.2 Sable Island

Ozone and CO measurements at Sable Island are available for 1993, 1994, and June-November 1997. Previously, *Lin et al.* [1998] used a 3-D regional chemistry model to simulate time series of ozone and CO observed in August 1993 at the site. Time series for June-November 1997 are shown in Figure 5.12. Model results are superimposed; the European contributions to ozone and CO, which are in general small (less than 2 ppbv for ozone), are also shown using tagged tracers. Contributions from other source regions are presented in *Li et al.* [2001b]. North American sources are dominant by far. Asian influence on ozone is less than 5 ppbv anytime. One major European pollution event at Sable Island is found in early June, which is highlighted by arrows in Figure 5.12 and will be discussed below.

Statistics of comparisons between the observed and simulated time series for the ensemble of 1993-1997 observations are shown in Figure 5.13. For ozone, the model has a positive bias of 4 ppbv but otherwise has some success in capturing the probability distributions, the frequencies and magnitudes of pollution events, and the day-to-day variations. Similar positive bias in the GEOS-CHEM simulated surface ozone in the United States has been found by *Fiore et al.* [2002]. There is a negative bias of 15 ppbv in the simulated CO concentrations. The simulated mean concentrations of ozone and CO are 38 ppbv and 122 ppbv, respectively, while the observed means are 34 ppbv and 139 ppbv. The correlation coefficients between the model results and measurements are 0.50 for ozone and 0.59 for CO.

Shown in the right panel of Figure 5.8 are the observed and simulated O_3 -CO correlations at Sable Island for 1993 when a full year of observations is available. The magnitude and seasonal



Figure 5.12: Hourly average surface concentrations of ozone and CO for June to November 1997 at Sable Island ($44^{\circ}N$, $60^{\circ}W$) (green: observations; blue: model). Contributions from European ozone and CO in the model are shown as red lines. The arrow indicates a major transatlantic transport event.



Figure 5.13: Cumulative probability distributions (top panels) and scatterplots (bottom panels) of simulated surface ozone and CO versus measurements for 1993, 1994, and 1997 at Sable Island (1993, 1994: light dots; 1997: dark dots). The y = x lines are also shown. Data points are 24-hour averages. The cumulative probability distribution is plotted on a probability scale such that a normal distribution would plot as a straight line.



Figure 5.14: Simulated seasonal variation of the European contribution to surface ozone at Sable Island. Values are 5-year statistics of 24-hour average data (1993-1997). Shown are monthly averages (white bar) and standard deviations (bracket). The black bars indicate the interannual range of the monthly averages. The whiskers represent the monthly maxima over the 5-year period.

variation of the O_3 -CO slope are similar to Mace Head, both in the model and in the observations. The ozone pollution season (positive O_3 -CO slope) at Sable Island extends longer than that at Mace Head, reflecting the higher latitude of Mace Head and the generally cooler and cloudier weather in Europe [*Doddridge et al.*, 1994].

Statistics of European influence on surface ozone at Sable Island during the 5-year simulation are shown in Figure 5.14. Monthly average European contributions are less than 2 ppbv throughout the year, but there are occasional events of 5-10 ppbv which occur in all five years. Similar to Mace Head, the transatlantic transport events at Sable Island occur mostly in spring and fall. The 1997 simulation indicates a particularly intense summertime event of transatlantic transport from Europe to Sable Island on June 3-8, 1997 (Figure 5.12). During the event, about 10 ppbv of ozone and 30-50 ppbv of CO are of European origin. Unfortunately, there are no measurements for that time period. This event at Sable Island was related to the event seen several days earlier on May 29-June 1 at Mace Head, with observed peak concentrations of 70 ppv ozone and 200 ppbv CO (Figure 5.5 and Figure 5.6).

Figure 5.15 illustrates the flow driving the European pollution event on June 3-8, 1997 at Sable Island. On June 3, two low pressure systems were merging to form an extensive low pressure system along 45°N latitude across the North Atlantic, while an extensive high pressure system was centered over Labrador. Thus an easterly flow from Europe to North America was established below 3 km altitude. This easterly flow is highly anomalous compared to the mean westerly flow pattern over the region (Figure 5.2 and Figure 5.4). It eventually broke up on June 7 when the low pressure system moved northeastward to Europe. The European ozone pollution persisted over northeast North America until June 11, when it extended as far south as Bermuda (5 ppbv European contribution to surface ozone).

We examined the other major European pollution events at Sable Island during the 5-year simulation and found they are all associated with similar anomalous direct transatlantic transport in the boundary layer. The more typical mechanisms for transport of European pollution to North America including northern circulation around the Icelandic low, southern circulation around the Bermuda-Azores high, and transport around the globe in the westerlies (see section 5.3) never generate high-O₃ events over North America.

5.5 Surface Ozone Enhancements From Intercontinental Transport of Pollution

Figure 5.16 shows the enhancements in the mean surface ozone concentrations in June-August 1997 over the northern hemisphere due to anthropogenic emissions from North America, Europe, and Asia, as determined from sensitivity simulations with these emissions shut off. These enhancements add up togethere to much less than the ozone concentrations in the standard simula-



Figure 5.15: European pollution episode at Sable Island: simulated daily average surface concentrations of European ozone on June 3, 1997 (top panel) and GEOS sea-level pressure and 925 hPa winds on that day (bottom panel). The solid circle indicates the location of Sable Island.



Figure 5.16: Sensitivity of simulated surface ozone concentrations in June-August 1997 to anthropogenic emissions in the individual continents. The plots show the mean decreases in concentrations when anthropogenic emissions from North America (top panel), Europe (middle panel), and Asia (bottom panel) are shut off separately. "Surface ozone" refers to the lower mixed layer (0-100 m), i.e., the lowest layer of the model.

tion, because of contributions from natural sources as well as chemical non-linearity. Shutting off North American anthropogenic emissions decreases the mean surface ozone concentrations in Europe by 2-4 ppbv, with maximum effect in northwest Europe. The relatively large North American influence over northern Africa and the Middle East is due to the deep boundary layer mixing over these arid regions which entrains North American ozone from aloft [*Li et al.*, 2001a].

We find that long-range transport of ozone itself is far more important in contributing to North American influence on surface ozone in Europe than transport of the precursors (NO_x and PAN) followed by ozone production in the European boundary layer. By difference with the standard simulation, we find that the monthly average influx of North American pollution ozone to the European boundary layer is 1.4 Gmold^{-1} in July 1997, while ozone production in the European boundary layer resulting from the influx of North American ozone precursors is 0.2 Gmol d⁻¹. Similarly, Jacob et al. [1999] found that Asian influence on surface ozone in the United States is driven by long-range transport of ozone rather than of its precursors. This influx of North American pollution ozone to the European boundary layer can be compared to its export out of the North American boundary layer. Our model simulation shows a monthly mean export flux of pollution ozone from the North American boundary layer of 6 $\text{Gmol}\,d^{-1}$ in July 1997, out of a net production in that region of 8.3 Gmold⁻¹, and this export is mostly by convection over the continent [*Jacob et al.*, 1993a]. The eastward flux of North American pollution ozone across the western North Atlantic (60°W) is 10 Gmol d^{-1} , higher than the export from the North American boundary layer because of subsequent production from exported ozone precursors. These results are consistent with previous 3-D model studies of the export of ozone pollution from North America [Chin et al., 1994; Liang et al., 1998] and imply that only 10-20% of this export goes on to enter the European boundary layer.

We examined the relative contributions of direct boundary layer advection versus subsidence from the free troposphere in contributing to North American influence on surface ozone in Europe in July 1997, and find the two to be of comparable importance. The mean influx of North American ozone to Europe from transport in the boundary layer below 2.6 km altitude is 0.8 Gmold^{-1} in the model, while downward influx from subsidence across the 2.6 km surface over Europe is 0.6 Gmold^{-1} . Again, these results were obtained by difference between the standard simulation and the simulation with North American anthropogenic emissions shut off.

The tagged tracer analysis in section 5.4 identified several events of transatlantic transport from North America to Mace Head during the summer of 1997, for instance, on June 18-20 and July 14-16 (Figure 5.5 and Figure 5.6). The sensitivity simulation with North American anthropogenic emissions shut off identifies the same events with comparable magnitudes. We find that these events are the forerunners of more general North American pollution events over the European continent during which North American anthropogenic emissions enhance surface ozone in the British Isles by up to 10 ppbv and in continental Europe by up to 8 ppbv (daily mean). For example, the North American plume observed on June 18-20 at Mace Head moved across the European continent, enhancing surface ozone levels by 4-8 ppbv in western Europe on June 21 and by 4-6 ppbv in central and eastern Europe on June 23 (not shown).

Such North American influence on surface ozone in Europe has important implications for achieving European ozone air quality standards. The current European Council Directive on air pollution by ozone (Council Directive 92/72/EEC) defines a health-based threshold of 55 ppbv (8-hour average) and a vegetation protection threshold of 65 ppbv (24-hour average) [*ECM*, 1992]. The World Health Organization (WHO) has recommended an air quality guideline of 60 ppbv (8-hour average) for Europe [*WHO*, 1996]. Figure 5.17 (top panel) shows the mean simulated surface ozone concentrations in Europe in July 1997. Maximum concentrations are in the southeast, consistent with observations [*Scheel et al.*, 1997; *Kley et al.*, 1997]. As pointed out in section 5.3, "surface" concentrations in the model are actually for the lower mixed layer (0-100 m altitude), and the corresponding 24-hour averages are more representative of 8-hour daily maxima rather than of 24-hour averages in surface air. With this assumption, Figure 5.17 (middle panel) shows the num-



Figure 5.17: (a) Simulated mean surface ozone concentrations for June-August 1997 in Europe; "surface" actually refers to the lower mixed layer (0-100 m altitude), i.e., the lowest layer of the model. (b) The number of days (out of 92) when the ozone standard of 55 ppbv is exceeded in the simulation. (c) The number of these days when the ozone standard would not have been exceeded in the absence of North American influence.



Figure 5.18: Simulated surface ozone enhancement over continental Europe from North American pollution, as determined by difference between the standard simulation and a simulation with North American anthropogenic emissions shut off, plotted as a function of local surface ozone concentrations. Values are daily (24-hour) averages for June-August 1997 and for the ensemble of continental Europe grid squares in the model. The curve is a locally weighted regression.

ber of daily violations of the 55 ppbv ozone standard in the model out of 92 days for June-August 1997. Violations are widespread, exceeding half of summer days over much of Italy. Figure 5.17 (bottom panel) shows the number of violations that would not occur in the absence of North American anthropogenic emissions. There are 5-10 such violations over much of Europe for the summer of 1997, with the largest number (> 10) in central Europe. The number of violations obviously depends on the formulation of the ozone standard, but we find that the pattern of North American influence is similar for different ozone standards. For example, we find that for higher standards of 65 ppbv and 75 ppbv, there are respectively 2-5 and less than 2 violations that would not occur in the absence of North American anthropogenic emissions over much of Europe for the summer of 1997.

Ozone concentrations in the range 50-60 ppbv, at the threshold of the European standards,

are in fact particularly susceptible to intercontinental transport of pollution. This was recently shown by [*Fiore et al.*, 2002] for the United States. It is shown here for continental Europe in Figure 5.18 as the ozone enhancement from North American anthropogenic emissions plotted as a function of the daily local surface ozone concentration, for the ensemble of continental Europe grid squares in June-August 1997. High ozone concentrations are usually associated with regional stagnation episodes when transport from outside Europe is suppressed. Low ozone concentrations tend to be associated with tropical rather than North American influence.

Shutting off European anthropogenic emissions in the model leads to a decrease of less than 2 ppbv in the monthly average surface ozone in North America in summer (middle panel, Figure 5.16). This again is consistent with our results using tagged ozone tracers for Sable Island in section 5.4. European pollution influence on surface ozone over eastern Asia is also weak, less than 2 ppbv on average, because of the prevailing Asian monsoon; greater European influence on Asia is found in spring [*Liu et al.*, 2002].

Shutting off Asian anthropogenic emissions in the model leads to a decrease of 1-4 ppbv in the monthly average ozone concentrations at the surface in North America in June-August 1997, with the maximum influence in the western United States (bottom panel, Figure 5.16). This Asian influence in North America is examined in more detail by [*Fiore et al.*, 2002]. We find that Asian pollution contributes less than 2 ppbv to surface ozone over Europe in the summer of 1997 (bottom panel, Figure 5.16).

Figure 5.19 shows the higher-altitude enhancements in the mean ozone concentrations at 45°N latitude in June-August 1997 due to anthropogenic emissions from North America, Europe, and Asia as determined from sensitivity simulations with these emissions shut off. We see that North American anthropogenic emissions enhance ozone in the middle/upper troposphere over Europe by about 10 ppbv on average. The impact of European anthropogenic emissions is largely limited to the lower troposphere, reflecting the relatively weak convective and frontal activity over Europe as



Figure 5.19: Mean ozone concentration enhancements in June-August 1997 at 45°N due to anthropogenic emissions in North America, Europe, and Asia, as determined from sensitivity simulations with these emissions shut off. The dashed lines indicate continental boundaries.

compared to North America or Asia [Stohl, 2001; Stohl et al., 2002].

5.6 Summary and Conclusions

We have used a 5-year (1993-1997) simulation of tropospheric ozone-NO_x-hydrocarbon chemistry with the GEOS-CHEM global 3-D model to quantify the impact of transatlantic transport of pollution on surface ozone in Europe and North America. Measurements of ozone and CO at Mace Head (Ireland) and Sable Island (Canada) were used to evaluate transatlantic transport in the model. The model reproduces well the frequencies and magnitudes of pollution events at these sites. The contributions from transatlantic transport of pollution are examined in the model through a combination of sensitivity simulations and tagged tracer analyses.

The contribution from North American pollution to surface ozone at Mace Head is 5 ppbv on average, with little seasonal variability, and up to 10-20 ppbv during transatlantic transport events. We find that these events are associated with low-level westerly flow (below 3 km altitude) channeled to northwest Europe by a strong Icelandic low centered between Iceland and the British Isles. We further find that transatlantic transport events at Mace Head are forerunners of broader events of long-range transport of North American pollution to the surface of Europe. North American ozone influence at Mace Head and more generally over Europe is strongly correlated with the North Atlantic Oscillation (NAO) index. This result suggests that long-term forecasts of the NAO, which are viewed with considerable interest for predicting precipitation and temperature in Europe, could also serve to predict the transatlantic transport of pollution.

European pollution influence on surface ozone at Sable Island is less than 2 ppbv on average and up to 5-10 ppbv during transatlantic transport events. These events are associated with low-level easterly flow (below 3 km altitude) driven by anomalous low pressure systems at 45°N over the North Atlantic. More typical pathways for transport of European pollution to North America include the circulations around the northern branch of the Icelandic low and around the southern branch of the Bermuda-Azores high, as well as the westerly flow around the globe. However, we find that none of these pathways lead to events of high European ozone over North America in our 5-year simulation record.

Our sensitivity simulation for the summer of 1997 indicates that North American anthropogenic emissions enhance surface ozone in Europe by 2-4 ppbv on average, and by 5-10 ppbv during transatlantic transport events. Asian anthropogenic emissions cause less than 2 ppbv enhancement of surface ozone over Europe. The North American influence on Europe is driven by the long-range transport of ozone rather than of its precursors, and includes comparable contributions from direct transatlantic transport of ozone in the boundary layer and subsidence from the free troposphere over Europe. Our model results suggest that 20% of the violations of the European Council ozone standard (55 ppbv, 8-hour average) in most of Europe in the summer of 1997 would not have occurred in the absence of North American anthropogenic emissions. North American influence on surface ozone in Europe is maximum when surface ozone concentrations are about 50-60 ppbv (i.e., at the threshold of the standard). North American influence is less during acute high-O₃ episodes associated with regional stagnation.

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Chapter 6

Atmospheric Hydrogen Cyanide (HCN): Biomass Burning Source, Ocean Sink?

[Li, Q., D. J. Jacob, I. Bey, R. M. Yantosca, Y. Zhao, and Y. Kondo, Atmospheric hydrogen cyanide (HCN): Biomass burning source, ocean sink? *Geophys. Res. Lett.*, *27*, 357-360, 2000.]

Abstract

The observed seasonal amplitude of atmospheric HCN concentrations implies an atmospheric lifetime of only a few months for HCN, much shorter than is commonly assumed from oxidation by OH (a few years). We propose that ocean uptake provides the missing sink, and show with a global 3-D model simulation that the observations of atmospheric HCN can be roughly reproduced in a scenario where biomass burning provides the main source $(1.4-2.9 \text{ Tg N yr}^{-1})$ and ocean uptake provides the main sink (HCN atmospheric lifetime of 2-4 months). Such a budget implies that HCN is a sensitive tracer of biomass burning on large scales, of particular value because it is readily observed from space. The ocean sink hypothesis can be tested with measurements of HCN concentrations in marine air and seawater.

6.1 Introduction

Spectroscopic measurements of the atmospheric column of HCN at northern midlatitudes indicate factors of 2-3 seasonal variation with maxima in spring-summer [*Mahieu et al.*, 1995, 1997; *Zhao et al.*, 2000]. Space-based measurements of HCN mixing ratios in the tropical upper troposphere indicate a range from 200 to 900 pptv [*Rinsland et al.*, 1998]. Such large variations are inconsistent with the conventional view that HCN has an atmospheric lifetime of a few years with oxidation by OH providing the main sink [*Cicerone and Zellner*, 1983]. There must be a large missing sink of HCN imposing a lifetime of a few months. Improved understanding is needed because HCN (1) interferes with measurements of total reactive nitrogen (NO_y) [*Kondo et al.*, 1997], (2) could play a non-negligible role in the biogeochemical cycling of nitrogen, and (3) provides a tracer of biomass burning readily observable from space [*Rinsland et al.*, 1998].

We propose here that ocean uptake could provide the missing sink for atmospheric HCN, and show with a global 3-D model that the available observations of atmospheric HCN are consistent with a scenario where biomass burning provides the main source and ocean uptake provides the main sink. The Henry's law constant of HCN is sufficiently high (12 Matm^{-1} at 298 K; *Edwards et al.* [1978]) for ocean uptake to impose an atmospheric lifetime of a few months if HCN(aq)/CN⁻ (*pKa* = 9.2) is consumed chemically or biologically in the ocean on a time scale of a few months or less, as discussed below. There are to our knowledge no data on HCN(aq)/CN⁻ concentrations in the oceans.

It is well established that biomass burning is a major source of atmospheric HCN, though different studies indicate a range of molar emission ratios relative to CO (0.03-1.1%) [*Lobert et al.*, 1990; *Hurst et al.*, 1994; *Yokelson et al.*, 1997; *Holzinger et al.*, 1999]. *Lobert et al.* [1990] estimate a global source of HCN from biomass burning of 0.4-1.9 TgNyr⁻¹. *Lobert* [1989] estimates a global fossil fuel combustion source of 0.04 TgNyr⁻¹, negligibly small in comparison. Higher plants and fungi are known to produce and release HCN, but the available data do not allow a quantitative estimate of emissions [*Cicerone and Zellner*, 1983]. A possible HCN source in the stratosphere is ion-catalyzed conversion of CH₃CN [*Schneider et al.*, 1997].

6.2 Model Simulation

We use the Harvard-GEOS global 3-D model [*Bey et al.*, 2001a] to simulate atmospheric HCN. The model is driven by 1993-1994 meteorological data updated every 6 hours from the Goddard Earth Observing System Data Assimilation System (GEOS-1 DAS) [*Schubert et al.*, 1993]. Advection is computed following *Lin and Rood* [1996]. Moist convection and boundary layer mixing are computed following *Allen et al.* [1996]. The spatial resolution is 4° latitude by 5° longitude, with twenty σ vertical levels up to 10 hPa. We use a zero-flux boundary condition at 10 hPa. A six-year simulation is conducted, recycling the meteorological fields for 1993-1994, to remove the effect of the initial condition (170 pptv HCN). Previous tracer model studies indicate that the GEOS fields provide a reasonable simulation of global atmospheric transport [*Allen et al.*, 1996; *Bey et al.*, 2001b]. We adopt in our standard simulation an HCN biomass burning emission ratio of 1.1% relative to CO on a molar basis, which is at the high end of laboratory data but is most consistent with observed HCN-CO column correlations [*Rinsland et al.*, 1998, 1999]. We could accommodate a smaller emission ratio depending on the efficacy of the ocean sink, as will be discussed later. We combine the HCN emission ratio with the biomass burning CO emission inventory of *Wang et al.* [1998]. This inventory has $1^{\circ} \times 1^{\circ}$ spatial resolution and monthly temporal resolution. The resulting global biomass burning source of HCN is 2.9 TgNyr⁻¹. There are no other HCN sources in our model.

The ocean uptake flux of HCN is $F = k_w C_g K_H RT$ [*Liss and Slater*, 1974], where k_w (ms⁻¹) is the air-to-sea transfer velocity, C_g (kgm⁻³) is the concentration of HCN in surface air, R is the gas constant, T is temperature, and K_H is the temperature-dependent Henry's law constant with $K_H = 12$ Matm⁻¹ at 298 K and $\Delta H_{298}/R = -5000$ K [*Edwards et al.*, 1978]. Diffusion in the liquid phase controls the oceanic uptake of HCN. We adopt $k_w = 0.31u^2(Sc/660)^{-1/2}$ with u in ms⁻¹ and k_w in cmhr⁻¹ [*Wanninkhof*, 1992], where u is the wind speed at 10 m height, Sc = v/D is the Schmidt number of HCN in seawater, v is the kinematic viscosity of water, and D is the diffusion coefficient of HCN in water. We assume that there is no reverse sea-to-air transfer flux, i.e., that HCN(aq)/CN⁻ is consumed in the oceans. A sensitivity simulation where k_w is reduced by a factor of 6 (to describe a situation where 5/6 of the HCN taken up by the oceans is returned to the atmosphere, i.e., a saturation ratio of 0.83) is still capable of reproducing the observed seasonal variations as discussed below. This sensitivity simulation corresponds to an HCN(aq)/CN⁻ lifetime of 2-3 months against consumption in the oceanic mixed layer.

Additional sinks for atmospheric HCN from photolysis and reactions with OH and $O(^{1}D)$ are specified following *Cicerone and Zellner* [1983]. Monthly varying concentration fields of tropospheric OH are taken from *Bey et al.* [2001a], and monthly varying concentration fields of stratospheric OH and $O(^{1}D)$ are taken from *Schneider et al.* [2000].

Total atmospheric burden (Tg N)	0.50			
Atmospheric lifetime (month)	2.1-4.4			
Sources $(TgNyr^{-1})$:				
Biomass burning	1.4-2.9			
Sinks $(TgNyr^{-1})$:				
Ocean uptake	1.1-2.6			
Reaction with OH	0.3			
Photolysis	0.2×10^{-2}			
Reaction with $O(^{1}D)$	0.3×10^{-3}			

Table 6.1: Global Atmospheric Budget of HCN (1000-10 hPa)

Our global budget of atmospheric HCN is shown in Table 6.1. The range is bounded by the standard simulation and by a sensitivity simulation where HCN emission is reduced by 53% and where 5/6 of HCN taken up by the ocean is returned to the atmosphere, resulting in the same atmospheric inventory of HCN as in the standard case (see Figure 6.1 and discussion below). The atmospheric lifetime of HCN is 2.1-4.4 months, with ocean uptake providing the main sink. The HCN ocean uptake of 1.1-2.6 TgNyr⁻¹ can be compared to an estimated 30 TgNyr⁻¹ total input of atmospheric fixed N to the oceans [*Duce et al.*, 1991]. Long-range transport of HCN could make a significant contribution to the deposition flux of fixed N to the central regions of the oceans.

6.3 **Results and Discussion**

Figure 6.1 compares model results to observed HCN columns at Jungfraujoch in the Swiss Alps [*Mahieu et al.*, 1995, 1997], Kitt Peak in Arizona [*Mahieu et al.*, 1995], Mauna Loa in Hawaii [*Rinsland et al.*, 1999], Rikubetsu and Moshiri in Japan [*Zhao et al.*, 2000], and Ny Ålesund in Spitsbergen (J. Notholt, unpublished data, 1999). Observations after September 1997 are not included in Figure 6.1 because of anomalous enhancements from massive fires in Indonesia [*Rinsland et al.*, 1999] which we will examine in a separate study.

The observations in Figure 6.1 were made by measuring absorption of solar radiation in



Figure 6.1: Seasonal variation of HCN column concentrations. Individual observations are shown as symbols. Monthly mean model values are shown as lines for the standard simulation (thick solid lines) and for three sensitivity simulations: 1) ocean uptake and biomass burning source reduced by factors of 6 and 2, respectively (thin solid lines); 2) ocean uptake and tropical HCN emission ratio reduced by factors of 6 and 2, respectively (dashed lines); 3) both ocean uptake and tropical HCN emission ratio reduced by a factor of 2 (dash dot lines). The top left panel shows zonally averaged model values in the standard simulation for different latitudes of the northern hemisphere.

the 3299.53 cm⁻¹ and 3287.25 cm⁻¹ HCN absorption bands; HCN columns were retrieved by assuming a vertical profile of HCN mixing ratios, typically uniform in the troposphere and decreasing with altitude in the stratosphere. In our model the tropospheric mixing ratio of HCN increases with altitude outside of source regions because of the ocean sink. We did not attempt to resolve inconsistencies between the model vertical profiles of mixing ratios and the assumed profiles used in the retrievals of the observed columns.

The observations show factors of ~ 2 seasonal amplitude with maxima in April-August. The model reproduces roughly the observed seasonal amplitudes but precedes the observed maxima by 1-2 months. As shown in the first panel of Figure 6.1, the model maxima reflect the northward propagation of the signal from biomass burning in the northern tropics which peaks in February, combined with the smaller signal from boreal forest fires which peaks in the summer.

The phase precession in the model compared to observations suggests either a flaw in the prescribed seasonal pattern of biomass burning emissions or a major HCN source other than biomass burning. *Mahieu et al.* [1995] attributed the spring maxima at Jungfraujoch and Kitt Peak to a biogenic source. However, the strong correlation observed between HCN and CO columns at Jungfraujoch (E. Mahieu, personal communication, 1999), at the Japanese sites [*Zhao et al.*, 2000] and at Mauna Loa [*Rinsland et al.*, 1999], supports a dominant biomass burning source. Ship measurements of atmospheric HCN columns over the tropical Atlantic in October [*Notholt et al.*, 2000] indicate elevated values associated with elevated CO and clearly associated with biomass burning. Our model values over the tropical Atlantic are twice those observed by *Notholt et al.* [2000], suggesting that our HCN tropical emission ratio is too high. Since HCN is a product of smoldering rather than flaming combustion [*Lobert et al.*, 1990], one would expect lower emission ratios from tropical savanna fires than from midlatitude forest fires. A sensitivity model simulation with tropical HCN emission ratios and ocean uptake both reduced by a factor of 2 (Figure 6.1) yields results over the tropical Atlantic that agree fairly well with the *Notholt et al.* [2000] observations (not shown).



Figure 6.2: Annual mean, zonally averaged mixing ratios of HCN in the standard simulation. Contour levels (ppbv) are 0.05, 0.1, 0.15, 0.18, 0.2, 0.22, 0.25, 0.3, and 0.35.

Figure 6.2 presents simulated zonal mean, yearly averaged mixing ratios of HCN. Simulated mixing ratios are minimum in the marine boundary layer (10-100 pptv) and maximum over biomass burning regions (up to 2000 pptv in the boundary layer and 500 pptv in the upper troposphere, consistent with the observations of *Rinsland et al.* [1998]). There are to our knowledge no measurements of HCN mixing ratios in the marine boundary layer (or, in fact, anywhere in the lower troposphere). Measurements in the stratosphere show HCN mixing ratios in the range 170-200 pptv [*Spreng and Arnold*, 1994]. The model simulates 180-220 pptv in the stratosphere; the stratospheric sink of HCN may be underestimated because of the zero-flux boundary condition at 10 hPa.

We have assumed in the standard simulation a relatively high air-to-sea transfer velocity [*Wanninkhof*, 1992] and neglected any reverse sea-to-air transfer. Our results are only moderately sensitive to these assumptions because the ocean uptake is largely limited by vertical transport from the free troposphere to the marine boundary layer. We could accommodate a decrease in the ocean sink by decreasing the biomass burning source down to a point limited by the ability of the model to reproduce the relative seasonal amplitude in the observations. As shown in Figure 6.1, a sensitivity simulation with the net ocean uptake reduced by a factor of 6 (see previous section) still provides a fair comparison to observations. This simulation corresponds to an atmospheric lifetime of HCN of

4.4 months and a 53% reduction in the biomass burning source (1.4 TgNyr^{-1}) to achieve the same atmospheric inventory of HCN as in the standard simulation.

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Chapter 7

A Global 3-D Model Analysis of the Atmospheric Budgets of HCN and CH₃CN: Constraints From Aircraft and Ground Measurements

[Li, Q., D. J. Jacob, R. M. Yantosca, C. L. Heald, H. B. Singh, M. Koike, Y. Zhao, G.
W. Sachse, and D. G. Streets, A global 3-D model analysis of the atmospheric budgets of HCN and CH₃CN: Constraints from aircraft and ground measurements, *J. Geophys. Res.*, accepted, 2003.]

Abstract

We construct global atmospheric budgets of HCN and CH₃CN through a 3-D model simulation of the HCN-CH₃CN-CO system constrained and evaluated with aircraft observations from the TRACE-P mission over the NW Pacific in February-April 2001. Observed background vertical gradients of HCN and CH₃CN imply a dominant ocean sink for both gases, with deposition velocity of 0.13 cm s⁻¹ for both and saturation ratios of 0.79 for HCN and 0.88 for CH₃CN. Observations for both gases in the free troposphere imply a dominant source from biomass burning. Enhancement of HCN observed in Chinese urban plumes is attributed tentatively to residential coal burning. Biomass burning and residential coal burning emission ratios relative to CO of 0.27% and 1.6% respectively for HCN, and of 0.20% and 0.25% respectively for CH₃CN, are consistent with observations in biomass burning and Chinese urban plumes. They provide the best model simulation of the ensemble of the TRACE-P observations including vertical profiles and HCN-CH₃CN-CO correlations. They also allow successful simulation of the long-term observations of HCN columns at sites in the northern hemisphere, and of CH₃CN vertical distribution observed over the northern Indian Ocean. Global biomass burning and Asian residential coal burning sources are 0.63 and 0.2 TgNyr⁻¹ respectively for HCN and 0.47 and 0.03 TgNyr⁻¹ respectively for CH₃CN. Ocean uptake is the dominant sink for both gases, with oxidation by OH representing an additional minor sink. The resulting tropospheric lifetimes are 5.3 months for HCN and 5.8 months for CH₃CN. The model predicts very low HCN and CH₃CN concentrations at high southern latitudes, reflecting the assumption of a uniform saturation ratio for ocean uptake; observations in that region are needed. In the free troposphere, the dominance of biomass burning sources (70-85% for HCN and 90-95% for CH₃CN) implies that both gases can be used as biomass burning tracers. In the boundary layer, CH₃CN appears to be a better biomass burning tracer. More work is needed to identify the Chinese urban source of HCN.

7.1 Introduction

Hydrogen cyanide (HCN) and methyl cyanide (CH₃CN, also called acetonitrile) are atmospheric tracers of biomass burning [*Lobert et al.*, 1990; *Holzinger et al.*, 1999] and could play a non-negligible role in the nitrogen cycle [*Li et al.*, 2000]. Ocean uptake has been hypothesized as their dominant sink, with corresponding lifetimes of a few months [*Hamm and Warneck*, 1990; *Li et al.*, 2000]. However, their atmospheric budgets are still poorly understood. We use here a global 3-D model analysis of HCN and CH₃CN observations in Asian outflow from the TRACE-P aircraft mission over the NW Pacific [*Singh et al.*, 2003] to improve the constraints on the sources and sinks of these two gases. The TRACE-P data represent the first in situ measurements for HCN in the troposphere, and one of the first for CH₃CN. Previous data for HCN are from remote sensing of the total column at several sites around the world [*Mahieu et al.*, 1995, 1997; *Rinsland et al.*, 1999, 2001, 2002; *Zhao et al.*, 2000, 2002]. Previous in situ measurements of CH₃CN have been made over the Indian Ocean [*de Laat et al.*, 2001] and over the Amazon [*Williams et al.*, 2001].

It is well established from laboratory and field experiments that biomass burning is a major source for both HCN (0.1-3.2 TgNyr⁻¹) and CH₃CN (0.2-1.1 TgNyr⁻¹) (Table 7.1). It is also well established that sources from automobile exhaust and industrial processes are negligible in comparison [*Lobert et al.*, 1991; *Bange and Williams*, 2000; *Holzinger et al.*, 2001]. A recent field experiment indicates no emission of HCN from domestic biofuels [*Bertschi et al.*, 2003, *Yokelson et al.*, 2003]. Atmospheric sinks of HCN and CH₃CN from reaction with OH and O(¹D), photolysis, and scavenging by precipitation yield lifetimes of a few years [*Cicerone and Zellner*, 1983; *Brasseur et al.*, 1983]. The solubilities of HCN and CH₃CN are sufficiently high for ocean uptake to impose atmospheric lifetimes of a few months if loss in the oceanic mixed layer is sufficiently rapid [*Hamm and Warneck*, 1990; *Li et al.*, 2000]. There is some evidence that HCN and CH₃CN are consumed biologically in the ocean [*Singh et al.*, 2003]. *Li et al.* [2000] showed in a global 3-D model study that the observed seasonal variation of the HCN column in different regions

of the world is consistent with a scenario where biomass burning provides the main source and ocean uptake provides the main sink. They inferred a global HCN biomass burning source of 1.4- 2.9 TgNyr^{-1} , and an oceanic saturation ratio of 0.83 or less. Observed vertical gradients of HCN and CH₃CN in remote marine air in TRACE-P confirm the importance of the ocean sink [*Singh et al.*, 2003].

The TRACE-P mission was conducted in February-April 2001 over the NW Pacific to study the transport and chemical evolution of Asian outflow over the Pacific [*Jacob et al.*, 2003]. It used two NASA aircraft, a DC-8 and a P-3B, operating out of Hong Kong and Japan, and with additional transit flights and sorties over the North Pacific. Biomass burning in SE Asia is an important component of Asian outflow in spring [*Liu et al.*, 1999; *Chan et al.*, 2000; *Bey et al.*, 2001b]. During TRACE-P, Asian biomass burning and anthropogenic sources had contributions of similar magnitude to CO concentrations observed in Asian outflow [*Liu et al.*, 2003].

^{*f*}Biomass burning sources based on HCN molar emission ratios relative to CO of 0.05% for savanna and grassland and 0.15% for tropical and extratropical forests, and CH₃CN molar emission ratios relative to CO of 0.11% for savanna, grassland, and tropical and extratropical forests. These ratios are combined with a global biomass buring CO source estimate of 700 TgCOyr⁻¹. Biofuel source estimates are based on molar emission ratios relative to CO of 0.20% for HCN and 0.16% for CH₃CN and a global biofuel CO source estimate of 210 TgCOyr⁻¹.

^{*g*}Based on biomass burning and biofuel molar emission ratios relative to CO of 0.27% for HCN and 0.15% for CH₃CN, and a global biomass burning CO source estimate of 700 TgCOyr⁻¹ [*Andreae and Merlet*, 2001]. Additional biogenic sources for both gases are invoked to balance estimated global loss from ocean uptake.

^{*h*}Global 3-D model study with biomass burning molar emission ratios relative to CO of 0.26% for HCN and 0.15% for CH₃CN and a global biomass burning CO source estimate of 487 TgCOyr⁻¹ [*Duncan et al.*, 2003]. The residential coal burning source is invoked to explain enhanced HCN and CH₃CN in Chinese urban plumes. It assumes molar emission ratios relative to CO of 1.6% for HCN and 0.25% for CH₃CN and an Asian residential coal burning CO source of 20 TgCOyr⁻¹.

^{*i*}The biomass burning source estimate is based on an emission ratio of $2.6\pm1.7\times10^{-4}$ gCH₃CN gC⁻¹ for straw and savannah grass [*Lobert*, 1989] and a global biomass burning carbon source estimate of 3.1×10^{3} TgCyr⁻¹ [*Seiler and Crutzen*, 1980]. The automobile exhaust source estimate is based on a CH₃CN emission factor of 1.3% g/g relative to organic compounds measured in the exhaust of a gasoline-powered engine [*Dulson*, 1978], combined with a global car exhaust source of organic compounds of 21 Tgyr⁻¹.

^{*j*}Based on biomass burning and biofuel CH₃CN molar emission ratios (relative to CO) of 0.13% [*Holzinger et al.*, 1999] and a global biomass burning and biofuel CO source estimate of 670 Tg COyr⁻¹.

Biomass burning	Biofuels	Car exhaust	Residential coal	Biogenic	Total	References
				HCN		
					0.2	<i>Cicerone and Zellner</i> [1983] ^{<i>a</i>}
0.37-1.89						Lobert et al. $[1990]^b$
0.64-3.18		0.04				Lobert et al. $[1991]^c$
0.1-0.3						Holzinger et al. $[1999]^d$
1.4-2.9					1.4-2.9	<i>Li et al.</i> $[2000]^e$
0.26	0.21				0.47	Andreae and Merlet [2001] ^f
0.7-0.9		< 0.02		0.2	1.1	<i>Singh et al.</i> [2003] ^{<i>g</i>}
0.63			0.2		0.83	this work ^h
				CH ₃ CN		
0.27		0.09			0.36	Hamm and Warneck [1990] ⁱ
0.14-0.75						Lobert et al. $[1990]^b$
0.23-1.13						Lobert et al. $[1991]^c$
0.14-0.34		0.01				<i>Holzinger et al.</i> [1999,2001] ^{<i>d</i>}
0.27	0.17				0.44	Andreae and Merlet [2001] ^f
					0.44	<i>de Laat et al.</i> [2001] ^{<i>j</i>}
0.4-0.5		< 0.02		0.2	0.7	<i>Singh et al.</i> [2003] ^{<i>g</i>}
0.47			0.03		0.5	this work ^h

Table 7.1: Literature Estimates of Global HCN and CH₃CN Sources (TgNyr⁻¹)

^{*a*}Source needed to balance the global sink from reaction of HCN with OH. However, we now know that this reaction makes only a small contribution to the total HCN sink [*Li et al.*, 2000].

^bBased on emission factors per unit nitrogen of $2.42\pm1.79\%$ for HCN and $0.95\pm0.74\%$ for CH₃CN measured in laboratory biomass burning experiments, and a global biomass burning nitrogen volatilization estimate of 24-57 TgNyr⁻¹ [*Crutzen and Andreae*, 1990].

^{*c*}Based on biomass burning molar emission ratios relative to CO of 1.1% for HCN and 0.25% for CH₃CN measured in laboratory biomass burning experiments, combined with a global biomass burning CO source estimate of 480-860 TgCOyr⁻¹. No detail of the car exhaust source estimate is given.

^{*d*}Biomass burning sources based on molar emission ratios (relative to CO) of 0.12% for HCN and 0.13% for CH₃CN measured in a laboratory biomass burning experiment, combined with a global biomass burning CO source estimate of 210-550 TgCOyr⁻¹. The automobile exhaust source of CH₃CN is based on a measured CH₃CN molar emission ratio of 0.06 relative to benzene, combined with an emission ratio of 0.6 g benzene per unit fuel (kg C) consumed in traffic [*de Fre et al.*, 1994] and a global fuel consumption estimate of 2.6×10^3 TgCyr⁻¹ [*Marland et al.*, 1998].

^eSource needed to balance the HCN loss derived from the relative seasonal amplitude of the column observations, when fitted in a global model simulation (GEOS-CHEM version 3.4) with biomass burning as the only source and ocean uptake as the dominant sink.

7.2 Model Simulation

We simulate the distributions of HCN, CH₃CN, and CO observed in TRACE-P with the GEOS-CHEM global 3-D model of tropospheric chemistry. A detailed description of the model is presented by *Bey et al.* [2001a]. We use here GEOS-CHEM version 4.33 (see http://www-as.harvard.edu/chemistry/trop/geos). The model is driven by assimilated meteorological fields from the Goddard Earth Observing System (GEOS) of the NASA Data Assimilation Office (DAO). We use meteorological fields for 2000-2001 (GEOS-3) which are provided with 6-hour temporal resolution (3-hour for surface variables and mixed layer depths), $1^{\circ} \times 1^{\circ}$ horizontal resolution, and 48 vertical sigma levels. We degrade the horizontal resolution to $2^{\circ} \times 2.5^{\circ}$ for application in GEOS-CHEM. The simulations are conducted for a 16-month period (January 2000-April 2001). The first 13 months are used for initialization and we present results for the February-April 2001 TRACE-P period.

Both HCN and CH₃CN were measured by gas chromatography aboard the DC-8 aircraft [*Singh et al.*, 2003]. The measurement accuracy was $\pm 25\%$ and the detection limit 30 pptv. Other measurements aboard the DC-8 used in this analysis include CO, perchloroethylene (C₂Cl₄), and methyl chloride (CH₃Cl). CO is a general tracer of combustion, C₂Cl₄ (a synthetic organic chemical used in dry cleaning) is an anthropogenic pollution tracer, and CH₃Cl can is a biomass burning tracer [*Blake et al.*, 2001]. These complementing measurements can be used to place constraints on the sources of HCN and CH₃CN [*Singh et al.*, 2003]. Some of the results shown in *Singh et al.* [2003] are reproduced here for purpose of comparison to model results. Throughout this paper, model comparisons to observations will use model results sampled along the DC-8 flight paths. All linear regressions are calculated using the reduced major axis (RMA) method, which allows for errors in both variables.

Sources and sinks of HCN and CH_3CN in the model are described in section 7.3. The CO simulation follows that of *Duncan et al.* [2003] and uses archived OH concentration fields

(monthly mean) from a full-chemistry simulation [*Li et al.*, 2002] to calculate CO loss. Anthropogenic sources of CO (including contributions from hydrocarbon precursors) are as described in *Duncan et al.* [2003], except for Asia where the *Streets et al.* [2003] inventory is used. Other TRACE-P studies have shown that the domestic fuel source of CO from China is too low in the *Streets et al.* [2003] inventory [*Carmichael et al.*, 2003, *Palmer et al.*, 2003]. For our simulation we double the residential coal source from China, resulting in a total anthropogenic (fossil fuel plus biofuel) source of CO from Asia of $184 \text{ Tg}COyr^{-1}$. Biomass burning sources are as described in *Heald et al.* [2003]. The global biomass burning CO source is $487 \text{ Tg}COyr^{-1}$ for 2000, while the global CO sources from fossil fuel and biofuel are 395 and 200 TgCOyr⁻¹, respectively. For the TRACE-P period (February-April 2001), the global biomass burning CO source is 129 TgCO and about half of that source is in SE Asia.

Since the model simulations of HCN, CH₃CN, and CO as implemented here are linear with respect to their sources, we resolve the contributions from different source regions and source types in the model by using tagged tracers [*Bey et al.*, 2001b], which can then be added to reconstitute the full concentration field. Tagged tracers resolve sources from biomass burning and residential coal burning, for Asia and for the rest of the world.

7.3 Model Sources and Sinks of HCN and CH₃CN

7.3.1 Sinks

Ocean Uptake

Constraints on ocean uptake for HCN and CH_3CN can be obtained from the vertical gradients of concentrations measured in background air over the North Pacific during TRACE-P [*Singh et al.*, 2003]. We implement this constraint here by using the observed gradients to infer a saturation ratio for these two gases that we can then extrapolate globally in the 3-D model simulation.



Figure 7.1: Vertical distributions of of HCN, CH₃CN, and CO for the ensemble of TRACE-P data over the NW Pacific (See *Jacob et al.* [2003] for a map of the aera covered). Individual observations are shown as dots. Solid circles, triangles, and horizontal bars represent means, medians, and standard deviations, respectively. Model results are shown for the standard simulation and for tagged combustion tracers. Additional sources of CO in the model include biofuel burning and oxidation of methane and biogenic nonmethane hydrocarbons.



Figure 7.2: Vertical distributions of HCN and CH_3CN observed in TRACE-P over the North Pacific under background conditions (CO < 120 ppbv and $C_2Cl_4 < 10$ pptv). Individual observations are shown as dots. Solid circles, triangles, and horizontal bars represent means, medians, and standard deviations, respectively.

Figure 7.1 shows the vertical distributions of HCN, CH₃CN, and CO observed for the ensemble of the data in TRACE-P (dots and red lines). The CO mixing ratios decrease from the boundary layer to the free troposphere, while the opposite is seen in the mixing ratios of HCN and CH₃CN. This is consistent with an ocean sink for HCN and CH₃CN and also with the dominant biomass burning source for these two gases, in contrast to the large fossil fuel source for CO. Biomass burning outflow during TRACE-P was largely confined to the free troposphere, while there was considerable fossil fuel outflow in the boundary layer [*Carmichael et al.*, 2003; *Liu et al.*, 2003].

Figure 7.2 shows the vertical distributions of HCN and CH₃CN (dots and red lines) observed in TRACE-P over the North Pacific under background conditions, defined here as CO < 120 ppbv and C₂Cl₄ < 10 pptv [*Singh et al.*, 2003]. Both gases show significantly reduced mixing ratios in the marine boundary layer compared with their free tropospheric values. Asian outflow influence for these conditions is minimal, and the shape of the profiles is evidence for ocean uptake. Median mixing ratios at 2-4 km for these background conditions are 201 pptv for HCN and 134 pptv for CH_3CN , while the corresponding values at 0-2 km are 161 pptv and 106 pptv, respectively.

Following *Singh et al.* [2003], the deposition velocities of HCN and CH₃CN to the ocean can be derived using a box model of the marine boundary layer (MBL) with no divergence of horizontal flux [*Lenschow*, 1983]. We calculate the flux across the MBL top as the concentration difference between 2-4 km (C_{FT}) and 0-2 km (C_{MBL}) multiplied by an entrainment velocity $K_e = 0.5$ cm s⁻¹ [*Heikes et al.*, 1996]. At steady state, this flux must be balanced by the ocean uptake flux ($v_d C_{MBL}$, where v_d is the deposition velocity). Loss by reaction with OH is negligible, since both HCN and CH₃CN can be considered chemically inert on the time scale for MBL turnover (a few days). It follows that

$$v_d = K_e \left(\frac{C_{FT}}{C_{MBL}} - 1\right) \tag{7.1}$$

The resulting deposition velocity is 0.13 cm s^{-1} for both gases.

The comparable deposition velocities despite greater solubility of CH₃CN imply faster consumption of HCN(aq)/CN⁻ in the ocean (see discussion below). *de Laat et al.* [2001] previously inferred a deposition velocity of 0.01-0.05 cm s⁻¹ for CH₃CN to the ocean in order to explain CH₃CN mixing ratios observed in South Asian outflow to the Indian Ocean (INDOEX mission). *Warneke et al.* [2001] estimated a deposition velocity of 0.34 cm s⁻¹ for CH₃CN from ship measurements taken during an oceanic upwelling event. They attributed the higher value compared to *de Laat et al.* [2001] to the lower surface temperature and higher biological activity in the upwelling water. More recently, *de Gouw et al.* [2003] estimated a deposition velocity of 0.17 cm s⁻¹ for CH₃CN from aircraft measurements over the NE Pacific.

Using a two-layer film model for air-to-sea exchange [*Liss and Slater*, 1974], *Singh et al.* [2003] estimated saturation ratios of 0.77 for HCN and 0.83 for CH₃CN from their TRACE-P data. Saturation ratio is related to deposition velocity by

$$v_d = (1 - S) K_g \tag{7.2}$$

where K_g is the air-to-sea transfer velocity and is calculated from conductances for mass transfer in the gas and liquid phases, for which we adopt the *Asher et al.* [1997] and the *Nightingale et al.* [2000] parameterizations, respectively. The resulting saturation ratios are 0.79 for HCN and 0.88 for CH₃CN. The difference with *Singh et al.* [2003] reflects different assumptions on the parameterizations of conductances for mass transfer. In our 3-D model calculation we extrapolate these saturation ratios globally, resulting in atmospheric lifetimes against ocean uptake of six months for HCN and eight months for CH₃CN.

Uptake of HCN and CH_3CN by the ocean must require consumption (presumably biological) in the ocean mixed layer (OML), and we can readily estimate the implied lifetimes. At steady state, the ocean uptake flux must be balanced by consumption in the OML

$$v_d C_{MBL} = \frac{Z}{\tau} C_{OML} \tag{7.3}$$

$$S = H \frac{C_{OML}}{C_{MBL}} \tag{7.4}$$

$$\tau = \frac{Z}{H} \frac{S}{v_d} \tag{7.5}$$

where Z is the oceanic mixed layer depth (about 50 m for the middle-latitude North Pacific in March [*Kara et al.*, 2000]), τ is the lifetime against consumption in the OML, C_{OML} is the concentration in the OML, and H is the dimensionless Henry's law constant defined as the ratio of the concentration in air to that in seawater. Values for H at 298 K are 3.4×10^{-3} ($\Delta H_{298}/R = 5000$ K) for HCN and 7.6×10^{-4} ($\Delta H_{298}/R = 4100$ K) for CH₃CN [*Sander*, 1999]. The resulting lifetimes against consumption in the OML are three months for HCN(aq)/CN⁻ and 14 months for CH₃CN(aq)/CN⁻.

Other Sinks

Additional known losses for atmospheric HCN and CH₃CN are reactions with OH and O(¹*D*), photolysis, and precipitation scavenging. Of these, only reaction with OH is significant [*Cicerone and Zellner*, 1983; *Brasseur et al.*, 1983] and is implemented in the model using rate constants from *Wine et al.* [2002] for HCN and *DeMore et al.* [1997] for CH₃CN, with monthly mean OH fields from a full chemistry simulation [*Li et al.*, 2002]. The recent laboratory study of *Wine et al.* [2002] indicates a factor of three lower rate constant for the HCN-OH reaction (low-pressure limit 7.4×10^{-33} cm⁶ molecule⁻² s⁻¹; high-pressure limit $9.0 \times 10^{-15} (T/300)^{3.2}$ cm³ molecule⁻¹ s⁻¹, where *T* is temperature) than previously measured [*Fritz et al.*, 1984]. The corresponding lifetimes against oxidation by OH are 4.3 years for HCN and 2.2 years for CH₃CN, much longer than the lifetimes against ocean uptake.

7.3.2 Sources

Biomass Burning

Both HCN and CH₃CN are mainly emitted in the low-temperature smoldering phase of biomass burning, similarly to CO [*Lobert et al.*, 1990]. Different fuel types and fire temperatures result in different emission ratios [*Lobert et al.*, 1991]. Past studies have indicated a large range of molar emission ratios for HCN (0.03-1.1%) and a narrower range for CH₃CN (0.12-0.25%) [*Lobert et al.*, 1991; *Hurst et al.*, 1994a,b; *Yokelson et al.*, 1997, 1999, 2003; *Holzinger et al.*, 1999; *Goode et al.*, 2000]. Emission ratios throughout this paper are in molar units relative to CO. When compounded with a range of global biomass burning CO emission estimates (200-800 TgCOyr⁻¹), one obtains global biomass burning sources of 0.1-3.2 TgNyr⁻¹ for HCN and 0.1-1.1 TgNyr⁻¹ for CH₃CN (Table 7.1).

The recent review of *Andreae and Merlet* [2001] recommends biomass burning HCN emission ratios of 0.05% (savanna and grassland) and 0.15% (tropical and extratropical forests)

and a biomass burning CH₃CN emission ratio of 0.11% for all vegetation types. The HCN recommendation for savanna and grassland is based on field experiments in Australia [*Hurst et al.*, 1994a,b]. Recent measurements in African savanna fires show much higher HCN emission ratios $(0.85\pm0.29\%)$ [*Yokelson et al.*, 2003]. By averaging measurements of biomass burning emissions from different fuel types and from different regions of the world, *Goode et al.* [2000] found an average biomass burning HCN emission ratio of 0.34%, much higher than the *Andreae and Merlet* [2001] value.

Correlations with CO in the TRACE-P observations provide important constraints on the emissions of HCN and CH₃CN. *Singh et al.* [2003] used these correlations in biomass burning plumes to derive emission ratios of $0.27\pm0.12\%$ for HCN and $0.15\pm0.05\%$ for CH₃CN. The HCN emission ratio is consistent with the average value reported by *Goode et al.* [2000], and is also in accord with the value of 0.28% estimated by *Heald et al.* [2003] based on multivariate analysis of the TRACE-P CO and HCN data. The CH₃CN emission ratio is consistent with the [*Andreae and Merlet*, 2001] value. We find in GEOS-CHEM that the best fit to the TRACE-P observations of HCN, CH₃CN, and CO, and to the global HCN column data is obtained with biomass burning emission ratios of 0.27% for HCN and 0.20% for CH₃CN, consistent with *Singh et al.* [2003]; we use these values in the simulations presented here. The corresponding sources of HCN and CH₃CN are 0.63 and 0.47 TgNyr⁻¹, respectively (Table 7.2), within the range of past estimates (Table 7.1).

Residential Coal Burning Source in Asia

It is well established that HCN and CH₃CN are produced in the early stages of hightemperature combustion but are subsequently oxidized within the combustion chamber [*Flagan and Seinfeld*, 198 Direct measurements in automobile exhaust [*Lobert et al.*, 1991; *Holzinger et al.*, 2001] as well as aircraft measurements by *Singh et al.* [2003] and *de Gouw et al.* [2003] over southern California support the view that the source from fossil fuel combustion is negligible.



Figure 7.3: Observed HCN (solid circles) and CH₃CN (open circles) correlations with CO in three Chinese urban plumes sampled during TRACE-P (DC-8 flights 9, 12, and 13) below 2 km altitude. Regression lines (RMA method) are also shown.



Figure 7.4: Observed CH₃CN:HCN correlations in plumes sampled during TRACE-P. Solid circles: sampled at 8-11 km on DC-8 flights 4, 7, 9, 12, 13, 14, 15, 17, 18, and 19; plumes at that altitude were largely devoid of anthropogenic influence [*Liu et al.*, 2003]. Open circles: Chinese urban plumes below 2 km (DC-8 flights 9, 12, and 13). Regression lines (RMA) are shown.

However, TRACE-P observations show a strong enhancement of HCN, and a much weaker enhancement of CH₃CN, in Chinese urban plumes sampled in the MBL less than two days downwind of the source [*Singh et al.*, 2003]. Figure 7.3 shows the HCN and CH₃CN correlations with CO observed in three major Chinese urban plumes (DC-8 flights 9, 12, 13) sampled in the MBL during TRACE-P. Asian outflow in the MBL was in general advected behind cold fronts and was devoid of biomass burning influence [*Carmichael et al.*, 2003; *Liu et al.*, 2003]. The peak mixing ratios of HCN and CO observed in the Shanghai plumes are 1.5 ppbv and 1 ppmv, respectively, while the peak mixing ratio for CH₃CN is 300 pptv, much less enhanced. These peak mixing ratios were associated with high mixing ratios of CH₃Cl (see Figure 7a of *Singh et al.* [2003]) and carbonyl sulfide (COS). The HCN-CO and CH₃CN-CO correlations show slopes of 0.17% and 0.04%, respectively (Figure 7.3).

Although there is widespread biofuel use in China [Streets et al, 2003], data from Africa

suggest negligible nitrile emission from biofuels [*Bertschi et al.*, 2003; *Yokelson et al.*, 2003]. Also, the CH₃CN/HCN enhancement ratio is much lower in the Chinese urban plumes than in biomass burning plumes (Figure 7.4). *Singh et al.* [2003] suggested that the enhancements of CH₃Cl and COS correlated with enhanced HCN in the Chinese urban plumes could indicate a source from hard coal burning, and we follow that suggestion here. Clearly, further work is needed to identify the Chinese source of nitriles.

We estimate the residential coal burning emission ratios of HCN and CH₃CN relative to CO from the Chinese urban plumes observed in TRACE-P (Figure 7.3). Residential coal burning accounts for about 15% of anthropogenic CO emissions for China in the model. Combined with the slopes of the HCN-CO and CH₃CN-CO correlations observed in the Chinese urban plumes (Figure 7.3), we obtain residential coal burning molar emission ratios of 1.2% for HCN and 0.26% for CH₃CN relative to CO. Simulation of the TRACE-P data with GEOS-CHEM (section 7.4) indicates a best fit for residential coal burning emission ratios of 1.6% for HCN and 0.25% for CH₃CN.

When scaling the above emission ratios by the fraction of urban CO from residential coal burning in China, the resulting HCN/CO source ratio (0.24% for Shanghai, for example) is comparable to biomass burning (0.27%) while the resulting CH₃CN/CO source ratio (0.04% for Shanghai, for example) is much lower than biomass burning (0.20%). The corresponding global sources are 0.2 for HCN and 0.03 TgNyr⁻¹ for CH₃CN (Table 7.2). This source could have a seasonal variation associated with heating [*Streets et al.*, 2003], but uncertainties are sufficiently large that we do not bother to include it here.

Biogenic Source

There is indication that HCN is produced by higher plants [*Cicerone and Zellner*, 1983; and references therein]. Recent laboratory results by *Fall et al.* [2001] show that wounded clover releases HCN in addition to large amounts of acetone. In the TRACE-P data, HCN is correlated with both acetone (r = 0.81, slope = 0.33 pptv ppbv⁻¹, n = 746) and methanol (r = 0.86, slope = 136.6



Figure 7.5: Observed HCN and CO correlations with Methanol for the ensemble of TRACE-P data. Regression lines are shown.

pptv ppbv⁻¹, n = 744), which have strong biogenic sources. In particular, methanol is generally considered a tracer for continental biogenic emissions [*Heikes et al.*, 2002]. Figure 7.5 (top panel) shows the correlation of HCN with methanol observed during TRACE-P. A similarly strong correlation was found for CH₃CN. The biogenic source of methanol is estimated to be 50-280 Tg yr⁻¹ [*Heikes et al.*, 2002]. If the HCN-methanol correlation were to reflect a common biogenic source, then the implied biogenic HCN source would be 3-17 Tg N yr⁻¹, far too large to be reconciled with the observed HCN concentrations [*Li et al.*, 2000]. Additionally, the highest methanol and HCN concentrations in TRACE-P were observed in the Chinese urban plumes. Methanol in TRACE-P was also strongly correlated with CO (r = 0.73, slope = 81.9 ppbv ppbv⁻¹, n = 1034) and was highest (together with HCN) in the Chinese urban plumes (Figure 7.5, bottom panel), implying an anthropogenic source. Thus we find no convincing evidence of a biogenic source of nitriles and do not include such a source in our simulations.

7.4 Simulation of Observations

We examine in this section the GEOS-CHEM model simulation of the TRACE-P observations for HCN and CH₃CN and discuss what constraints this simulation provides. The model evaluation also considers CO, since our source specifications for HCN and CH₃CN are based on relationships with CO. We also examine the consistency of our simulation with the global data sets of HCN columns previously used as constraints by *Li et al.* [2000] and with the INDOEX data of *de Laat et al.* [2001].

As a general assessment of our simulation, we show in Figure 7.6 the frequency distributions of the observed and simulated HCN, CH₃CN, and CO concentrations along the ensemble of TRACE-P flight tracks. The simulated mean and median values agree with the observed values to within 10 pptv for HCN, 5 pptv for CH₃CN, and 5 ppbv for CO. There are no systematic biases or obvious anomalies in the simulated frequency distributions. Figure 7.7 shows scatterplots of



Figure 7.6: Frequency distributions of observed (solid line) and simulated (dashed line) mixing ratios of HCN, CH₃CN, and CO for the ensemble TRACE-P data over the North Pacific.



Figure 7.7: Scatterplots of simulated versus observed mixing ratios of HCN and CH_3CN for the ensemble of TRACE-P data. The y = x line is also shown.

simulated versus observed concentrations of HCN and CH_3CN for the ensemble of TRACE-P data. The bulk of the points are strongly correlated, but the correlations are much smaller at high mixing ratios (primarily in the boundary layer), likely because of model errors in the location of plumes [*Kiley et al.*, 2003]. For further evaluation of the simulation we examine vertical distributions and correlations between species.

7.4.1 Vertical Distributions

The observed and simulated vertical profiles of HCN, CH₃CN, and CO for the ensemble of TRACE-P measurements are shown in Figure 7.1. The model reproduces the increase of CO mixing ratios and the decrease of HCN and CH₃CN mixing ratios from the free troposphere to the MBL. For the background conditions over the NW Pacific (Figure 7.2), the model reproduces the gradients of HCN and CH₃CN between the free troposphere and the MBL driven by ocean uptake. Without ocean uptake in the model there would be no such gradients. Also shown in Figure 7.1 are the relative contributions from biomass burning and residential coal burning simulated in the



Figure 7.8: Vertical distribution of CH₃CN concentrations over the northern Indian ocean in March 2001. Median aircraft observations from the INDOEX campaign [*de Laat et al.*, 2001] are shown as symbols with standard deviations. Monthly mean model results for the corresponding month and region $(0-10^{\circ}N, 65^{\circ}E-80^{\circ}E)$ are shown as the solid line.

model using tagged tracers. Biomass burning accounts for 70-85% of total HCN and 90-95% of total CH₃CN in the free troposphere (above 2 km), while in the boundary layer the fractions are 45% and 75%, respectively. Thus it appears that CH₃CN is a better tracer for biomass burning. Simulated and observed mean vertical profiles of HCN and CH₃CN show enhancements at 2-4 and 8-11 km (Figure 7.1). These correspond to preferential altitudes for frontal and convective outflow of biomass burning pollution, respectively [*Bey et al.*, 2001b; *Liu et al.*, 2003].

We also compare model results in Figure 7.8 to aircraft measurements of CH_3CN made over the northern Indian Ocean during the INDOEX campaign [*de Laat et al.*, 2001]. In contrast to TRACE-P, the INDOEX observations show maximum concentrations in the MBL due to boundary layer outflow from the Indian subcontinent associated with the winter-spring monsoon. The model reproduces this enhancement, which is thus consistent with our representation of the ocean sink.

7.4.2 Correlations Between HCN, CH₃CN, and CO

Figures 7.9 and 7.10 compare the observed and simulated correlations between HCN, CH₃CN, and CO for the ensemble of the TRACE-P data in the free troposphere and in the boundary layer. The model reproduces the slopes of the correlations to within their expected errors. Differences in slopes between the free troposphere and the boundary layer reflect the dominant influence of biomass burning in the free troposphere, and the added influences from the urban source and the deposition sink in the MBL. The CH₃CN-CO correlation is poor in the boundary layer (r = 0.29) in the observations and r = 0.24 in the model), while the HCN-CO correlation is strong (r = 0.85in the observations and r = 0.77 in the model), reflecting the similarity between urban and biomass burning emission ratios for HCN/CO but the much lower urban ratios for CH₃CN/CO. The CH₃CN-HCN correlation in the free troposphere above 2 km (Figure 7.9) shows less variability in the model than in the observations, which likely reflects the assumption of uniform biomass burning emission ratios of HCN and CH₃CN in the model, while in reality these emission ratios vary for different fuel types and fire temperatures [Lobert et al., 1991]. The CH₃CN-CO relationship in the boundary layer (Figure 7.10) shows two branches, both in the model and in the observations, reflecting (1) the subsidence of biomass burning influence from the free troposphere (high CH₃CN, low CO), and (2) the urban outflow influence (low CH₃CN, high CO).

7.4.3 HCN Columns

Spectroscopic measurements of HCN atmospheric columns were made at three Japanese sites during TRACE-P as part of a long-term observational program [*Zhao et al.*, 2000, 2002]. The three sites are Moshiri (44°N, 142°E, 0.28 km altitude), Rikubetsu (43.5°N, 144°E, 0.37 km altitude), and Tsukuba (36°N, 140°E, 0.03 km altitude). The data for the TRACE-P period are shown in Figure 7.11 (solid circles). The columns at Tsukuba show much higher variation than at Moshiri and Rikubetsu, reflecting the latitudinal difference and the proximity of Tsukuba to the



Figure 7.9: Observed and simulated HCN-CH₃CN-CO correlations in the free troposphere (above 2 km) during TRACE-P. Regression lines and correlation coefficients are shown.


Figure 7.10: Same as Figure 7.9 but for the boundary layer (below 2 km).



Figure 7.11: Time series of observed (solid circles) and simulated (open circles) 24-hour average HCN columns (molecules cm⁻²) at the three Japanese stations of Moshiri (44°N, 142°E, 280 m altitude), Rikubetsu (43.5°N, 144°E, 370 m altitude), and Tsukuba (36°N, 140°E, 30 m altitude) during TRACE-P (February-April 2001).



Figure 7.12: Scatter plot of observed and simulated daily HCN columns (molecules cm^{-2}) at Moshiri, Rikubetsu, and Tsukuba in TRACE-P. Values are averages over the three sites. The regression line is calculated without the outlier.

main channel of Asian outflow at 25-35°N [*Bey et al.*, 2001b; *Liu et al.*, 2003]. The increases in the columns from February to April are consistent with the previous observation of a spring-summer HCN column maximum at these sites [*Zhao et al.*, 2000, 2002], and can be explained by the seasonal variation of biomass burning emissions [*Li et al.*, 2000].

Figure 7.11 compares model results for the TRACE-P period with observed HCN columns at the three Japanese sites. The averaging kernel and *a priori* vertical profile from the retrievals [*Zhao et al.*, 2000, 2002 were applied to the model results. The HCN columns average 4×10^{15} molecules cm⁻² with high values of $5 \cdot 7 \times 10^{15}$ molecules cm⁻², both in the observations and the model, consistent with previous column measurements at northern middle latitudes [*Mahieu et al.*, 1995, 1997; *Zhao et al.*, 2000, 2002]. A scatterplot of simulated versus observed HCN columns is shown in Figure 7.12. There is strong correlation (r = 0.82), reflecting in part the seasonal increase



Figure 7.13: Monthly mean HCN total columns (molecules cm⁻²) retrieved from spectroscopic measurements at Moshiri and Rikubetsu in Japan [*Zhao et al.*, 2000,2002], Kitt Peak in Arizona [*Mahieu et al.*, 1995], Jungfraujoch in the Swiss Alps [*Mahieu et al.*, 1995,1997], and Ny Ålesund in Spitsbergen [*Li et al.*, 2000]. Data for the two Japanese sites are monthly means and vertical bars indicate standard deviations. The solid lines represent simulated daily average HCN total columns for 2000.

from February to April (Figure 7.13), and no significant bias.

Multi-year measurements of HCN columns are available from several sites in the northern hemisphere and provide another important test for the model. We used these data in *Li et al.* [2000] to evaluate our previous simulation of HCN. The present model has a weaker HCN source and a longer HCN lifetime to match the TRACE-P constraints, and it is imperative to determine whether these changes degrade the simulation of the HCN column data. Figure 7.13 compares model results for 2000 to the seasonal variations in these multi-year records, including data from the Japanese sites [*Zhao et al.*, 2000, *Zhao et al.*, 2002], Kitt Peak in Arizona [*Mahieu et al.*, 1995], Jungfraujoch in

the Swiss Alps [*Mahieu et al.*, 1995, *Mahieu et al.*, 1997], and Ny Ålesund in Spitsbergen [*Li et al.* [2000]. Observations for 1998 were excluded because of anomalous fire influence throughout the northern hemisphere [*Rinsland et al.*, 1999, *Rinsland et al.*, 2000, *Zhao et al.*, 2002]. We find that we achieve a similar or better simulation than in the study of *Li et al.* [2000]. The reader is referred to that paper for discussion of the seasonal features.

7.5 Global Budgets and Distributions of HCN and CH₃CN

	HCN	CH ₃ CN
Atmospheric burden (TgN)	0.426	0.28
Atmospheric lifetime (months)	6.2	6.7
Tropospheric burden $(TgN)^a$	0.38	0.25
Tropospheric lifetime (months)	5.3	5.8
Sources $(TgNyr^{-1})$		
Biomass burning	0.63	0.47
Residential coal burning	0.2	0.03
Sinks $(TgNyr^{-1})$		
Ocean uptake	0.73	0.36
Reaction with OH	0.1	0.14

Table 7.2: Global Atmospheric Budgets of HCN and CH₃CN

^{*a*}For the 1000-100 hPa column.

The global atmospheric budgets of HCN and CH₃CN in the model are shown in Table 7.2. Biomass burning contributes 0.63 TgNyr^{-1} to global HCN and 0.47 TgNyr^{-1} to global CH₃CN, while the corresponding sources from residential coal burning are 0.2 and 0.03 TgNyr⁻¹, respectively. Ocean uptake dominates the loss of both HCN (0.73 TgNyr⁻¹) and CH₃CN (0.36 TgNyr⁻¹), while the sink from reaction with OH is relatively small (0.1 TgNyr⁻¹ for HCN and 0.13 TgNyr⁻¹ for CH₃CN). The resulting tropospheric lifetimes are 5.3 months for HCN and 5.8 months for CH₃CN.

Our HCN lifetime is longer, and the implied global source smaller, than in our previous study using the constraints from the observed relative seasonal variation of HCN columns [*Li et al.*, 2000]. In that study we used the relative seasonal amplitude of the observed columns at constraint on the HCN lifetime and derived a global source by mass balance. We considered that the seasonal amplitude of the columns constrained the lifetime to be less than 4 months, where as the TRACE-P constraints imply a longer lifetime (5.3 months). As shown in Figure 7.13, it appears that this longer lifetime is still compatible with the constraints from the HCN column observations.

Figures 7.14 shows simulated global mean distributions of HCN and CH₃CN in April 2001. Surface concentrations are maximum over biomass burning regions in SE Asia, central America, and central Africa (> 1000 pptv). Surface concentrations are very low (< 50 pptv) at high southern latitudes, reflecting the remoteness from sources and the sink from ocean uptake under our assumption of uniform saturation ratios. Observations in this part of the world are evidently needed. Concentrations in the middle troposphere at 500 hPa are highest over SE Asia and downwind, with a circumpolar band of relatively high concentrations (> 200 pptv for HCN) at 5°N-40°N due to biomass burning influence.

7.6 Conclusions

We used a global 3-D model analysis of in situ HCN-CH₃CN-CO aircraft observations made over the NW Pacific during the TRACE-P aircraft mission (February-April 2001) to improve understanding of the atmospheric budgets of both gases. Vertical gradients of HCN and CH₃CN observed in remote marine air confirm the previous hypotheses of a dominant ocean sink for HCN [*Li et al.*, 2000] and CH₃CN [*Hamm and Warneck*, 1990]. Following *Singh et al.* [2003], we used these gradients to derive deposition velocities of 0.13 cm s⁻¹ for both gases, corresponding to saturation ratios of 0.79 for HCN and 0.88 for CH₃CN. These deposition velocities imply lifetimes of three months for HCN(aq)/CN⁻ and 14 months for CH₃CN(aq)/CN⁻ against consumption in the oceanic mixed layer.

Biomass burning plumes from SE Asia observed during TRACE-P confirmed the impor-



Figure 7.14: Simulated global distributions of HCN and CH₃CN concentrations in surface air and at 500 hPa for April 2001.

tance of biomass burning as a global source for HCN and CH₃CN, while observations in southern California confirmed that automobile exhaust is not a significant source for either gas [*Singh et al.*, 2003]. However, HCN and CH₃CN observed in fresh Chinese urban plumes indicate emissions of anthropogenic origin with a much higher HCN/CH₃CN ratio than from biomass burning. We tentatively attribute these enhancements to residential coal burning.

Our global model uses biomass burning and residential coal burning emission ratios (molar) relative to CO of 0.27% and 1.6% respectively for HCN, and 0.2% and 0.25% respectively for CH₃CN, as providing the best fit to the TRACE-P observations within the constraints offered by the HCN-CH₃CN-CO relationships observed in biomass burning and urban plumes. The resulting simulation captures the observed frequency distributions of HCN and CH₃CN, their vertical distributions, and their correlations with CO. It offers a good simulation of ground-based measurements of HCN columns, at sites in Japan and elsewhere in the northern hemisphere, both during TRACE-P and over the multi-year record. It also reproduces the mean CH₃CN vertical distribution observed over the northern Indian Ocean during the INDOEX aircraft campaign.

Our global budgets of HCN and CH₃CN indicate biomass burning sources of 0.63 and 0.47 Tg N yr⁻¹, respectively, and residential coal burning sources of 0.2 and 0.03 Tg N yr⁻¹, respectively. Ocean uptake is the dominant sink for both; oxidation by OH is an additional minor sink. The resulting tropospheric lifetimes are 5.3 months for HCN and 5.8 months for CH₃CN. The HCN lifetime is longer, and the global source smaller, than in our previous model analysis [*Li et al.*, 2000], but it still provides an unbiased simulation of the relative seasonal cycle of HCN columns which was the main constraint in that previous analysis. The model predicts maximum surface air concentrations of HCN and CH₃CN over biomass burning regions and very low (< 50 pptv) concentrations at high southern latitudes due to ocean uptake under the assumption of a uniform saturation ratio. Observations are evidently needed to test this assumption. Concentrations in the middle troposphere are highest over tropical biomass burning regions and downwind, with a circumpolar band of high

concentrations at 5° N-40°N. Although both HCN and CH₃CN appear to be good tracers of biomass burning in the free troposphere, CH₃CN is a better tracer in the boundary layer due to the relatively large Chinese urban source of HCN. More work is needed to characterize the nature of this Chinese urban source.

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