SPRING TO SUMMER TRANSITIONS OF OZONE AND ITS PRECURSORS OVER NORTH AMERICA AND PHOTOCHEMISTRY OVER ANTARCTICA

A Dissertation
Presented to
The Academic Faculty

By

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In Partial Fulfillment
Of the Requirements for the Degree
Doctor of Philosophy in the School of Earth and Atmospheric Sciences

Georgia Institute of Technology

August 2007

Spring to Summer Transitions of Ozone and Its Precursors over North America and
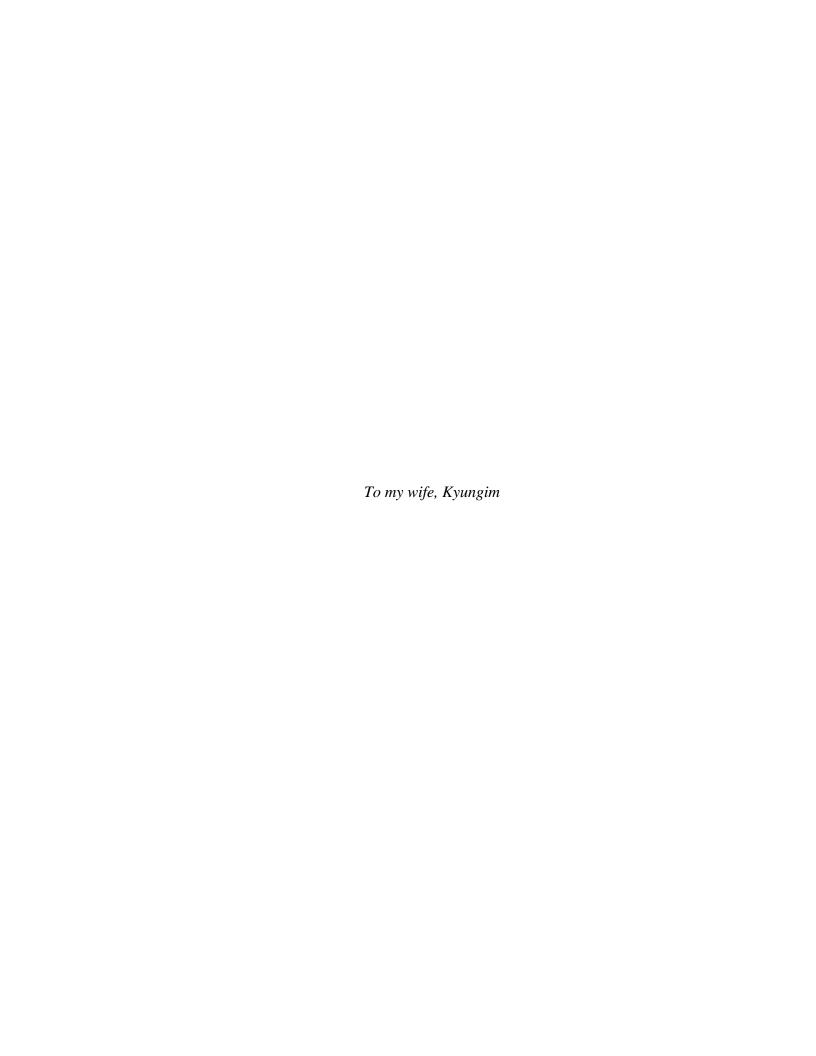Photochemistry over Antarctica

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To my wife, Kyungim

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS AND ABBREVIATIONS

AK	averaging kernel
AMF	air mass factor
ANTCI	Antarctic Tropospheric Chemistry Investigation
ARO	Atmospheric Research Observatory
ASDC	Atmospheric Science Data Center
AVHRR	Advanced Very High Resolution Radiometer
AWS	Automatic Weather Station
CAPE	convective available potential energy
CFCs	chlorofluorocarbons
CG	cloud-to-ground
CH_3OOH	methyl hydroperoxide
CO	carbon monoxide
CTM	Chemical Transport Model
DAAC	Distributed Active Archive Center
DAO	Data Assimilation Office
DFS	degree of freedom
DOAS	Differential Optical Absorption Spectroscopy
ECC	electrochemical concentration cell
ECMWF	European Centre for Medium-Range Weather Forecasts
ERBS	Earth Radiation Budget Satellite
ERS-2	European Remote Sensing-2 (satellite)
FDDA	four-dimensional data assimilation
GEIA	Global Emissions Inventory Activity
GEOS-Chem	global Goddard Earth Observing System – Chemistry (model)
GEOS-3	GEOS assimilated meteorological fields
GES	Goddard Earth Sciences
GMAO	Global Modeling Assimilation Office
GOCART	Global Ozone Chemistry Aerosol Radiation and Transport
GOME	Global Ozone Monitoring Experiment
GOMECAT	GOME cloud retrieval algorithm
GSFC	Goddard Space Flight Center
Halon-1211	Bromochlorodifluoromethane
HANK	Regional Episodic Chemical Transport Model
HCHO	formaldehyde
HNO_3	nitric acid
hPa	hecto Pascal
H_2O_2	hydrogen peroxide
IC	intracloud
INTEX-NA	intercontinental chemical transport experiment – North America
IPCC	Intergovernmental Panel on Climate Change
ISCAT	Investigation of Sulfur Chemistry in the Antarctic Troposphere
ITCT	Intercontinental Transport and Chemical Transformation

K	temperature
LAI	leaf area index
LIDORT	linear discrete ordinary radiative transfer
LT	Local Time
MDL	method detection limits
MLS	Microwave Limb Sounder
MOPITT	Measurement of Pollution in the Troposphere
MOZAIC	Measurement of Ozone and Water Vapor by Airbus In-Service Aircraft
MOZART	Model for OZone And Related chemical Tracers
MYJ	Mellor-Yamada-Janjic
NAPAP	National Acid Precipitation Assessment Program (NAPAP)
NCEP	National Center Environmental Prediction
NEI99	EPA 1999 National Emission Inventory
NLDN	National Lightning Detection Network
NMHC	non-methane hydrocarbon
NO	nitric oxide
NO_2	nitrogen dioxide
NOx	nitrogen oxides ($NO + NO_2$)
NOy	total reactive, oxidized nitrogen
OH	hydroxyl radical
O_3	ozone
OMI	Ozone Monitoring Instrument
Pa	Pascal
PAN	peroxyacetyl nitrate
PBL	periodic boundary layer
PDF	probability distribution function
ppbv	parts per billion by volume
ppmv	parts per million by volume
pptv	parts per trillion by volume
PV	potential vorticity
REAM	Regional chEmical trAnsport Model
SAGE	Stratospheric Aerosol and Gas Experiment
SCIAMACHY	Scanning Imaging Absorption spectroMeter for Atmospheric CartograpHY
SEARCH	Southeastern Aerosol Research and Characterization Study
SODAR	Sound Detecting and Ranging
SONEX	SASS (Subsonic Assessment) Ozone and NOx Experiment
SP	South Pole
TES	Tropospheric Emission Spectrometer
TOA	top of the atmosphere
TOPSE	Tropospheric Ozone Production about the Spring Equinox
3-D	three-dimensional
TOMS	Total Ozone Mapping Spectrometer
UT	upper troposphere
VOCs	volatile organic compounds

WCB   Warm Conveylor Belt
WOUDC   World Ozone and Ultraviolet Data Center

SUMMARY

The horizontal and vertical distributions of ozone and its precursors over North America during the spring and the summer are frequently determined by several factors: cloud convection, lightning NO_X production, mixing depth, and long-range transport. The critical factors that contribute to the spatial distribution of air pollutants are studied using the Regional chEmical trAnsport Model (REAM) with diverse satellite measurements as well as in-situ surface and aircraft measurements. Among the space-borne measurements, GOME and OMI NO_2 column measurements show enhanced lightning NO_X over the continent and the western North Atlantic. Concurrent convective transport-causing CO column peaks and high CO enhancements in the upper troposphere (UT) over the ocean are shown from the modeling analysis of the CO column by MOPITT and UT CO by TES. Likewise, TOMS-SAGE II and OMI-MLS O_3 column peaks and TES UT O_3 enhancements due to convective outflow and lightning NO_X are also observed. Lightning NO_X production in REAM is much larger than that in GEOS-CHEM, resulting in better simulations of GOME NO_2 columns over the western North Atlantic. Consequently, REAM simulates larger O_3 increasing trends in better agreement with TOMS-SAGE II and OMI-MLS O_3 columns over the southern United States and the western North Atlantic than GEOS-CHEM. Another factor, mixing depth, is a key parameter for the boundary layer structure of the model. Simulated spring to summer transitions of O_3 and its precursors over North America indicate that the simulated boundary layer structure plays a key role in differentiating REAM from GEOS-CHEM. Large enhancements of columns and upper tropospheric O_3 comparable to those over the eastern United States

are found over the western North Atlantic in the satellite measurements and REAM simulations. The O_3 enhancement region migrates northward from the spring to the summer. A model analysis indicates that the northward shift is driven by O_3 in the stratospheric flux, convective outflow and production from lightning NO_X. In addition, long-range transport affects the spatial distributions of air pollutants, particularly during the spring. During the late spring, large enhancements of NO_X, PAN, O_3, CO, CFCs, and Halon-1211 in UT are found over North America due to a surge of trans-Pacific pollutant transport from observations during the TOPSE 2000 experiment. The transition occurs later than that of the typical low-altitude trans-Pacific transport, which peaks around March or April.

Surface and aircraft measurements show a large amount of reactive nitrogen tracers over the Antarctic plateau during the summer. These enhanced measurements are investigated, and their photochemical impact is assessed by 1-D CTM and 3-D CTM, REAM. The 1-D model and REAM reasonably simulate the surface measurements of NO, HNO_3, HNO_4, and balloon NO measurements at the South Pole. However, compared with the Twin Otter NO measurements, REAM underestimates NO concentrations over plateau regions because parameterization based on surface measurements at the South Pole underestimates emissions in higher-elevation plateau regions. After all, around 50% of reactive nitrogen is scavenged by deposition, and the other is lost by transport. Thus, a shallow but highly active oxidizing canopy surrounds the Antarctic plateau due to snow NO_X emissions.

CHAPTER I

INTRODUCTION

1.1 Motivation

North America is a large source of O_3, aerosols, and their precursors in the Northern Hemisphere, which results in air pollution and adversely affects climate [IPCC, 2001]. Well-established as a typical climate issue, ozone in the UT functions as an efficient greenhouse gas, particularly in the mid-latitude Northern Hemisphere [Lacis *et al.*, 1990; Mickley *et al.*, 2004]. A critical aspect of determining air pollution caused by O_3 and its precursors and their impact on climate is to better constrain their horizontal and vertical distributions. The spatial distributions of O_3 and its precursors during the spring and the summer are affected by several factors: convection, lightning NO_X production, mixing depth, long-range transport, and their associated chemistry. Among these factors, cloud convection, along with the warm conveyor belt (WCB), is a major pathway for the outflow of North American pollution [Li *et al.*, 2005]. With cloud convection, lightning NO_X production is a dominant factor for O_3 production in the UT over North America during the summer [Li *et al.*, 2005; Cooper *et al.*, 2006]. From space-borne measurements, lightning NO_2 signals are evident in the Global Ozone Monitoring Experiment (GOME) [Richter and Burrows, 2002] and the Scanning Imaging Absorption spectroMeter for Atmospheric CartograpHY (SCIAMACHY) [Martin *et al.*, 2006]. Martin *et al.* [2006] and Hudman *et al.* [2007] quadrupled the northern mid-latitude lightning NO_X emissions in the global 3-D CTM, the Goddard Earth Observing System-CHEMistry (GEOS-CHEM) to reproduce observed lightning-caused NO_2

enhancements over North America. In the model, simulating plausible lightning NO_X production consistent with in-situ and satellite observed lightning occurrence is still difficult. Another factor that affects the spatial distributions of air pollutants, the mixing depth, changes rapidly as the season advances towards the summer [Holzworth, 1964, 1967]. Since O_3 concentrations over the surface are sensitive to uncertainties in the mixing depth [Rao *et al*., 1994; Sistla *et al*., 1996], a reliable mixing depth is critical for reasonable model performance [Berman *et al*., 1999]. Long-range transport also affects the spatial distributions of air pollutants. Increasing pollution from Asia, driven by rapid regional economic growth, affects O_3 concentration in the United States [Bernsen *et al*., 1999; Jacob *et al*., 1999]. Due to the subsidence of the trans-Pacific transported high O_3, the National Ambient Air Quality Standard could be significantly exceeded at California mountain sites [Hudman *et al*., 2004].

Thus, it is imperative that a three-dimensional regional chemical transport model (CTM) be used with higher temporal and spatial resolutions that incorporate detailed cloud convection, an observation-constraint lightning scheme, regional scale mixing depth, and increased vertical resolution. Various regional and global 3-D CTM's [McKeen *et al*., 1991; Brasseur *et al*., 1998, Wang *et al*., 1998; Lawrence *et al*., 1999; Levy *et al*., 1999; Hess *et al*., 2000; Bey *et al*., 2001, Song and Carmichael, 2001] have been developed to study the chemical and physical processes of air pollutants in the atmosphere. Meanwhile, to explain the various tropospheric chemistry problems, we have also developed a regional CTM. In this thesis, we apply the resulting CTM (hereafter referred to as REAM: the Regional chEmical trAnsport Model) to examine spring-to-summer transitions of O_3 and its precursors, largely driven by rapid changes in the factors

and their associated photochemistry. We also examine the role of the factors on the optimization of NO_X emissions and the budget of the tracers.

Even with regional-scale CTMs such as REAM, estimating the quantitative impact of the various factors on air pollutants is still difficult because of the lack of in-situ surface or aircraft measurements in extreme environments such as thunderstorms. Despite the drawback of cloud interference of space-borne measurements, satellite observations can potentially be a complementary method of overcoming this limitation [e.g., Li *et al.,* 2005; Jing *et al.,* 2006]. Therefore, the validation of REAM and an examination of the impact of these factors on O_3 and its precursors necessitate the following: corresponding surface observations of O_3, NO_x, and CO from the EPA AIRNow and the Southeastern Aerosol Research and Characterization Study (SEARCH); the vertical profiles of O_3 from the Measurement of Ozone and Water Vapor by Airbus In-Service Aircraft (MOZAIC) and ozonesondes; NO_2 tropospheric columns from the Global Ozone Monitoring Experiment (GOME) and the Ozone Monitoring Instrument (OMI); CO columns from the Measurement of Pollution in the Troposphere (MOPITT); O_3 and CO vertical profiles from the Tropospheric Emission Spectrometer (TES); and tropospheric O_3 columns from the Total Ozone Mapping Satellite (TOMS) and the Stratospheric Aerosol and Gas Experiment II (SAGE II), and OMI and the Microwave Limb Sounder (MLS).

From the Investigation of Sulfur Chemistry in the Antarctic Troposphere (ISCAT) experiments during 1998 and 2000, high concentrations of NO at the South Pole (SP) have been identified. NO concentrations reached over 500 pptv [Davis *et al.*, 2001, 2004], significantly higher than those in the Arctic [Honrath *et al.,* 1999; Ridley *et al.,*

2000]. The high NO concentrations occurred due to the emissions of NO_X, resulting from nitrate photolysis inside snow pack [Davis *et al.*, 2001, and references therein]. As a result, measurements show higher 24-hour average concentrations of OH at SP than they show in the tropical marine boundary [Mauldin *et al.,* 2001, 2004]. In addition, active photochemistry driven by snow NO emissions leads to significant ozone production [e.g., Crawford *et al.,* 2001, Chen *et al.*, 2004]. Davis *et al.* [2004] further speculated that given the rate of nitrate photolysis, most of the plateau should exhibit high levels of O_3 as well as OH near the surface. Today, the spatial extent and overall impact of snow NO_X emissions on photochemistry over Antarctica is not clear. Interestingly, flux estimated by Jones *et al.* [2001] at the German Antarctica station, Neumayer (70°S, 8°W), was only about one-third of that estimated by Oncley *et al.* [2004] at SP. Snow emissions clearly vary over Antarctica. In order to address the various issues related to reactive nitrogen and its coupling to atmospheric oxidizing species such as OH, we need to extend the measurements of NO_X so that they include a larger area of Antarctica and extend the previous box model analysis to 1-D CTM and 3-D CTM, REAM analyses.

1.2 **Space-borne Measurements and Models**

1.2.1 Tropospheric NO_2 Column from GOME and OMI

The GOME instrument is on board the European Remote Sensing-2 (ERS-2) satellite that passes over the equator at 1030 AM local time and its horizontal resolution is 40 km latitude by 320 km longitude. In the Differential Optical Absorption Spectroscopy (DOAS) algorithm, an air mass factor (AMF), is used to translate a slant column to a vertical column, as described by previous studies [Palmer *et al.,* 2001;

Martin *et al., 2002*]. AMF considers not only the geometrical configuration of the atmosphere but also its atmospheric states. In other words, AMF is mathematically expressed by an integral of the products of the relative vertical profiles, the shape factors of NO_2 from the two models, REAM and GEOS-CHEM, and the sensitivity of backscattered radiance to changes in tracer concentration [Martin *et al., 2002*]. Sensitivity is estimated from the linearized discrete ordinate radiative transfer (LIDORT) model [Spurr *et al*., 2001], one of the exact algorithms that accurately accounts for multiple scatterings in the atmosphere. The detailed retrieval method of tropospheric NO_2 columns from GOME measurements and the estimation of its uncertainty are described in a previous study by Martin *et al*. [2002]: First, fitting directly backscattered radiance spectra from GOME instruments produces a slant column; then a stratospheric column determined from an NO_2 column over the central Pacific is subtracted from the total column with an assumption that stratospheric columns are zonally constant; and finally, the subtracted slant column is converted into a vertical column using AMF. The calculation of AMF requires information about clouds and aerosols. The cloud fraction and cloud-top pressure are from GOME [Kurosu *et al., 1999*]. Also, the monthly mean fields of aerosol mass concentrations between February and May of 2000 are from the Global Ozone Chemistry Aerosol Radiation and Transport (GOCART) model [Chin, 2002], which includes 3-D dimensional sulfate, mineral dust, sea salt, hydrophobic and hydrophilic black carbon, and organic carbon [Mian Chin, Personal Comm., 2004]. Data that show >40% cloud cover are disregarded, as suggested by Martin *et al*. [2002]. Retrieval uncertainties are mostly due to spectral fitting, spectral artifacts from a diffuser

plate, the removal of stratospheric columns, and the AMF calculation [Martin *et al*., 2002].

OMI onboard the NASA Aura satellite, which passes over the equator at 1345 PM local time have horizontal resolutions of 13 km × 24 km. Algorithms for retrieving the OMI total and tropospheric NO_2 columns are described in previous studies by Boersma *et al*. [2001] and Bucsela *et al.* [2006]. Parameters such as viewing geometry, surface albedo, and the shape factor of NO_2 are needed to estimate AMF. Two AMF's are estimated using two shape factors from the Goddard Space Flight Center (GSFC) CTM and GEOS-CHEM, which are for unpolluted (the stratosphere and upper troposphere) and polluted (the lower and middle troposphere) NO_2 profiles, respectively. The radiance-weighted sum of clear and cloudy conditions is used to estimate each AMF. A detailed explanation about OMI NO_2 retrievals and total and tropospheric NO_2 data are available from http://disc.gsfc.nasa.gov/Aura/OMI/omno2.shtml.

1.2.2 Total CO Column from MOPITT

The MOPITT instrument on board the NASA Terra satellite provides the capability of globally monitoring CO through observations of two spectral bands: a solar band around 2.3 μm and a thermal band around 4.6 μm. The satellite passes over the equator at around 1045 AM and 2245 PM local time, and the horizontal resolution of MOPITT is 22×22 km^2. MOPITT detectors measure filtered radiance from the top of the atmosphere (TOA) from a gas correlation radiometer that produces gas correlation spectroscopy composed of an average response signal (A) and a different response signal (D) rather than capturing TOA radiance directly [Pan *et al*., 1995, 1998]. The retrieval

procedure of passive remote sensing measurements does not allow one to get delta function-type vertical profiles. Therefore, the solution of an inverse problem needs to be solved by an optimum estimate method with a priori information, filtered radiances, and data from the gas correlation radiometer [Rodgers, 2000]. If the probability distribution function (PDF) of a state vector (CO vertical profile) is proportional to that of an observed signal measured by a MOPITT instrument, an inverse problem with an ill-posed condition is resolved by minimizing the cost function.

MOPITT CO columns are obtained from a data pool of the NASA Langley Atmospheric Science Data Center (ASDC). The uncertainty of the CO columns, as reported by the data, averages 2×10^{17} molecules cm^{-2} for each datum. When compared to the MOPITT observations, simulated CO concentrations are processed with the MOPITT retrieval averaging kernel (AK), described in previous studies by Deeter *et al.* [2003] and Emmons *et al.* [2004]. First, corresponding simulated CO concentrations are estimated for the standard pressure levels of MOPITT: surface, 850, 700, 500, 350, 250 and 150 hPa; second, the AK matrix is estimated from the retrieval error covariance and the a priori covariance matrix; then the seven levels of CO concentrations processed with AK are calculated; and finally, the total number of CO columns is estimated with the retrieved CO concentrations at the pressure levels.

1.2.3 Tropospheric O$_3$ from TOMS-SAGE II and OMI-MLS

TOMS on board the Earth Probe satellite with an equator crossing time of 1116 AM local time measures incident solar radiation and backscattered ultraviolet sunlight, resulting in deriving total ozone; TOMS has a horizontal resolution of 39×39 km^2 and a

measurement uncertainty of about 5% (the random error is 2% and the systematic error about 3%) [ftp://toms.gsfc.nasa.gov/pub/eptoms/EARTHPROBE_USERGUIDE.PDF]. SAGE II on board the Earth Radiation Budget Satellite (ERBS) measures the Earth's limb extinction via the solar occultation technique during each spacecraft sunrise and sunset. The horizontal and vertical resolutions of SAGE are about 30×250 km^2 and 1 km, respectively. The scatter-plots of SAGE II (retrieval version 6.2) O_3 versus potential vorticity (PV) on isentropic surfaces are used to produce the O_3 profiles in the stratosphere [Jing *et al.,* 2004], which are coincident with the TOMS (version 8) total column O_3 measurements in latitude, longitude, and time. When the TOMS data indicate a reflectivity less than 20%, tropospheric O_3 columns are inferred by subtracting the SAGE II-based stratospheric columns from the TOMS columns. The PV values are obtained from the NCEP reanalysis data set, and the value of the 3.5 PV units is used to define the location of the tropopause. Based on comparisons with the ozonesondes, two previous studies by H. J. Wang *et al*. [2002, 2006] indicate that SAGE O_3 has an accuracy of 10% or better down to the tropopause with SAGE values almost 5% higher than the ozonesondes at an altitude between 15 and 20 km. A previous study by Jing *et al*. [2004] suggested that mapping produces individual O_3 values in the stratosphere with a precision of about 10%. However, this error tends to be random, and stratospheric columns averaged several days, for example, are expected to have significantly better precision.

OMI and MLS onboard the NASA Aura satellite that passes over the equator at 1345 PM local time have horizontal resolution of 13 km $\times$ 24 km and spatial resolution of 30 km $\times$ 150 km $\times$ 2.5 km, respectively. To derive a tropospheric O_3 column by

implementing a residual method, we have used a combination of MLS profiles above 215 hPa and averaged OMI level 2 total O_3, which satisfies a coincidence criterion with MLS profiles. OMI and MLS coincidence criteria are $\pm$ 1.25° longitude by 1.25° latitude and on the same day. The location of the tropopause is derived from the NCEP reanalysis data. Mid-latitude stratospheric O_3 columns for between 215 hPa and the tropopause are obtained by the SAGE II mapping profiles. Tropospheric O_3 columns are then obtained by subtracting the stratospheric O_3 columns from the OMI total columns. To prevent interference from clouds on the OMI total O_3 column, we use only total columns obtained under clear conditions, which is defined by a reflectivity of less than 10% based on OMI 360 nm reflectivity datasets. Yang *et al*. [2007] provide a detailed explanation.

1.2.4 3-D Global Chemical Transport Model, GEOS-CHEM

In order to prepare the initial and boundary chemical conditions for and cross-validate REAM, we use the GEOS-CHEM model [Bey *et al.,* 2001] driven by the assimilated meteorological observations for 2000, updated three to six hours from the GEOS of the NASA Data Assimilation Office (DAO) [Schubert *et al.,* 1993] for the 2000 simulations, and the assimilated meteorological data from GEOS-4 at the NASA Global Modeling and Assimilation Office (GMAO) for the 2005 simulations. The horizontal resolution of the used model (GEOS-CHEM 7.2) is 2° latitude by 2.5° longitude. The model has thirty vertical layers on a sigma level, reaching from the surface to 0.01 hPa. Thirty chemical tracers describing tropospheric O_3 chemistry are transported. A detailed photochemistry module, algorithms for dry and wet deposition, and emissions from vegetation and soils are described in a study by Bey *et al.* [2001].

1.2.5 3-D Regional Chemical Transport Model, REAM

1.2.5.1 Model framework

GEOS-CHEM is used to specify the initial and boundary conditions of chemical species in REAM. Lateral and top boundary conditions are updated hourly or daily. The REAM domain covers North America and the portion of the North Atlantic with a 70 km horizontal resolution. The numbers of horizontal grid points are 80 and 60, respectively, for west to east and south to north on a Lambert conformal map projection. REAM has 23 vertical layers from the surface to 10 hPa, and terrain-following σ coordinates are used. MM5 is run with four-dimensional data assimilation (FDDA) with the National Center Environmental Prediction (NCEP) reanalysis, rawinsonde, and surface observations [Zeng *et al.*, 2003]. Meteorological fields are also provided for 23 vertical sigma-coordinate levels from MM5. For the advection and diffusion processes, meteorological and physical variables are stored every half hour and interpolated every five minutes. The variables are archived every 2.5 minutes for cloud convection and lightning NO_X production. The integration of the chemical reaction, wet and dry deposition, and emissions are performed every hour.

For the transport of air pollutants, MM5 produces input variables (in unit): temperature (K), wind scalar velocities (m s^{-1}), cloud water mixing ratio (kg kg^{-1}), the rain water mixing ratio (kg kg^{-1}), diffusion coefficients (m^2 s^{-1}), pressure (Pa), convective precipitation (cm), non-convective precipitation (cm), surface albedo (fraction), land use (category), the periodic boundary layer (PBL), the top layer (dimensionless), PBL height (m), PBL regime (dimensionless), sensible heat flux (Wm^{-2}), frictional velocity (ms^{-1}), surface radiation (Wm^{-2}), soil temperature (K), 10-meter horizontal velocities (ms^{-1}), and

10

surface roughness (cm). As described, these variables are similarly used in other studies [McKeen *et al.*, 1991; Hess *et al*., 2000]. A photochemical module, the algorithms for dry and wet deposition, and emissions from vegetation and soils are adopted from GEOS-CHEM [Bey *et al*., 2001, and references hereafter]. REAM includes a detailed photochemical mechanism that includes about 200 reactions, the chemical concentration changes of 120 species are estimated, and 24 tracers (family or species) are transported to describe O_3-NO_X-hydrocarbon [Bey *et al*., 2001]. Detailed explanations follow.

1.2.5.2 Model components

Like conservation of energy and momentum, a chemical tracer needs to be conserved during the transport and vertical mixing processes. A transport module consists of horizontal advection, deep and shallow vertical convections, and diffusion. Transport caused by diffusion includes molecular diffusion caused by molecular collisions and eddy diffusion driven by mechanical shear and thermal buoyancy. The strength of the former is substantially weaker than that of the latter, so the former is not considered in REAM. The deposition process includes dry and wet depositions. The dry deposition of oxidants and soluble gases is estimated using a resistance-in-series model [Wesely *et al*., 1989] with some modifications [Wang *et al.,* 1998]. Large-scale wet deposition consists of washout and rainout. The former is caused by wet scavenging inside a cloud, and the latter rain scavenging below a cloud [Liu *et al*., 2001]. The convective scavenging of soluble species is separately considered in REAM, as described by Liu *et al*., [2001].

1.2.5.3 Advection and convection

11

We adopt an efficient and accurate tracer transport model scheme [Walcek, 2000, Zeng *et al*., 2003] to treat advection. Among the four different cumulus convection schemes [Jacobson, 1999], which include the moist convective adjust, Kuo, Arakawa-Schubert, and Grell schemes, we use the Grell scheme [1993] for cumulus convection parameterization in order to be consistent with the dynamic model, MM5. Transport through a cloud, which is on a sub-grid scale, is parameterized based on earlier studies [Lin *et al.,* 1994; Jacobson, 1999]. In order to incorporate deep cumulus convections in the model, we use the top levels of cloud, originating levels, and air mass fluxes for updraft and downdraft processes from MM5. The sub-grid scale updrafts of air masses are considered during updrafts from originating levels to cloud-top levels. The convective wet scavenging of soluble tracers is also considered during an updraft process. Large-scale downward subsidence follows. In nature, the mass of species is conserved. Likewise, during a downdraft process, as in an updraft process, a downdraft flux to the bottom layer is considered, and large-scale transport follows a downdraft process. The Grell scheme assumes that an entrainment occurs at the cloud bottom, a detrainment occurs at the cloud top, and neither entrainment nor detrainment occurs between the cloud top and bottom [Grell, 1993].

For shallow convection, the top and bottom layers of a shallow convection are determined by MM5, and a cloud fraction is estimated using relative humidity, as described by Geleyn [1981] and Lin *et al.* [1994]. A shallow convection that mixes chemical tracers between the two adjacent layers at a time exhibits neither precipitation nor a downdraft process.

1.2.5.4 Diffusion

For stable and weakly unstable conditions, turbulent (i.e., eddy) diffusion transports are considered using the K-theory (i.e., the gradient transport theory) [Holton, 1992; Jacob, 1999; Jacobson, 1999], which allows mixing between two adjacent layers. Under strong, unstable conditions, a full mixing method such as a free convective-plume scheme [Blackadar, 1978; Zhang and Anthes, 1982] is used to simultaneously mix a tracer for all layers within a boundary layer. Eddy diffusivities for the K-theory are from MM5, which depend on wind speed, surface roughness, surface heating, and altitude.

1.2.5.5 Chemical and photolysis reactions

We incorporate a chemistry module using a fast and numerically accurate Gear-type solver [Jacobson and Turco, 1994] in which an original Gear's code is combined with a sparse-matrix and computer optimization technique [Jacobson, 1999]. Inside the chemistry module, one hundred twenty species are included in a chemistry mechanism. Moreover, the surface areas of sulfate aerosols are calculated using the concentrations of aerosols from Chin *et al*., [1996], as described by Y. Wang *et al*., [1998]. Photolysis rates are calculated with the fast and flexible FAST-J algorithm of Wild *et al*. [2000], which accounts for cloud, aerosol, and Mie scattering. Cloud optical depths are calculated using MM5 cloud water content [Stephens *et al*., 1978; Weele *et al.,* 1993; Salby, 1996]. The source of UV surface albedo is the TOMS satellite [Herman and Celarier, 1997].

1.2.5.6 Dry and wet depositions

Dry deposition velocities are calculated using a resistance-series scheme [Wesley, 1989; Seinfeld and Pandis, 1998]. These resistances are calculated, with some modifications, using Monin-Obukhov length, momentum, temperature, friction velocity, solar irradiation, and resistance variables on the basis of the formulas of Wesely [1989] [Y. Wang *et al.,* 1998; Bey *et al.,* 2001]. Variables are calculated or directly archived from MM5. Ozone, NO_2, nitric acid (HNO_3), hydrocarbon peroxide (H_2O_2), formaldehyde (HCHO), peroxyacetic acid (PAN), and NO are considered in the dry deposition process. For the wet scavenging process, two scavenging processes are considered: One accounts for scavenges that occur during the updraft convection of deep cumulus convection [Hess *et al.,* 2000; Liu *et al.,* 2001], and the other is from large-scale precipitation due to rainout and washout by stratiform and convective anvil precipitation, respectively [Giorgi and Chameides, 1986; Liu *et al.,* 2001]. Wet scavenging accounts for the scavenging of tracers with high solubility, which include HNO_3, H_2O_2, HCHO, and methyl hydroperoxide (CH_3OOH).

1.2.5.7 Emissions

For NO_X emissions, the EPA 1999 National Emission Inventory (referred to as NEI99) Version 2, the National Acid Precipitation Assessment Program (NAPAP), and the Global Emission Inventory Activity (GEIA) [Benkovitz *et al*., 1996; Yienger and Levy, 1995] are used in the United States, Canada, and Mexico, respectively. For CO emissions, NEI99 is used in the United States, and CO emissions developed at Harvard [Bey *et al*., 2001] are used in the other regions. Industrial non-methane hydrocarbon (NMHC) emissions are based on a study by Y. Wang *et al.* [1998]. For biogenic

emissions, the emission rates of isoprene and monoterpene are estimated by a modified version by Y. Wang *et al.* [1998] using an algorithm by Guenther *et al.* [1995]. The biogenic emissions of acetone are by Jacob *et al.* [2002]. Propene and CO productions due to the oxidation of isoprene and monoterpene are scaled to isoprene and monoterpene emissions as described by Bey *et al.* [2001]. The monthly averaged leaf area index (LAI) is from 1 km Advanced Very High Resolution Radiometer (AVHRR) data between April 1992 and March 1993 [Bonan *et al.*, 2002]. A detailed explanation of lightning NO_X production parameterization follows.

1.2.5.8 Lightning NO_X parameterization

NO_X production due to lightning flash is estimated, and the produced NO molecules are distributed vertically to the top cloud layer in the model. There are two flash types, cloud-to-ground (CG) and intracloud (IC) flashes. Lightning consists of a number of strokes, but NO_X is primarily produced during the high-energy return stroke phase of the flash [Price *et al.*, 1997]. The NO molecules per IC flash are estimated to be one-tenth that of a CG flash (6.7×10^{26} NO molecules flash^{-1}) in some previous studies [Prince *et al.*, 1997; Pickering *et al.*, 1998; Allen *et al.*, 2000; Allen and Pickering, 2002]. Compared with the NO production rates of CG flash, equivalent rates are used for IC flash in several more recent studies [DeCaria *et al.*, 2000; Ott *et al.*, 2003; Zhang *et al.*, 2003; Fehr *et al.*, 2004; Choi *et al.*, 2005, 2007a, 2007b]. Based on cloud-resolving modeling output compared with anvil aircraft NO_X observations over the U.S., the average NO production per flash for both IC and CG flashes is about $2\text{-}4\times10^{26}$ NO molecules [K. Pickering, Personal Comm., 2005]. Ott *et al.* [2003] use 3.0×10^{26}

molecules per flash for IC and CG flashes. We assume that NO production per IC flash is the same as that per CG flash. The NO production rate per flash used by Choi *et al.* [2005, 2007a] is 6.0×10^{26} NO molecules during the spring of 2000 and 3.0×10^{26} molecules [Choi *et al.*, 2007b] during the summer of 2005. Sensitivity results suggest that these values show better agreement with GOME and OMI measurements. Lightning NO_X is distributed vertically following a mid-latitude profile by Pickering *et al.* [1998].

Two separate parameterizations are constructed for continental and oceanic regions [Price and Rind, 1993] using measurements from the National Lightning Detection Network (NLDN). The detection efficiency reported by Cummins *et al.* [1981] is used. We parameterize the lightning NO_X production rate as a function of meteorological variables so that the emissions are consistent with the dynamic model, MM5. We experiment with cloud top height [Price and Rind, 1993], convective mass flux [Allen and Pickering, 2002], and convective available potential energy (CAPE) [Choi *et al.*, 2005, 2007a, 2007b]. We use both CAPE and cloud mass fluxes to take advantage of the different distributions of the two variables. However, the two meteorological variables must be normalized. The CG flashing rate for continental and oceanic regions are mathematically expressed in terms of normalized convective mass flux (M) and CAPE (C):

$$
\begin{aligned}
LF_{cg} = a_0 &+ aM + bM^2 + cM^3 + dC + eC^2 + fC^3 + gMC \\
&+ hM^2C + iMC^2 + jM^4 + kM^3C + lM^2C^2 + mMC^3 + nC^4
\end{aligned}
,
$$

where for a continental region, $a_0 = 0.00495$, $a = 4.219$, $b = 15.5064$, $c = -112.492$, $d = -2.089$, $e = 48.143$, $f = -53.983$, $g = -121.956$, $h = 358.118$, $i = 208.105$, $j = 108.613$, $k = -$

216.226, l = -330.354, m = -134.307, n = 16.742 and for an ocean region, a_0 = 0.126, a = 2.669, b = -0.854, c = -61.793, d = -2.482, e = 24.35, f = 26.739, g = -31.732, h = 288.129, i = -185.419, j = 63.089, k = -178.063, l = -151.659, m = 204.120, n = -34.408.

Once the CG flashing rate is estimated, the IC to CG flash rate ratio is calculated following Y. Wang *et al.* [1998].

1.3 Scope of This Dissertation

This dissertation focuses on the modeling analysis of the transitions of O_3 and its precursors over North America from the spring to the summer and the photochemistry over Antarctica from in-situ and satellite observations. Chapter 2 provides evidence from satellite observations over North America of lightning NO_X production and the convective transport of pollutants. Column observations of NO_2 and CO by GOME and MOPITT, measured separately over North America for April 2000, are investigated using REAM and the transient enhancements in these measurements due to lightning NO_X production and the convective process are examined. Chapter 3 presents the modeling analysis of the transition of air pollutants over North America from late winter to spring on the basis of in situ and satellite measurements. Trace gas simulations using REAM over North America between February and May of 2000 are analyzed to elucidate the impact of the springtime transition derived by the following factors: cloud convection, lightning NO_X production, soil NO_X emissions, and mixing depth on the concentrations and exports of key tracers. In situ observations from the EPA AIRNow and SEARCH ground network, aircraft observations from the TOPSE and MOZAIC experiments,

ozonesondes, and space-borne observations from GOME, MOPITT, TOMS and SAGE II satellite measurements are analyzed.

Chapter 4 presents a modeling analysis of the spring to summer transitions of O_3 and its precursors over North America between April and August of 2005 on the basis of satellite observations and examines the seasonal trend of tropospheric O_3 from OMI-MLS satellite observations. O_3 column peaks are generally constrained by the stratospheric input, convective outflows of the O_3 precursors and lightning NO_X production during the spring and the summer. Chapter 5 shows the late-spring increases of the transport of trans-Pacific pollution in UT using O_3 and other key tracers. In this chapter, large enhancements of air pollutants such as NO_X, PAN, CO, CFCs, and Halon-1211 in UT are shown over North America in the late spring. An analysis of these observations and model results indicates that enhancements are driven by trans-Pacific pollutant transport. Chapter 6 presents a modeling analysis that assesses the photochemical impact of snow NO_X emissions over Antarctica during ANTCI 2003. 1-D CTM and 3-D CTM, REAM are used to analyze these measurements and assess the photochemical impact of snow emissions. The polar version of MM5 with a modification of the ETA turbulence scheme is used to simulate the heights of the boundary layer from Sound Detecting and Ranging (SODAR) measurements at SP. Daytime snow NO_X emissions are parameterized as a function of temperature and wind speed. The emission fluxes, deposition fluxes, and transported fluxes of nitrogen tracers over Antarctica are also estimated. Chapter 7 concludes.

CHAPTER II

EVIDENCE OF LIGHTNING NO$_X$ AND CONVECTIVE TRANSPORT OF POLLUTANTS IN SATELLITE OBSERVATIONS OVER NORTH AMERICA

2.1 Introduction

Convective outflow is an important pathway for ventilating pollutants from the boundary layer to the free troposphere; subsequent transport of these pollutants has significant ramifications for hemispheric and global air quality. The effects of such processes over North America have been previously investigated using 3-D chemical transport simulations and surface and aircraft observatio[1]ns [e.g., Thompson *et al.,* 1994; Horowitz *et al.*, *1998*; Liang *et al.*, 1998; Park *et al.*, 2004b; Li *et al.*, 2005]. However, in situ observations of convective outflow are limited because of the sporadic nature of convection and aircraft operational difficulties. Recent advancements in satellite observations could potentially provide additional constraints on model simulated convective outflow.

Satellite observations of trace gases and aerosols have been used to detect forest fire plumes [Thomas *et al.,* 1998; Spichtinger *et al.*, 2001; Lamarque *et al.*, 2003]. In comparison, convective outflow is more difficult to detect due in part to cloud interference. Li *et al.* [2005] showed that despite this interference, satellite observations of CO and aerosol optical depth are useful for mapping convective outflow from North America to the western North Atlantic. In addition, indications were found for lightning

activity in the monthly/seasonally averaged NO_2 columns over the tropical Atlantic observed by the Global Ozone Monitoring Experiment (GOME) [Richter and Burrows, 2002; Edwards *et al.,* 2003].

In this work, we make use of GOME NO_2 observations and Measurements Of Pollution In The Troposphere (MOPITT) observations of CO to evaluate the simulations of REAM. Both NO_2 and CO are good chemical tracers for convection. Lightning during convection provides a major source of NO_X ($NO+NO_2$) in the free troposphere [e.g., Price and Rind, 1993].

We analyze model simulations and satellite observations for April 2000 because of frequent cyclonegenesis and convective events over North America during that period. The analysis is carried out on a daily basis to emphasize the transient nature of convection. We conduct two model simulations with and without lightning NO_X production and compare these results with GOME observations. Carbon monoxide has much higher concentrations near the surface due to combustion and industrial emissions over North America. To test the effects of convection on CO concentrations, we conduct a sensitivity simulation in which convective transport of CO is turned off and then the standard and sensitivity simulations in light of MOPITT observations are compared.

2.2 GOME and MOPITT Retrievals

The retrieval of tropospheric NO_2 columns from GOME measurements and its uncertainty are calculated using the algorithms by Martin *et al.* [2002]. The retrieval uncertainties are due to spectral fitting, spectral artifact from the diffuser plate, the removal of the stratospheric column, and the calculation of the air mass factor. The

MOPITT CO columns are obtained from the data pool at the NASA Langley Atmospheric Science Data Center (ASDC). Only MOPITT retrievals with an a priori fraction of <50% were used. The uncertainty of CO columns as reported by the data is about 2×10^{17} molecules cm^{-2} in this work. When compared with the observations, the simulated CO results were processed using the MOPITT retrieval averaging kernel described by Deeter *et al.* [2003] and Emmons *et al.* [2004]. The horizontal resolutions of GOME and MOPITT are 40×320 and 22×22 km^2, respectively.

2.3 Model Description

REAM has a horizontal resolution of 70 km with 20 vertical layers below 100 hPa. The National Center for Atmospheric Research/Penn State MM5 was used to simulate the meteorological fields using four-dimensional data assimilation with the National Center for Environmental Prediction reanalysis, surface, and rawinsonde observations. Most meteorological variables were archived every 2.5 minutes. The horizontal domain of MM5 has five extra grids beyond that of REAM on each side to minimize potential transport anomalies near the boundary. As in the work by Zeng *et al.* [2003], spring 2000 simulations using the global GEOS-CHEM model [Bey *et al.*, 2001] provide the initial and boundary conditions for trace gases. The regional simulations were spun up during the last week of March.

REAM was updated from the previous model by McKeen *et al*. [1991]. The transport scheme by Walcek [2000] was adopted. Twenty-four chemical tracers describing tropospheric O$_3$ chemistry [Bey *et al.,* 2001] were transported. The convective scheme by Grell [1993] was implemented so that it was consistent with the

meteorological model. The photochemistry module, and the algorithms for dry and wet deposition and emissions from vegetation and soils are adopted from GEOS-CHEM [Bey *et al.* 2001, and references therein]. Biogenic emissions of hydrocarbons are limited to the regions south of 30°N in April. The monthly mean leaf area index distribution was derived from the Advanced Very High Resolution Radiometer data by Bonan *et al.* [2002]. Emission inventories for combustion and industrial sources were also taken from GEOS-CHEM [Bey *et al.*, 2001], except that fossil fuel NO_X and CO emissions over the United States were taken from the 1999 US Environmental Protection Agency National Emission Inventory. The lightning NO_X algorithm is described in Appendix 2.A. Cloud-to-ground flashes in the model are constrained by observations from the National Lightning Detection Network (NLDN).

2.4 Results and Discussion

2.4.1 Is Lightning NO_X Evident in GOME Observations?

Monthly mean-simulated tropospheric NO_2 column compares well with the GOME observations (not shown). We find a correlation coefficient of 0.95 with little mean bias (-3%). Our main goal in this work is to determine if transient convection features such as lightning NO_X production can be detected in the GOME observations. Large convective or cyclonegenesis events were simulated on April 7-10, 14-16, 18-22, 25-27, and 29-30. Generally, we find corresponding NO_2 column enhancements associated with these events. We illustrate four specific days of April 20, 21, 27, and 29 (Figure 2.1).

Figure 2.1 GOME retrieved and the corresponding REAM simulated tropospheric NO_2 vertical column on April 20, 21, 27, and 29, 2000. GOME columns less than the spectral fitting uncertainties are not included. Simulations with and without lightning NO_X production are shown. The last column shows the simulated lightning NO_2 enhancements.

The model simulations with lightning NO_X are clearly in much better agreement with the observations. All four cases show various degrees of lightning enhancements over the western North Atlantic. The April 29 case also shows significant continental enhancements from western Texas to Kansas. However, the lightning signals are more difficult to detect over the continent because of surface emissions. The standard model underestimates NO_X concentrations over the western North Atlantic on April 20 and 21 but tends to overestimate them on April 27.

The lightning enhancements are 0.5-1 $\times$ 10^{15} molecules cm^{-2} on April 20 and 21 and >1 $\times$ 10^{15} molecules cm^{-2} on April 27 and 29. Following Martin *et al.* [2002], we estimate the uncertainties of GOME NO_2 vertical columns to be 50-100% of the lightning enhancements simulated in the model. The relative uncertainties are at the high end for April 20 and 21, when the model underestimates lightning NO_X enhancements over the western North Atlantic. Satellite observations with improved spatial coverage and lower uncertainty than GOME should provide better quantitative constraints on lightning production of NO_X.

We select a grid box with large lightning NO_X enhancements on April 27 to illustrate the altitude dependence of the lightning NO_X contribution to the NO_2 column (Figure 2.2). NO_2 lightning enhancements are in the lower and upper troposphere, corresponding to the "C"-shaped NO_X profile by Pickering *et al.* [1998]. Enhancement of the upper tropospheric NO is far more prominent than that of NO_2 because the NO/NO_2 ratio increases with decreasing temperature. The large enhancements in the lower troposphere are due to convective downdrafts. The contribution to column enhancement

Figure 2.2 Scattering weights under clear and cloudy sky conditions for the standard model NO_2 simulation on April 27 over the grid box indicated by the black circle in Figure 2.1. Also shown as a function of pressure is the simulated enhancement of NO_2 due to lightning NO_X production. The scattering weight represents the sensitivity of backscattering radiance measured by GOME to NO_2 concentrations at a given level.

by NO_2 above 600 hPa is larger than in the lower troposphere (below 850 hPa) in part because of the larger scattering weight at higher altitudes (Figure 2.2).

2.4.2 Signals of Convective Transport in MOPITT CO Observations

The simulated monthly mean CO column also compares well with MOPITT observations (not shown). We find a linear correlation coefficient of 0.88 with little mean bias (-2%). As in the previous section, we select three cases on April 20, 21, and 27 to illustrate the effects of convection on CO column concentrations (Figure 2.3). The effects are found over the ocean because the only difference between standard and sensitivity simulations is the convective transport of CO. Its effect is to lift CO, emitted from the surface, into a higher altitude, where wind speeds are higher than they are near the surface. As a result, higher-altitude CO lifted by convection is carried over the ocean faster in a more westerly flow compared to that near the surface, creating the enhancements seen in Figure 2.3. The April 29 case is not shown because the convection is mostly limited to land (Figure 2.1).

The simulations without the convective transport of CO clearly underestimate CO columns over the western North Atlantic. The standard simulations agree much better with the observations. The model tendencies that underestimate CO enhancements on April 20 and 21 but overestimate CO enhancements on April 27 are consistent with the results for lightning NO_X enhancements. The simulated CO column enhancements are above the MOPITT retrieval uncertainty of 2×10^{17} molecules cm^{-2}.

Figure 2.3 The same as Figure 2.1, but for MOPITT-retrieved and REAM-simulated CO columns on April 20, 21, and 27, 2000. The model results with and without convective transport have been processed with the MOPITT averaging kernel.

Figure 2.4 Simulated CO concentrations with and without convective transport as a function of pressure on April 27 over the grid box indicated by the orange circle in Figure 2.3.

The altitude dependence of the CO enhancement contribution for a selected grid box on April 27 is shown in Figure 2.4. The profile with the convective transport of CO compared to that without is much higher at 300 hPa and 700-980 hPa, but it is lower near the surface due to the redistribution of CO by convective transport. The 700-980 hPa enhancement due to shallow convection is much larger than that at 300 hPa due to deep convection. This result is consistent with our finding that mass fluxes of shallow convection are much larger than deep convection in MM5 simulations during this period.

2.5 Conclusions

Chemical tracer distributions are strongly affected by convective transport and, in the case of NO_X, lightning production. We show that column observations of NO_2 by GOME and CO by MOPITT can be used to identify these transient features when used in combination with 3-D chemical transport model simulations. The two independent measurements show consistent convection related enhancements in terms of geographic location and model bias. While the middle and upper tropospheric contribution from lightning NO_2 to the column enhancements is more significant, the major contribution to CO column enhancements is from the lower troposphere. The model results indicate large enhancements in the lower atmosphere of lightning NO_2 (due to convective downdrafts) and transported CO (due to shallow convection), suggesting that low-altitude aircraft in situ observations can potentially provide valuable and critical observations for evaluating model simulations and validating satellite observations.

Appendix 2.A: Lightning NO_X parameterization

We parameterize the lightning NO_X production rate as a function of meteorological variables so that this emission is consistent with model dynamics. In our work, we experimented with cloud top height [Price and Rind, 1993], convective mass flux [Allen and Pickering, 2002], and convective available potential energy (CAPE). We found that the parameterization with CAPE produces a similar but better lightning flash distribution than cloud top height when compared with NLDN observations and that CAPE is a better variable for parameterizing lightning flashes than convective mass flux over the southern part of North America and the western Atlantic. To take advantage of the distribution difference between CAPE and convective mass flux, both variables are used in the parameterization (up to the 4th order, including cross terms). Two parameterizations are created separately for the land and the ocean. The intracloud (IC) to cloud-ground (CG) flash ratio is calculated following Y. Wang *et al.* [1998]. We assume that IC and CG flashes have the same energy [Ott *et al.*, 2003]. The rate of NO produced per unit energy is that of Pickering *et al.* [1998]. Lightning NO_X is distributed vertically following the mid-latitude profile by Pickering *et al.* [1998].

MODELING ANALYSIS OF SPRINGTIME TRANSITION OF NO$_2$, CO, AND O$_3$ OVER NORTH AMERICA ON THE BASIS OF IN SITU AND SATELLITE MEASUREMENTS

3.1 Introduction

Ozone (O$_3$), carbon monoxide (CO) and nitric oxides (NO$_X$ = NO+NO$_2$), which are regulated under EPA's National Ambient Air Quality Standards, are among the six EPA criterion pollutants that adversely affect human health and biological ecosystems [NRC, 1991]. Ozone is a major precursor of the hydroxyl radical (OH), which plays a key role in oxidation chemistry in the troposphere. It is also considered a greenhouse gas, particularly in the upper t^{2}roposphere. NO$_X$ and CO are major O$_3$ precursors produced during combustion. NO$_X$ is also emitted from soils and lightning, and CO is produced during the oxidation of anthropogenic and biogenic hydrocarbons.

Previous studies show that spring is the season of rapid transitions in trace gas concentrations and photochemical activity [Blake *et al*., 2003; Cantrell *et al*., 2003; Davis *et al*., 2003; Emmons *et al*., 2003; Y. Wang *et al*., 2003; Kondo *et al*., 2004]. Besides changes in solar insolation, a number of physical processes change drastically during the spring. Among them, we are particularly interested in NO$_x$ emissions from lightning and soils, convective transport, and the mixing depth in the boundary layer. These factors lead to higher surface concentrations and tropospheric columns of ozone. They also affect the

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[2]This chapter is for "Modeling analysis of springtime transition of NO$_2$, CO, and O$_3$ over North America on the basis of in situ and satellite measurements," prepared for the submission to *Journal of Geophysical Research* in 2007. Authors are Y. Choi, *et al*.

export of pollutants from North America. The following will discuss each factor and its observational constraints.

Warmer temperature and the increasing abundance of water vapor result in more frequent convection and lightning [Rind, 1998; Price, 2000; Soden, 2000]. Choi *et al.* [2005] showed that day-to-day enhancements of lightning NO_X can be detected from Global Ozone Monitoring Experiment (GOME) measurements but stressed that satellite retrieval uncertainties [Martin *et al.*, 2002] must be taken into account. Edward *et al.* [2003] showed a linkage between lightning NO_X over southern Africa and South America, and the Total Ozone Mapping Spectrometer (TOMS) measured O_3 in the tropical southern Atlantic. Therefore, lightning NOx production could be a major contributor to the increase in the tropospheric O_3 column over North America during the spring. In this study, we use TOMS total ozone columns and the Stratospheric Aerosol and Gas Experiment (SAGE) II stratospheric ozone columns to derive tropospheric ozone columns and investigate any trends. We then evaluate the derived tropospheric ozone columns with ozonesonde measurements. We find that CO is a good tracer for convective transport [e.g., Choi *et al.*, 2005]. In situ observations of free tropospheric CO are available from the Tropospheric Ozone Production about the Spring Equinox (TOPSE) experiment of 2000. Although the measurement region is not affected by convective transport, these measurements can be used to evaluate the results of the Measurement of Pollution In The Troposphere (MOPITT). Soil NO_X emissions also increase during spring as temperature increases [Yienger and Levy II, 1995]. Although no direct in situ measurements are available to constrain this source, GOME measurements may be useful to constrain this source [e.g., Martin *et al.*, 2003; Jaegle *et al.*, 2005]. It

remains to be seen if this source is large enough to detect in the satellite measurements in the spring.

For the identification of seasonal changes in ozone, CO, and NO_x, a large number of surface in situ measurements from AIRNow and Southeastern Aerosol Research and Characterization Study (SEARCH) observation networks can be examined. These networks show that one key process that affects pollutant surface concentrations is the rapid change of mixing depth during the spring [Holzworth, 1964, 1967]. Although routine meteorological measurements do not provide measurements of daytime mixing depth, 3-D CTMs can be used to determine this effect.

Regional [McKeen *et al*., 1991; Hess *et al*., 2000; Song and Carmichael, 2001; Choi *et al*., 2005] and global 3-D CTM [Brasseur *et al*., 1998; Y. Wang *et al*., 1998; Lawrence *et al*., 1999; Levy *et al*., 1999; Lelieveld and Denter, 2000; Bey *et al*., 2001; Park *et al*., 2004a] have been developed to explain chemical and physical processes in the atmosphere. In this work, we apply the Regional chEmical trAnsport Model (REAM) [Zeng *et al*., 2003, 2006; Choi *et al*., 2005; Jing *et al*., 2006; Y. Wang *et al*., 2006, 2007] to simulate the seasonal transition of ozone and its precursors over North America during spring 2000. The model results will be evaluated based on surface, balloon, aircraft, and satellite measurements.

Through the combination of model simulations and satellite measurements, "top-down" estimates of emissions have been used to constrain "bottom-up" inventories [Leue *et al*., 2001; Martin *et al*., 2003, 2006; Arellano *et al*., 2004; Jaegle *et al*., 2004, 2005]. In this work, we apply the same approach to estimate surface NO_X emissions and compare them with the a priori inventories. In particular, we test the sensitivities of the a posteriori

inventories to the air mass factor (AMF), which is calculated using the vertical profiles of NO_2 from the model results. For this purpose, two model results will be used in the comparison. Finally, using the results of the REAM model, we examine the export of O_3 and its precursors from the boundary layer of North America [Horowitz *et al*., 1998; Liang *et al*., 1998; Park *et al*., 2004b] and the springtime transitions of pollutant exports. We also examine the vertical profiles of the import and export fluxes of these tracers and the factors affecting the fluxes.

We first described the measurement data, including the surface measurements of O_3 from the EPA AIRNow network and of NO, CO, and O_3 from the surface SEARCH, aircraft measurements of CO from the TOPSE experiment and of O_3 from the Measurement of Ozone and Water Vapor by Airbus In-Service Aircraft (MOZAIC) program, and ozonesondes. Satellite measurements include GOME NO_2, MOPITT CO, and TOMS-SAGE II O_3. The regional REAM and global GEOS-CHEM models are described in Section 3.3. We evaluate the REAM simulated springtime transitions of O_3 and its precursors with surface, ozonesonde, aircraft, and satellite measurements in Section 3.4. In this section, we also analyze the top constraints of surface NO_X emissions and the exports of O_3 and its precursors from North America. Conclusions are given in Section 3.5.

3.2 In situ and Satellite Measurements

3.2.1 Surface Measurements

3.2.1.1 The EPA AIRNow network

Hourly O_3 concentrations are obtained from the EPA AIRNow data archives [www.epa.gov/ttnairs1/airsaqs/detaildata/downloadaqsdata.htm]. The EPA network contains considerably more O_3 measurement sites than NO_X and CO sites. The sites are divided into three categories: urban, suburban, and rural. Since they are more representative of the region, the 291 rural sites are used. The CO and NO_X measurements are not used because of their high method detection limits (MDL) of 0.5 ppmv of CO and 5 ppbv of NO_x [Jake Summers, Personal Comm., 2004]. However, rural CO and NO_X measurements are usually below the MDL values, reported at one-half the MDL. The MDL value for O_3 was 5 ppbv. We focus on the afternoon (1300 to 1700 LT) when surface observations are more representative due to strong turbulent mixing in the planetary boundary layer (PBL).

3.2.1.2 The SEARCH network

Hourly O_3, NO, and CO are measured at eight SEARCH sites: Yorkville (YRK, rural), Jefferson Street (JST, urban), Centreville (CTR, rural), Outlying Landing Field #8 (OLF, suburban), Pensacola (PNS, urban), Gulfport (GFP, urban), Oak Grove (OAK, rural), and North Birmingham (BHM, urban). The SEARCH data of trace gases are obtained from the web [www.atmospheric-research.com/public/index.html]. For our analysis, we use observations from the following rural and suburban sites: YRK, CTR, OLF, and OAK. The detection limits of O_3, NO, and CO are 1 ppbv, 50 pptv, and 10 ppbv, respectively [E. S. Edgerton, Personal Comm., 2007].

3.2.2 Aircraft Observations

3.2.2.1 MOZAIC

The MOZAIC program was designed to automatically collect O_3 and water vapor data on five commercial Airbus A340 aircraft [Marenco *et al*., 1998]. For recent updates, see http://www.aero.obs-mip.fr/mozaic/. We use MOZAIC O_3 measurements recorded from February to May 2000. For the ascent and descent portions of the flights, MOZAIC raw data (4s time resolution) are averaged over 150 m height intervals. The MOZAIC analyzer is the dual-beam UV absorption Model 49-103 from Thermo Environment Instruments [Thouret *et al.,* 1998]. The instruments are laboratory-calibrated before and after flight and re-calibrated every 12 to 18 months. During any flight operation, each instrument is checked for zero and the calibration factor using a built-in ozone generator.

3.2.2.2 TOPSE

The TOPSE experiment took place from February to May 2000 [Atlas *et al.,* 2003]. The objective of TOPSE was to investigate the chemical and dynamical changes in the tropospheric chemical components over North America covering the region from Colorado to north of Thule, Greenland, during the late winter to spring transition. Thirty-eight science flights were conducted in seven deployments that were one to two weeks apart. Diverse trace gases related to tropospheric O_3 chemistry were measured from the surface up to 8 km. Several aircraft flights between March and May are concurrent with MOPITT overpasses.

3.2.3 Ozonesondes

We use ozonesonde data from February to May of 2000 from six mid-latitude stations located between 35°N and 53°N: Huntsville (35°N, 87°W), Wallops Island (38°N, 75°W), Boulder (40°N, 105°W), Trinidad Head (41°N, 124°W), Richland (46°N, 119°W), and Goose Bay (53°N, 50°W). The electrochemical concentration cell (ECC) sensor is typically used and the accuracy is about ±6% on the ground and -7% to 17% in the middle and upper troposphere [Komhyr *et al.,* 1995]. The ozonesonde data are mainly obtained from the World Ozone and Ultraviolet Data Center (WOUDC) [http://www.woudc.org].

3.2.4 Satellite Retrievals

The GOME instrument is on board the European Remote Sensing-2 (ERS-2) satellite that passes over the equator at 1030 AM local time, and its horizontal resolution is 40 km latitude by 320 km longitude. The DOAS algorithm with AMF calculation is described by Chance *et al.* [2000] and Martin *et al.* [2002]: First, the slant column is determined by fitting directly backscattered radiance spectra from GOME; then a stratospheric column determined from the NO_2 column over the central Pacific [Martin *et al.,* 2002] is subtracted from the total column; and finally, the subtracted columns are converted to a vertical column with AMF, which is an integral of the product of the shape factor from model-calculated vertical profiles and the perturbation of backscattered radiance of NO_2. The radiance perturbation due to the change of NO_2 is calculated from the Linearized Discrete Ordinate Radiative Transfer (LIDORT) model [Spurr *et al.,* 2001], which considers multiple scattering in the atmosphere. Data of the cloud optical depth and fraction are from GOME [Kurosu *et al.,* 1999]. The monthly mean fields of

aerosol mass concentrations are taken from the Global Ozone Chemistry Aerosol Radiation and Transport (GOCART) model [Chin, 2002], which simulates 3-D distributions of sulfate, mineral dust, sea salt, hydrophobic and hydrophilic black carbon, and organic carbon [Mian Chin, Personal Comm., 2004]. We do not use the measurements when the cloud cover is >40% [Martin *et al*., 2002]. The retrieval uncertainties are mostly due to spectral fitting, spectral artifact related to the diffuser plate, removal of the stratospheric column, and AMF calculations [Martin *et al.,* 2002; Choi *et al.,* 2005]. The uncertainties are generally 0.6-1.2 $\times$ 10^{15} molecules cm^{-2} over the ocean and 1.0-3.5$\times$10^{15} molecules cm^{-2} over the continent.

The MOPITT instrument on board the NASA Terra satellite is capable of globally monitoring CO through observations of two spectral bands: a solar band around 2.3 μm and a thermal band around 4.6 μm. The satellite passes over the equator at around 1045 AM and 2245 PM local time, and the horizontal resolution of MOPITT is 22$\times$22 km^2. MOPITT measures filtered radiance from the top of the atmosphere (TOA) from a gas correlation radiometer that produces gas correlation spectroscopy composed of an average response signal (A) and a different response signal (D) rather than capturing TOA radiance directly [Pan *et al.,* 1995, 1998]. If the probability distribution function (PDF) of a state vector (CO vertical profile) is proportional to that of an observed signal measured by a MOPITT instrument, an inverse problem with an ill-posed condition is resolved by minimizing a cost function. MOPITT CO columns are obtained from the data pool of the NASA Langley Atmospheric Science Data Center (ASDC). The uncertainty of CO columns, as reported by the data, averages 2 $\times$ 10^{17} molecules cm^{-2}. In our model evaluation, simulated CO concentrations are processed with the MOPITT

retrieval averaging kernel (AK), described in previous studies [Deeter *et al.*, 2003, Emmons *et al.*, 2004].

TOMS on board the Earth Probe satellite that crosses the equator at 1116 AM local time measures incident solar radiation and backscattered ultraviolet sunlight, resulting in deriving total ozone. TOMS has a horizontal resolution of 39×39 km^2 and a measurement uncertainty of about 5% (the random error is 2% and the systematic error is about 3%) [ftp://toms.gsfc.nasa.gov/pub/eptoms/EARTHPROBE_USERGUIDE.PDF]. SAGE II on board the Earth Radiation Budget Satellite (ERBS) measures the Earth's limb extinction via the solar occultation technique during each spacecraft sunrise and sunset. The horizontal and vertical resolutions of SAGE are about 30×250 km^2 and 1 km, respectively. Scatter-plots of SAGE II (retrieval version 6.2) O_3 versus Potential Vorticity (PV) on isentropic surfaces are used to produce the O_3 profiles in the stratosphere [Jing *et al.,* 2004], which are coincident in latitude, longitude, and time with TOMS (version 8) total column O_3 measurements. When the TOMS data indicate a reflectivity less than 20%, tropospheric ozone columns are inferred by subtracting the SAGE II-based stratospheric from the TOMS columns. The PV values are obtained from the NCEP reanalysis data set, and a value of 3.5 PV units is used to define the location of the tropopause.

By comparison with the ozonesonde measurements, two previous studies [H.-J. Wang *et al.,* 2002, 2006] indicate that SAGE O_3 has an accuracy of 10% or better down to the tropopause, the SAGE values being almost 5% higher than the ozonesonde values at an altitude between 15 and 20 km. A previous study [Jing *et al.,* 2004] suggested that PV mapping produces individual O_3 values in the stratosphere with a precision of about

10%. Thus, the measurement uncertainties of TOMS-SAGE become about 21%. However, this error tends to be random, and stratospheric columns averaged for several days, for example, are expected to have significantly better precision, resulting in smaller measurement uncertainties of TOMS-SAGE II.

3.3 Model Descriptions

3.3.1 Regional chEmical trAnsport Model (REAM)

3.3.1.1 General description

In this work, REAM has a horizontal resolution of 70 km with 23 vertical layers reaching 10 hPa, 20 of which are below 100 hPa. The National Center for Atmospheric Research/Penn State MM5 is used to simulate meteorological fields using four-dimensional data assimilation (FDDA) [Stauffer *et al*., 1991] with the National Center for Environmental Prediction reanalysis, surface, and rawinsonde observations. Most of the meteorological variables are archived every 30 minutes, except convection and lightning, which are archived every 2.5 minutes because of the highly variable nature of these processes. The horizontal domain of MM5 has five extra grids beyond that of REAM on each side to minimize potential transport anomalies near the boundary. We use the ETA Mellor-Yamada-Janjic (MYJ) 2.5-order closure scheme [Black, 1994] for turbulent calculations.

The photochemical, dry, and wet deposition modules of REAM are adopted from the GEOS-CHEM model [Bey *et al.,* 2001]. The altitude-dependent cloud optical depth is calculated using MM5 liquid water content [Stephens *et al*., 1978]. The UV surface albedo for photolysis rate calculations is obtained from TOMS observations [Herman and

Celarier, 1997]. The transport scheme is from Walcek [2000]. The convective scheme by Grell [1993] is implemented to be consistent with the meteorological model; sub-grid scale updraft and downdraft processes and large-scale subsidence are considered. The top and bottom layers of shallow convection are determined by MM5 simulations; the cloud fraction is determined using the scheme described by Geleyn [1981]. Previously, the model was used to analyze the effects of lightning and convection [Choi *et al.*, 2005], the trans-Pacific transport [Y. Wang *et al.*, 2006], the tropospheric O_3 column [Jing *et al.*, 2006], and polar tropospheric chemistry [Zeng *et al.*, 2003; Y. Wang *et al.*, 2007].

Spring 2000 GEOS-CHEM model simulations provide initial and boundary conditions for trace gases. Regional simulations are spun up in the last week of January 2000. Emission inventories for combustion and industrial sources are taken from GEOS-CHEM [Bey *et al.*, 2001], except the fossil fuel NO_X and CO emission inventories over the United States, which are taken from the 1999 US Environmental Protection Agency National Emission Inventory (NEI99). These values are scaled with the national total emissions of 2000 [EPA, 2003]. Emission algorithms for vegetation and soils are taken from GEOS-CHEM, but meteorological inputs are from MM5. The monthly mean leaf area index (LAI) distribution is derived from 1-km Advanced Very High Resolution Radiometer data [Bonan *et al.,* 2002]. The lightning NO_X algorithm follows.

3.3.1.2 Lightning NO_X parameterizations

NO_X production due to lightning is estimated and distributed vertically up to the cloud top layer in the model. NO_X is primarily produced during the high-energy return stroke phase of a flash [Price *et al.,* 1997]. There are two flash types: cloud-to-ground

41

(CG) and intracloud (IC) flashes. The NO produced per IC flash is estimated to be one-tenth that of a CG flash (6.7×10^{26} NO molecules flash^{-1}) in some previous studies [Price *et al.,* 1997; Pickering *et al.,* 1998; Allen *et al.,* 2000; Allen and Pickering, 2002]. Higher or equivalent NO production per IC as CG flash is used in several more recent studies [DeCaria *et al.,* 2000; Ott *et al.,* 2003; Zhang *et al.,* 2003; Fehr *et al.,* 2004; Choi *et al.,* 2005]. Based on cloud-resolving modeling output compared with anvil aircraft NO_X observations over the U.S., the average NO production per flash for both IC and CG flashes is about $2\text{-}4 \times 10^{26}$ molecules [K. Pickering, Personal Comm., 2005]. Ott *et al.* [2003] use 3.0×10^{26} NO molecules per flash for IC and CG flashes. We assume that NO production per IC flash is the same as that per CG flash. The NO production rate per flash used by Choi *et al.* [2005] is 6×10^{26} NO molecules per flash. Sensitivity results suggest that this value gives better agreement with GOME measurements. Lightning NO_X is distributed vertically following the mid-latitude profile by Pickering *et al.* [1998].

Two separate parameterizations are constructed for continental and oceanic regions [Price and Rind, 1993] using measurements from the National Lightning Detection Network (NLDN). The detection efficiency reported by Cummins *et al.* [1998] is used. We parameterize the lightning NO_X production rate as a function of meteorological variables so that this emission is consistent with the dynamic model. Using the parameterizations, we experimented with cloud top height [Price and Rind, 1993], convective mass flux [Allen and Pickering, 2002], and convective available potential energy (CAPE) [Choi *et al.,* 2005]. To take advantage of the different distributions, we use both CAPE and cloud mass flux and had to normalize them. The CG

flashing rate for continental and oceanic regions are mathematically expressed in terms of

normalized convective mass flux (M) and CAPE (C):

$$LF_{cg} = a_o + aM + bM^2 + cM^3 + dC + eC^2 + fC^3 + gMC$$
$$+ hM^2C + iMC^2 + jM^4 + kM^3C + lM^2C^2 + mMC^3 + nC^4,$$

where for continental regions, a_o = 0.00495, a = 4.219, b = 15.5064, c = -112.492, d = -

2.089, e = 48.143, f = -53.983, g = -121.956, h = 358.118, i = 208.105, j = 108.613, k = -

216.226, l = -330.354, m = -134.307, n = 16.742 and for ocean regions, a_o = 0.126, a =

2.669, b = -0.854, c = -61.793, d = -2.482, e = 24.35, f = 26.739, g = -31.732, h =

288.129, i = -185.419, j = 63.089, k = -178.063, l = -151.659, m = 204.120, n = -34.408.

Once the CG flashing rate is determined, the IC to CG flash rate ratio is calculated

following Y. Wang *et al.* [1998].

3.3.2 Global Earth Observing System (GEOS)-CHEM

GEOS-CHEM is driven by GEOS assimilated meteorological fields (GEOS-3) for

2000 [Schubert *et al.*, 1993]. The horizontal resolution of GEOS-CHEM is 2° latitude by

2.5° longitude. Thirty chemical tracers describing tropospheric O_3 chemistry are

transported. Detailed algorithms for photochemistry, dry and wet deposition, and

emissions are described by Bey *et al.* [2001]. Chemical initial and hourly boundary

conditions for REAM are taken from GEOS-CHEM model simulations (version 7.2)

[Bey *et al.*, 2001]. In addition, the results of GEOS-CHEM are compared with those of

the REAM simulations.

3.4 Seasonal Transitions of NO$_X$, CO, and O$_3$

3.4.1 Nitrogen Oxides (NO$_X$ = NO+NO$_2$)

3.4.1.1 Time series of SEARCH NO

We compare REAM simulated NO mixing ratios with SEARCH observations at four rural or suburban sites, CTR, OAK, OLF, and YRK, during February and May of 2000, in order to examine the seasonal trends of surface NO data. Hourly NO concentrations vary significantly between day and night because of the shallow boundary layer at night. We show only daily 1-5 pm (LT) NO comparisons between SEARCH and REAM (Figure 3.1). Simulated mean NO concentrations during the four months (CTR: 290 pptv, OAK: 216 pptv, OLF: 314 pptv, YRK: 936 pptv) agree with the observed means (240 pptv, 241 pptv, 275 pptv and 1048 pptv) to within 10% and 20%. The correlation coefficients between REAM and SEARCH NO are 0.66, 0.56, 0.40, and 0.23 at the sites. High NO peaks at YRK are due to nearby power plant emissions [B. Hartsell and E. S. Edgerton, Personal Comm., 2006]. The model resolution is too coarse to simulate the influence of power plant plumes. As a result, of the four sites, YRK has the lowest correlation coefficient. Decreasing NO concentrations from spring to summer are clear from both observations and REAM simulations, reflecting in part an increasing photochemical loss of NO$_X$.

3.4.1.2 GOME tropospheric NO$_2$ column

3.4.1.2.1 Dependence of GOME NO$_2$ retrievals on the a priori profiles

The monthly means of tropospheric NO$_2$ columns derived from GOME measurements are calculated between February and May 2000 in order to investigate

Figure 3.1 Averaged observed and simulated NO mixing ratios (ppbv) during the afternoon (1300-1700, LT) at four SEARCH surface sites: Centerville (CTR), Oak Grove (OAK), Outlying Landing Field #8 (OLF), and Yorkville (YRK). The solid black lines represent the SEARCH measurements and red lines the REAM results.

seasonal changes in tropospheric NO_2 patterns. The retrieval process is described in Section 3.2.4. Both GEOS-CHEM and REAM vertical profiles are applied to calculate the AMFs as a way of examining the sensitivity of GOME retrievals to the simulated NO_2vertical profiles. GEOS-CHEM and REAM have different profiles due in part to the shallower boundary layers in MM5 than GEOS-3 (to be discussed in Section 3.4.3.3). Despite the differences in the NOx profiles (to be shown in Figure 3.11), Figure 3.2 shows good agreement between GOME NO_2 column retrievals using the REAM and GEOS-CHEM profiles. The correlation coefficient is > 0.99. The monthly mean NO_2 columns of the retrievals using REAM profiles are higher by 6.1, 12.0, 5.5, and 0.4% from February to May than that using GEOS-CHEM because the AMF values are smaller. Generally, about 40% is used to calculate the AMF-associated retrieval uncertainty for each datum [Martin *et al.*, 2002], which is in agreement with our results.

3.4.1.2.2 *Comparisons of the model results with GOME NO_2 retrievals*

Figure 3.2 also shows that the REAM and GEOS-CHEM simulated NO_2 columns are generally in agreement with the GOME NO_2 retrievals. The mean biases are within 11%, and the correlations are high (R>0.85). In February, compared with GOME observations, both models overestimate the NO_2 columns due to the negative retrieval values over high-latitude regions. While REAM tends to overestimate GOME NO_2 columns in April and May due to larger lightning NO_X productions in REAM, GEOS-CHEM tends underestimate them in the same months.

Due to its coarse spatial resolution, the GEOS-CHEM model fails to capture NO_2 column peaks ($>5\times10^{15}$ molecules cm^{-2}) in California, but REAM captures GOME NO_2

Figure 3.2 Monthly mean tropospheric NO_2 vertical columns (in molecules cm^{-2}) during February-May 2000 from GOME retrievals using the REAM-derived shape factor (first column), the REAM model (second), GOME retrievals using the GEOS-CHEM-derived shape factor (third), and the GEOS-CHEM model (last). The text provides more details. The model results are obtained by averaging NO_2 data during the satellite overpass time period (1000-1100, LT).

columns. In April and May, both models slightly underestimate NO_2 columns in the western United States likely due to underestimated soil NO_X emissions [Martin *et al.*, 2003; Bertram *et al.*, 2005; Jaegle *et al.*, 2005]. The GEOS-CHEM model also underestimates NO_2 columns in GOME over the western North Atlantic due to their lower lightning NO_X production over the region.

3.4.1.2.3 NO$_2$ column sensitivities to lightning and soil emissions and convection

We compute the contributions of lightning production, convective transport, and soil emissions by comparing sensitivity simulations with each process turned off and the standard REAM simulation. Figure 3.3 shows monthly mean column differences between the standard model and sensitivity simulations. The largest impact on the tropospheric NO_2 column appears to be from lightning production, and enhancements are found over the southern United States, the Gulf, and the western North Atlantic. The smallest impact is from convection, and some enhancements are seen over western Texas and some regions of the western North Atlantic Ocean. Enhancements from soil emissions are seen over the central United States.

In contrast to the decreasing trend of tropospheric NO_2 columns (Figure 3.2), lightning and soil contributions increase significantly as solar insolation and atmospheric moisture increase. Surface heating and abundant moisture, which lead to more convection and lightning and soil emissions, are driven in part by surface temperature. The lightning and soil emission contributions increase to about 10% and 7%, respectively, in May. The contribution of lightning is larger than that of soil emission, except in February.

Figure 3.3 The monthly mean contributions of lightning production, convection, and soil emissions to tropospheric NO_2 vertical columns (in molecules cm^{-2}).

In February and March, lightning NO_2 enhancements are typically less than 3.0×10^{14} molecules cm^{-2}, but in April and May, they increase to $0.5 - 2.0 \times 10^{15}$ molecules cm^{-2} over the southern United States, the Gulf, and the western North Atlantic. By using an algorithm in Martin *et al*. [2002], we estimate monthly mean uncertainties for GOME retrievals to $1 - 2 \times 10^{14}$ molecules cm^{-2} over the ocean and $1 - 8 \times 10^{14}$ molecules cm^{-2} over the continent. Therefore, the detection of lightning enhancements is much easier over the ocean than it is on land. Large enhancements from lightning and soil emissions simulated in May are larger than the retrieval errors on a monthly mean basis.

3.4.1.3 *Optimization of fossil fuel NO_X emissions*

Optimized NO_X emissions are estimated by combining top-down NO_X emissions from satellite measurements with a priori bottom-up emissions, weighted by relative errors for the two estimates [Martin *et al*., 2003]. NO_X emission inventories used in REAM [Choi *et al*., 2005; Jing *et al.,* 2006; Y. Wang *et al.,* 2006] and GEOS-CHEM [Bey *et al*., 2001; Martin *et al.,* 2002, 2003; Jaegle *et al.,* 2005] are used as a priori bottom-up emissions. REAM and GEOS-CHEM use the same EPA 1999 NEI inventory for surface fossil fuel NO_X emissions in the United States.

The top-down NO_X fossil fuel emission inventory (E_t) is first calculated following Martin *et al*. [2003] by fitting E_t to a priori bottom-up emission E_a with the ratio of the retrieved NO_2 column (Ω_r) to the simulated column (Ω_s):

$$E_t = E_a \times \Omega_r / \Omega_s .$$ (3.1)

Monthly a posteriori emissions (E) are then calculated by the weighted averages of E_a and E_t [Martin *et al*., 2003]:

$$\ln E = \frac{(\ln E_t)(\ln \varepsilon_a)^2 + (\ln E_a)(\ln \varepsilon_t)^2}{(\ln \varepsilon_a)^2 + (\ln \varepsilon_t)^2} \, , \qquad\qquad (3.2)$$

where ε_a and ε_t are the a priori inventory and retrieval errors, respectively. The inventory

errors are from a study by Martin *et al*. [2003]. Table 3.1 shows the monthly a priori,

top-down, and a posteriori emissions derived using REAM and GEOS-CHEM results,

respectively. The a priori emissions from REAM and GEOS-CHEM are almost the same,

but the top-down estimates sometimes differ significantly. The top-down emissions

Table 3.1 Monthly North America (20 - 62°N) fossil fuel NO_X emissions (Tg N month^{-1})

	REAM derived			GEOS-CHEM derived		
	A priori	Top-down	A posteri	A priori	Top-down	A posteri
Feb	0.57	0.49	0.52	0.55	0.41	0.47
Mar	0.61	0.76	0.69	0.61	0.66	0.64
Apr	0.59	0.66	0.63	0.58	0.64	0.61
May	0.61	0.59	0.60	0.60	0.71	0.66
Avg.	0.60	0.63	0.61	0.59	0.61	0.60

derived by REAM are larger by 3% to 16% than those of GEOS-CHEM between

February and April, but lower by 20% than those of GEOS-CHEM in May. REAM

generally has lower mixing depths than GEOS-CHEM, which results in lower AMFs and

higher NO_2 retrievals (discussed previously). Therefore, the emissions derived by REAM

are usually larger than those derived by GEOS-CHEM. In May, however, REAM has

larger lightning NO_X production than GEOS-CHEM, which results in smaller top-down

emissions.

Optimized emissions derived by REAM are 3% to 9% higher than those derived

by GEOS-CHEM during the period of February to April, but lower by 10% in May.

Differences between the two a posteriori emissions are caused by top-down emissions.

The seasonal agreement between top-down and a posteriori emissions are fortuitous because the boundary layer height and lightning NO_X production differences in the models are not correlated. We note that the difference between the two model-derived a posteriori emissions is well within the uncertainties of the GOME NO_2 retrievals. The large month-to-month variation in top-down emissions also suggests that this approach requires that GOME measurements be taken throughout the entire season.

3.4.2 Carbon Monoxide

3.4.2.1 Time series of SEARCH CO

Figure 3.4 shows a comparison of REAM simulations with SEARCH surface CO measurements between February and May. The seasonal change in CO is small during the spring. Increasing CO loss due to increasing OH oxidation is compensated by faster CO production from VOC oxidation. Observations show that simulated seasonal change is small. REAM also simulates multi-day variations in CO observations reasonably well, but the simulated mean CO concentrations (CTR: 242 ppbv, OAK: 213 ppbv, OLF: 228 ppbv and YRK: 261 ppbv) are higher than the observed concentrations (CTR: 226 ppbv, OAK: 187 ppbv, OLF: 168 ppbv and YRK: 193 ppbv). The EPA NEI emissions used in the model may also have a high bias. The correlation coefficients between hourly REAM simulations and SEARCH CO observations are 0.52, 0.56, 0.63, and 0.48 at the four sites, respectively.

3.4.2.2 MOPITT CO

3.4.2.2.1 Evaluation of MOPITT CO with TOPSE observations

Figure 3.4 The same as Figure 3.1, but for hourly observed and REAM simulated CO mixing ratios at four surface SEARCH sites.

53

Figure 3.5 The monthly mean cross sections of the MOPITT CO concentrations (ppbv) (left column) along TOPSE aircraft tracks, corresponding TOPSE CO concentrations processed with the MOPITT averaging kernel (middle), and TOPSE CO observations (right). Data selection criteria are described in the text.

TOPSE CO observations processed with MOPITT AK are compared with MOPITT CO observations (Figure 3.5) in order to validate MOPITT retrievals. In order to maximize data coverage, we use TOPSE observations as long as MOPITT passing over the same region was within a day. MOPITT retrievals with a priori fraction <60 % are used. MOPITT CO retrievals are in reasonably good agreement with AK-processed TOPSE CO concentrations, although high CO peaks from TOPSE observations near 6 km, particularly in May. Those high peaks are caused by long-range trans-Pacific transports in the upper troposphere [Y. Wang *et al*., 2006]. These upper tropospheric enhancements are not captured by MOPITT mostly likely due to the low vertical resolution of MOPITT measurements [Deeter *et al*., 2004].

To further illustrate the AK effects, we group the MOPITT CO profiles along the TOPSE flight tracks into three latitudinal bins (< 52°N, 52-57°N, >57°N), as a vertical sampling by TOPSE is inadequate to construct the profiles (Figure 3.5). We obtain a ratio of TOPSE measurements to REAM simulations at the measurement altitudes and then apply the ratio-to-scale REAM simulations for the altitudes without measurements. Figure 3.6 shows the regional profile comparison for March to May 2000. Close agreement between MOPITT and TOPSE-REAM is found except in May at higher latitudes because very few TOPSE measurements went into the profile. In addition, after AK processing, the vertical information in the TOPSE-REAM profiles is clearly lost.

3.4.2.2.2 Comparison of simulated CO columns with MOPITT

For the model evaluation, we compare only the column concentrations because of insufficient vertical information obtained from MOPITT measurements. During March

Figure 3.6 Regional profiles by latitudes for the MOPITT measurements and the TOPSE-REAM results with and without AK processing. Region 1 covers the lower-latitude region of the TOPSE aircraft campaign (latitude < 52°N, in the left column), region 2 the middle-latitude region (52°N < latitude < 57°N, in the middle column), and region 3 the higher-latitude region (latitude > 57°N, in the right column). The scaling of the REAM results with the TOPSE measurements is explained in the text.

Figure 3.7 Mean CO columns (in molecules cm^{-2}) from MOPITT (left panel) during April-May of 2000, the corresponding REAM CO columns processed with the MOPITT averaging kernel (middle), and the GEOS-CHEM CO columns processed with the averaging kernel (right). Model results are sampled at the MOPITT measurement time and location.

2000, the first month when MOPITT data were collected, large amounts of data are missing due to calibrations. Therefore, we show only comparisons in April and May 2000. REAM and GEOS-CHEM CO columns processed using MOPITT AK reproduce MOPITT CO retrievals well (Figure 3.7). The correlation coefficients between simulated and MOPITT monthly mean CO columns are about 0.9 for both REAM and GEOS-CHEM. REAM mean biases are 1.1 and -1.1% in April and May, respectively. The GEOS-CHEM mean biases are 2.45% and -0.49%, respectively. REAM mean columns are slightly lower than GEOS-CHEM due to the lower mixing depth in REAM (to be discussed in Section 3.4.3.3).

3.4.3 Ozone

3.4.3.1 Time series of SEARCH surface O_3

REAM simulated O_3 concentrations are compared with SEARCH observations from February to May 2000 (Figure 3.8). In addition to capturing background concentrations and multi-day episodes of O_3, REAM reproduces the gradual increase in surface O_3 at SEARCH sites well from spring to early summer. Simulated mean O_3 concentrations during the four months (CTR: 34 ppbv, OAK: 38 ppbv, OLF: 42 ppbv and YRK: 33 ppbv) are in good agreement with observed mean concentrations (CTR: 38 ppbv, OAK: 43ppbv, OLF: 40 ppbv and YRK: 36 ppbv). The correlation coefficients between hourly REAM simulations and SEARCH observations at these sites are 0.69, 0.69, 0.65 and 0.68, respectively.

3.4.3.2 Monthly mean EPA AIRNow O_3

Figure 3.8 The same as Figure 3.4 but for surface O₃. The black lines are SEARCH measurements, and the red lines are REAM results.

Figure 3.9 Monthly mean afternoon (1300-1700, LT) surface O_3 concentrations (ppbv) over the United States in February-May 2000. Shown are the EPA AIRNow observations (left column), the REAM simulation results (middle), and the GEOS-CHEM simulation results (right).

Monthly mean afternoon (1300-1700, LT) O_3 concentrations measured by the EPA AIRNow surface sites are compared with REAM and the GEOS-CHEM simulations from February to May (Figure 3.9). High O_3 peaks are generally captured by REAM to within 10 ppbv. The correlation coefficients of the REAM results and the EPA measurements range between 0.56 and 0.65. The correlation coefficients of the GEOS-CHEM results and the EPA observations range from 0.44 to 0.68. The correlations of the GEOS-CHEM and EPA observations decrease as the season progresses towards summer. Surface O_3 concentrations are low in February in part because weak solar influx limits photochemical activity. In addition, the titration of O_3 by high NO emissions from automobiles and power plants can occur. As the season processes towards summer, increasing solar influx and water vapor activates photochemistry [Y. Wang *et al.*, 2003]. Both REAM and GEOS-CHEM simulate a resulting increase in surface O_3. The rate of photochemical activation and surface O_3 increase are better simulated in REAM than in GEOS-CHEM. The global model simulates higher O_3 concentrations over the eastern United States in April and May than the EPA observations. Inspections of the model difference between REAM and GEOS-CHEM reveal that a major contributing factor is the differences in the mixing heights used in the model.

3.4.3.3 *Mixing depth and surface O_3*

From February to May, both MM5 and GEOS-3 predict increasing boundary layer mixing depths as solar insolation increases (Figure 3.10). However, MM5 predicted mixing depths used in REAM are in general lower than GEOS-3 predictions used in GOES-CHEM. The difference is particularly large over the eastern United States, where

61

Figure 3.10 Average afternoon (1200-1600, LT) mixing depths over North America in February-May 2000. The data used in REAM (left column) are simulated by MM5, and those used in GEOS-CHEM (right column) are simulated by GEOS-3.

Figure 3.11 The comparisons of averaged afternoon (1200-1600, LT) vertical profiles of CO and NO_X concentrations from the REAM and GEOS-CHEM models. The solid lines represent the REAM simulations, and the dotted lines represent the GEOS-CHEM simulations.

of difference up to a factor of 2 is observed. The shallower mixing depth in REAM results in a stronger boundary layer vertical gradient and higher surface concentrations of CO and NO_X than GEOS-CHEM (Figure 3.11). Surface CO and NO_X over North America are larger by 15-20 ppbv and 200-300 pptv in the REAM results. In contrast, GEOS-CHEM CO and NO_X are generally higher at the pressure altitudes of 600-800 hPa. During the spring, when the radical source largely driven by photon flux and water vapor [Y. Wang *et al.*, 2003] is limited, high concentrations of NO_X decrease photochemical activity because of increasing radical loss through the reaction of OH and NO_2. Thus, less active mixing in REAM predicts lower surface O_3 concentrations than in GEOS-CHEM, and the simulated O_3 concentration in REAM is in better agreement with the EPA surface measurements (Figure 3.9).

3.4.3.4 MOZAIC O_3

Most of the MOZAIC flights are in the upper troposphere. We first look at the measurements below 350 hPa. The data coverage is limited in these take-off and landing flights. Figure 3.12 shows a comparison of the MOZAIC data and the REAM results. Most of the data are for the eastern United States because the measurements are taken on commercial flights between the United States and Europe. Tropospheric O_3 mixing ratios are between 30 and 80 ppbv, showing a clear O_3 increase as the season shifts towards summer, which is consistent with the ozone climatology by Thouret *et al.* [2006]. REAM results reproduce reasonably well MOZAIC observations, except in the southern United States in March and May, when REAM overestimates O_3 (<10 ppbv) in the lower troposphere.

Figure 3.12 O$_3$ concentration (ppbv) below 350 hpa from the MOZAIC measurements during February-May 2000 (left column) and the corresponding REAM results (right column). The REAM data for comparison with the MOZAIC data are sampled along MOZAIC aircraft tracks.

Figure 3.13 The same as Figure 3.12, but for 250-350 hPa. The O_3 data > 200 ppbv from MOZAIC and REAM are filtered out.

Figure 3.14 Observed and simulated O_3 monthly mean vertical profiles (ppbv) for six ozonesonde sites at 30-55°N in February-May 2000. The solid lines represent the ozonesonde measurements, and the dotted lines represent the corresponding REAM results. The error bars represent the standard deviations of the measurements.

Figure 3.14 (continued.)

MOZAIC measurements in the upper troposphere show large influences from stratospheric air masses, which have high O_3 concentrations. We filtered out mixing ratios > 200 ppbv in the measurements (and model results) to minimize the effects of extreme values. Figure 3.13 shows a comparison of MOZAIC measurements with REAM results at 250-350 hPa. In general, REAM underestimates high O_3 concentration measurements, except in May. Thouret *et al*. [2006] found that maximum ozone in the MOZAIC measurements is found in the spring in the lower stratosphere, where ozone concentrations range from 150 to 500 ppb with a strong vertical gradient near the tropopause region. REAM underestimates O_3 concentrations compared with MOZAIC at that level. We will show the model bias in the comparison of the REAM results with the ozonesonde measurements (Figure 3.14). The upper tropospheric O_3 simulations in REAM are strongly affected by the specified upper boundary conditions at 100 hPa from GEOS-CHEM, which exhibits difficulties in simulating the sharp O_3 gradient across the tropopause [Bey *et al*., 2001].

3.4.3.5 Ozonesonde measurements

Ozonesonde observations at the six sites over North America are compared with the REAM results in Figure 3.14. The observed seasonal trend of increasing tropospheric O_3 concentration is captured reasonably well by REAM. However, the large concentration gradients near the tropopause in the ozonesonde observations are underestimated in the model. Stratospheric intrusion events are more frequent in the winter and the spring than in the summer. Therefore, the discrepancies between the REAM results and the MOZAIC and ozonesonde measurements decrease as the season

shifts towards summer. The monthly ozone concentrations and their changes below 350 hPa are better simulated than they are in the region above.

Simulated low-altitude O_3 concentrations are generally close to the ozonesondes measurements (within 10 ppbv). While the measurements at Boulder, Huntsville, and Wallops Island show O_3 increases in the lower troposphere, those at Trinidad Head and Goose Bay do not undergo large seasonal changes. The latter two stations are not as affected by North American NO_X emissions as the other stations. The underestimation of REAM is the largest at Wallops Island, located at a baroclinic zone that has large ozone gradients, described previously by Thouret *et al*. [2006].

3.4.3.6 TOMS-SAGE II tropospheric column O_3

Section 3.2.4 describes tropospheric column O_3 derived from TOMS and SAGE II measurements. PV mapping is a promising method of deriving tropospheric O_3 at mid-latitudes. However, the resolution and accuracy of PV mappings largely depend on the relatively sparse number of ozonesonde observations [Bithell *et al*., 1999], and ozonesonde observations are usually not coincident with SAGE measurements. Therefore, capturing events in synoptic or smaller scales is difficult using the PV mapping method. We use tropospheric O_3 products here to qualitatively examine the seasonal transition. Figure 3.15 compares TOMS-SAGE II tropospheric O_3 column with REAM and GEOS-CHEM results from February to May 2000. Both the satellite products and the models show a springtime increase in tropospheric O_3 over North America, even though absolute amounts of column O_3 from the PV mapping method do not agree well with either model. High O_3 columns are clearly shown over the western North Atlantic in the satellite

Figure 3.15 Monthly mean tropospheric O$_3$ columns derived from TOMS total columns and SAGE II stratospheric columns (first column), the REAM standard simulation (second), the REAM sensitivity simulation without lightning NO$_X$ production (third), and the GEOS-CHEM simulation (last).

derived columns, particularly in May. The standard REAM model produces significant enhancements over the region while GEOS-CHEM does not. A sensitivity REAM simulation without lightning NO production exhibits much weaker enhancements, suggesting that lightning NO production is the main contributor to O_3 enhancements over the western North Atlantic. REAM-simulated lightning NO_x enhancements (Figure 3.3) cover regions similar to TOMS-SAGE-derived O_3 enhancements. However, the resulting O_3 enhancements are mainly in the southern region, where solar influx is large.

3.4.4 Pollutant Export/Import Fluxes and Budget Calculations

3.4.4.1 Longitudinal pollutant fluxes

Fluxes of NO_X, NO_y, CO, and O_3 imported to and exported from the troposphere in North America are estimated using the REAM results. Fluxes throughout the western and eastern boundaries are a factor of 18 larger than throughout the north and south boundaries. Here, we focus on longitudinal fluxes. Figure 3.16 shows the longitudinal import and export fluxes of these pollutants as a function of latitude. We find net import in the western boundary region and net export in the eastern boundary region. Import fluxes are generally smaller than export fluxes. The import and export fluxes of NO_X are smaller than those of NO_y, CO, and O_3 due to the relatively low concentrations of NO_x caused by its shorter lifetimes. The latitudes of maximum NO_X export are different from those of NO_y, CO and O_3. The shorter lifetimes of NO_X dictate that the export flux reflects more the locations of NO_x emissions, where longer-lived species are affected more by meteorology. The latitudes of NO_X, NO_y, CO, and O_3 export peaks in May are similar to those in June 1985 from PK04 [Park *et al*., 2004b, hereafter referred to as

Figure 3.16 The longitudinal import and export fluxes of NO_X, NO_y, CO, and O_3 over North America in the troposphere as a function of latitude. The western and eastern boundaries are the same as those depicted in Figure 3.15. The solid lines represent export fluxes while the dotted lines represent import fluxes.

Figure 3.17 The same as Figure 3.16, but for altitude.

PK04], but the NO_X export in May in this study is higher by a factor of 3 than that by PK04, reflecting higher lightning NO_x production. The peak NO_y export in this study is also higher than PK04 by 25%. The net export of NO_x increases from February to May because of increasing emissions from lightning and soils (Figure 3.3). The net exports of CO and O_3 at 20-40 °N are most significant in May, driven in part by more activate convection in the region.

Figure 3.17 shows longitudinal import and export fluxes as a function of altitude. REAM shows that significant pollution import from the West takes place in the upper troposphere, and that export fluxes of NO_X and NO_y are much larger than import fluxes at high altitudes. This trend is also shown in PK04. The peak NO_X export in May in this study is larger than that from PK04 by a factor of 5. The peak export of NO_y in this study is larger than that of PK04 by 38%. Import fluxes of NO_X and NO_y in this study are similar to those from PK04. In addition, in PK04, less CO was exported than imported above 7 km in March-May due to a stronger jet stream over the Pacific than over the Atlantic, which is also shown in this study. PK04 shows that less O_3 is exported than imported above 9 km. By comparison, we find that O_3 export fluxes are similar to the import fluxes in the upper troposphere in this study, likely due to higher lightning NO_X production.

Export of NO_X in the upper troposphere is enhanced due to lightning production [Pickering *et al.*, 1998; Choi *et al.*, 2005]. Simulated NO_X export fluxes at 12 km increase from 1.8×10^7 moles day^{-1} to 4×10^7 moles day^{-1} from February to May. This increase is associated with active lightning NO_X production as the season shifts towards summer. Sensitivity studies (not shown) indicate that lightning production enhances NO_X

and NO_y exports in the upper troposphere (8-12 km) by 252% and 66%, respectively, in May.

Maximum NO_X fluxes occur at about 10 km in February, March, and April, and at about 12 km in May due to lightning NO_X enhancements at high altitudes. The maximum O_3 and NO_y fluxes are located at about 10-15 km. Maximum CO fluxes occur at about 9 km. Maximum CO fluxes take place at a lower altitude because the source of CO emissions is primarily at the surface. By comparison, the sources of NO_X (and hence, NO_y) are aircraft and lightning in the upper troposphere, and O_3 has net production in the upper troposphere [e.g., Y. Wang *et al.*, 2003].

3.4.4.2 Net fluxes in the free troposphere and boundary layer
3.4.4.2.1 Net flux in the lower and middle troposphere

We chose 7 km as the top of the middle troposphere in order to compare our results with those of PK04. Net fluxes of NO_X in the lower and middle troposphere (<7 km) are 0.037, 0.014, 0.023, and 0.024 Gmol day^{-1}, and those of NO_y are 0.47, 0.32, 0.36, and 0.43 Gmol day^{-1} from February to May 2000 (Table 3.2a). NO_X and NO_y net fluxes decrease from February to March, but beginning in April, the net fluxes increase due to enhanced lightning and soil NO_X emissions. Compared with the net fluxes of NO_X and NO_y in June from PKO4, NO_X, and NO_y the net fluxes in May in this study are larger by 50% and 79%, respectively.

Export CO fluxes from North America in the lower and middle troposphere are 93, 61, 53, and 49 Gmol day^{-1} from February to May, compared with imports of 61, 61, 52, 39 Gmol day^{-1} (Table 3.2a). The import and export fluxes in May in this study are larger

than those from PK04. However, the net CO flux over North America in May is 10 Gmol day^{-1}, which is similar to the 12 Gmol day^{-1} in June from PK04. Net flux is largest in the winter due to slow photochemical loss, but net flux in May is larger than in March and April in part due to the increase of photochemical CO production. The difference in import CO fluxes between PK04 (20 Gmol day^{-1}) and those in this study (39 Gmol day^{-1} in May) could stem from a number of factors, including an underestimation of Asian fossil fuel emissions and an overestimation of OH concentrations in the spring and the summer in PK04 [Park *et al.,* 2004a]. Other contributors could be the month and interannual differences.

The net O_3 flux in the lower and middle troposphere in May in this study (6 Gmol day^{-1}) is smaller than that in PK04 (10 Gmol day^{-1} in June). Photochemistry is more active in June than it is in May. PK04 used meteorological fields from GEOS-3 Stretched Grid Data Assimilation System (SG-DAS) [Fox-Rabinovitz *et al*., 2002], which may also

Table 3.2a The import and export fluxes of tracers in the lower and middle troposphere (<7 km) over North America (20 – 62°N, Gmol day^{-1})

	Import fluxes				Export fluxes			
	Feb	Mar	Apr	May	Feb	Mar	Apr	May
NO$_x$	0.003	0.006	0.007	0.006	0.04	0.02	0.03	0.03
NO$_y$	0.11	0.14	0.13	0.09	0.58	0.46	0.49	0.52
CO	61	61	52	39	93	61	53	49
O$_3$	21	21	20	16	30	22	21	22

Table 3.2b Same as table 3.2a, but in the boundary layer (<2.5 km)

	Import fluxes				Export fluxes			
	Feb	Mar	Apr	May	Feb	Mar	Apr	May
NO$_x$	0.00	0.00	0.00	0.00	0.02	0.01	0.01	0.01
NO$_y$	0.01	0.02	0.02	0.007	0.31	0.20	0.19	0.21
CO	18	17	13	9	33	19	14	16
O$_3$	5.2	4.5	3.8	2.5	8.2	5.2	4.2	5.3

have deeper mixing depths than MM5 simulations in REAM, resulting in higher O_3 concentrations near the surface, as in the case of GEOS-CHEM (see Figure 3.9).

3.4.4.2.2 Net flux in the boundary layer

We chose 2.5 km as the top of the boundary layer in order to compare our results with those of PK04. NO_X exports in the boundary layer are 0.02, 0.01, 0.01, and 0.01 Gmol day^{-1}, and NOy exports 0.31, 0.20, 0.19, and 0.21 Gmol day^{-1} from February to May, respectively (Table 3.2b). PK04 shows NO_x and NO_y exports of 0.01 and 0.11 Gmol day^{-1}, respectively, in the boundary layer in the month. Whereas the net flux difference in NO_X in the troposphere (<12 km) of the two studies is large, the net fluxes of NO_X in the boundary are the same (Table 3.2b) because the impact of lightning NO_X is primarily in the upper troposphere. Some of the lightning NO_X in the free troposphere is transported to the boundary layer. During transport, NO_X is oxidized into longer-lived NO_y species such as HNO_3. As a result, the NO_y export is larger.

Export CO fluxes in the boundary layer are 33, 19, 14, and 16 Gmol day^{-1} and import CO fluxes 18, 17, 13, and 9 Gmol day^{-1} from February to May, respectively. Net CO fluxes over North America are 15, 2, 1, and 7 Gmol day^{-1} for the February to May period. The net CO flux in May is comparable to that of 7.2 Gmol day^{-1} in June from PK04.

Exports of O_3 in the boundary layer are 8.2, 5.2, 4.2, and 5.3 Gmol day^{-1} and imports 5.2, 4.5, 3.8, and 2.5 Gmol day^{-1} from February to May. Net exports are 3.0, 0.7, 0.4 and 2.8 Gmol day^{-1} from February to May. The net flux in May is smaller than the

4.88 Gmol day^{-1} in June from PK04 for the same reasons discussed for the lower and middle tropospheric flux comparison.

3.4.4.2.3 Export efficiencies for NO$_X$

North American NO$_X$ emissions (20-62°N) are about 1.47 Gmol day^{-1}. About 1.4%, 0.7%, 0.6%, and 0.7% of the emission are exported as NO$_X$, and 20%, 12%, 12%, and 14% are exported as NO$_y$ from the boundary layer from February to May, respectively. Because of more active convection (and lightning production) towards May, the export efficiency of NO$_x$ increases while that of photo-oxidation decreases. The ratio of NO$_X$ fluxes in the boundary layer to total emissions in May is comparable to that of PK04 (0.6%), but the ratio for NO$_y$ is twice as large as that of PK04 (7%), suggesting a large difference between the two models with regard to reactive nitrogen speciation. Considering the region below 7 km, 2.5%, 1.0%, 1.6%, and 1.6% are exported as NO$_X$ and 32%, 22%, 24%, and 29% as NO$_y$ from February to May, respectively. PK04 showed that 1% and 15% of NO$_X$ emissions were exported as NO$_X$ and NO$_y$, respectively. The export efficiencies of NO$_X$ and NO$_y$ fluxes from the lower and middle troposphere in this study are 60% and 100% larger than those of PK04, respectively.

3.5 Conclusions

We apply a regional chemical transport model (REAM) to analyze surface, ozonesonde, aircraft, and satellite measurements over North America from February to May 2000, in order to investigate the transitions of the concentrations and fluxes of O$_3$ and its precursors during the rapid photochemical and dynamical changes that occur in

the spring. The GEOS-CHEM model is used to provide not only chemical initial and boundary conditions but also targeted comparisons with REAM results. Pollutant fluxes from this work are compared with earlier work by PK04. Surface observations from the EPA AIRNow and SEARCH networks, aircraft observations from the TOPSE and MOZAIC experiments, ozonesondes, and satellite measurements from GOME, MOPITT, TOMS, and SAGE II are analyzed.

The REAM results are generally in good agreement with observations in the troposphere. Comparisons of surface measurements from EPA AIRNow (O_3) and SEARCH networks (O_3, CO, and NO_X) show that REAM performs reasonably well in simulating multi-day variations and seasonal transitions. The model is in reasonable agreement with MOZAIC and ozonesonde O_3 measurements in terms of seasonal transitions, but simulated O_3 concentrations above 350 hPa are biased low because the specified upper boundary condition for O_3 is also biased low. The low bias decreases towards May as tropospheric chemistry becomes more important. Qualitative agreement between the model results and TOMS-SAGE II-derived tropospheric O_3 column are found. Lightning NO_X production is found to contribute large O_3 enhancements over the western North Atlantic in May.

MOPITT CO measurements are found to be in good agreement with column concentrations derived from TOPSE in situ measurements and REAM-simulated vertical CO profiles. However, after AK processing, the vertical information in the in situ measurements is clearly lost. The two model results are in good agreement with MOPITT CO columns with high correlation coefficients (R>0.89) and small mean biases

($< \pm 2.45\%$). The mixing depth in REAM is lower than in GEOS-CHEM, contributing to slightly lower a REAM mean CO column.

Comparisons of GOME NO_2 columns with REAM and GEOS-CHEM show that the model captures GOME spatial variation well in the spring ($R > 0.85$) with small mean biases ($< \pm 11\%$). While active photochemical oxidation leads to lower NO_2 columns from February to May, NO_x emissions from lightning and soils also increase. The resulting monthly mean enhancements are $0.5\text{-}2\times10^{15}$ and $0.5\text{-}1.0\times10^{15}$ molecules cm^{-2}, respectively. Some NO_X enhancements in May due to lightning and soil emissions are larger than GOME retrieval uncertainties, suggesting that satellite measurements may be used to constrain the emissions.

A major difference found between REAM and GEOS-CHEM simulations is that the increase in surface O_3 concentrations from February to May over the eastern United States in GEOS-CHEM is larger than it is in the REAM or EPA surface observations. A key factor driving the model difference is mixing depth, which is much lower in REAM (simulated by MM5) than it is in GEOS-CHEM (simulated by GEOS-3). With limited supplies of radicals in the springtime, a larger mixing depth in GEOS-CHEM results in faster photochemical activation because radical loss by the reaction of OH and NO_2 decreases.

Another difference between REAM and GEOS-CHEM is that lightning NO_x production is larger in REAM, particularly over the western North Atlantic, where REAM results are in better agreement with GOME NO_2 measurements. Because the mixing depth is shallower and lightning NO_X production is larger, REAM simulates larger NO_x vertical gradients in the lower and upper troposphere than GEOS-CHEM.

Higher surface concentrations and a larger boundary layer gradient in REAM leads to smaller AMFs in GOME NO_2 retrievals, which leads to higher top-down estimates of fossil fuel NO_X emissions (3-16%) than GEOS-CHEM from February to April. In May, however, higher lightning NO_X emissions in REAM leads to a smaller top-down estimate (20%) than those in GEOS-CHEM. Over the course of the season, the top-down estimates from the two models are essentially the same and in close agreement with those from the EPA NEI inventory.

Lightning NO_X production is a major contributor to the seasonal increase in the exports of NO_X and NO_y from North America in the upper troposphere. As a result, simulated NO_X export fluxes at 12 km increase by more than a factor of 2 from February to May (1.8 to 4×10^7 moles day^{-1}). In May, lightning production enhances NO_X and NO_y exports in the upper troposphere (8-12 km) by 252% and 66%, respectively. The effects of lightning on the net fluxes of NO_X and NO_y in the lower and middle troposphere are smaller. The model estimates 0.6-0.7 and 12-14% of NO_X and NO_y, respectively, are exported from the boundary layer from March to May.

CHAPTER IV

**EVIDENCE OF SPRING-SUMMER NORTHWARD MIGRATION OF HIGH O$_3$
OVER THE WESTERN NORTH ATLANTIC**

4.1 Introduction

A major pathway for North American pollution outflow is cloud convection along

with the warm conveyor belt (WCB) during the spring and summer [Li *et al*., 2005; Kiley

et al., 2006]. Cloud convection, which is associated with lightning, enhances the

precursor of ozone in the upper troposphere (UT) during the spring and summer. Due to

convection, the enhanced precursors in the upper troposphere (UT) [Bertram *et al*., 2007]

are largely exported to the North Atlantic due to stronger westerly winds [Park *et al.,*

2004; Choi *et al*., 2005, 2007a]. The chemical consequences of the addition of NO$_X$ in

the UT due to aircraft or lightning NO$_X$ production on HO$_X$ and O$_3$ chemistry over the

western North Atlantic have been studied from previous aircraft campaigns such as the

[3] SASS (Subsonic Assessment) Ozone and NO$_X$ Experiment (SONEX), the NOAA

Intercontinental Transport and Chemical Transformation (ITCT 2004), and the NASA

Intercontinental Transport Experiment-North America, Phase A (INTEX-A) [Brune *et al*.,

1999; Jaegle *et al*., 1999; Liu *et al*., 1999; Singh *et al*., 1999; Crawford, J., 2000; Bertram

et al., 2007; Hudman *et al*., 2007]. Jaegle *et al*. [1998, 1999] also showed that NO$_X$

concentration to transfer North America from NO$_X$-limited to NO$_X$-saturated regimes in

the spring is higher than that in the fall. Choi *et al*. [2005] also demonstrated that the

transient enhancements of lightning NO$_X$ and the convective transport of CO have large

enough signals for satellites to detect. Their impact on pollutant distributions averaged

over a long time period become more difficult over land, but the signals are easier to

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[3]This Chapter is for "Evidence of spring-summer northward migration of high O$_3$ over the western North
Atlantic," prepared for the submission to *Geophysical Research Letter* in 2007. Authors are Y. Choi, *et al*.

detect over the ocean [e.g., Li *et al.*, 2005; Choi *et al.*, 2005, 2007a]. In this work, we examine pollutant enhancements and their chemical consequences over the western North Atlantic during the transition from spring to summer in 2005 using measurements from recent satellite instruments, OMI, MLS, and TES, onboard the NASA Aura satellite. The Regional chEmical and trAnsport Model (REAM) [Choi *et al.*, 2005, 2007a] is applied to analyze the satellite measurements.

Many investigators have reported better agreement between the satellite measurements and the model results in tropical regions than at mid- and high-latitudes [e.g., Chandra *et al.,* 2003, 2004; Edwards *et al.*, 2003; Martin *et al.*, 2006a, 2006b; Ziemke *et al.*, 2006]. Recent GEOS-CHEM studies show increased lightning NOx production at higher latitudes from the standard model [e.g., Martin *et al.*, 2006b; Hudman *et al.,* 2007]. In the REAM model, lightning NOx production shows reasonably good agreement with measurements [Choi *et al.*, 2005]. Convective transport of CO is in agreement with MOPITT measurements [Choi *et al.*, 2005]. Simulated transient tropospheric O_3 column changes are in general agreement with OMI-MLS derived tropospheric O_3 column observations [Jing *et al.*, 2006]. More detailed REAM evaluations with surface, ozonesonde, aircraft, and satellite measurements are presented by Choi *et al.* [2007a]. In this work, we conduct sensitivity analyses to investigate the effects of surface pollutant emissions and lightning NO production on the spring-summer migration of high O_3 over the western North Atlantic.

4.2 Satellite Measurements: OMI-MLS Tropospheric Column O_3, OMI Tropospheric Column NO_2, and TES O_3 and CO

OMI, MLS, and TES are onboard the NASA Aura satellite, which passes over the equator at 1345 PM local time. The horizontal resolutions of OMI, MLS and TES are 13 km×24 km, 30 km×150 km×2.5 km, and 5 km×8 km. The tropospheric O_3 column is derived using a residual method. We use a combination of MLS profiles above 215 hPa and OMI level 2 total column O_3. The OMI and MLS coincidence criteria are ± 1.25° longitude by 1.25° latitude on the same day. The mid-latitude stratospheric O_3 columns between 215 hPa and the tropopause are obtained by SAGE II mapping profiles [Yang *et al*., 2007]. The tropospheric O_3 column is then obtained by subtracting stratospheric O_3 columns from the OMI total columns. To avoid the interference of clouds on satellite measurements, we use only the OMI total column obtained under clear sky conditions defined as the reflectivity of < 10% based on OMI 360 nm reflectivity data. A detailed validation of the OMI-MLS tropospheric O_3 products was performed by Yang *et al.* [2007].

The retrieval of tropospheric NO_2 columns from OMI measurements [Bucsela *et al.*, 2006] and their uncertainty are obtained from the NASA Goddard Earth Sciences Distributed Active Archive Center (GES DAAC). We use only OMI tropospheric NO_2 column data with a cloud fraction of < 40%. TES O_3, and CO data are obtained from the NASA Langeley Atmospheric Science Data Center (ASDC). Only TES O_3 and CO retrieval data with a degree of freedom (DFS) of > 3.5 and 1.0, respectively, are used. When compared with the results of the observations, the REAM results are processed with TES retrieval averaging kernels for O_3 and CO, described by Worden *et al.* [2007] and Luo *et al.* [2007], respectively. TES O_3 and CO are interpolated onto 3° latitude by 4° longitude using measurement locations.

4.3 Model Description

The model set up in this study is the same as that set up by Choi *et al*. [2005, 2007a]. REAM has a horizontal resolution of 70 km, with 23 vertical layers reaching 10 hPa. The National Center for Atmospheric Research/Penn State MM5 is used to simulate meteorological fields using four-dimensional data assimilation (FDDA) [Stauffer *et al*., 1991] with the National Center for Environmental Prediction reanalysis, surface, and rawinsonde observations. Most meteorological variables are archived every 30 minutes. For convection and lightning, they are archived every 2.5 minutes. Spring and summer 2005 GEOS-CHEM model simulations provide initial and boundary conditions for trace gases. Regional simulations were spun up during the last two weeks of March 2005. Emission inventories for combustion and industrial sources are taken from GEOS-CHEM [Bey *et al*., 2001], except for the fossil fuel NO_X and CO emissions over the United States, which are taken from the 1999 US Environmental Agency National Emission Inventory. Our previous lightning NO_X production in REAM using convective available potential energy and cloud mass flux resulted in evidence of the lightning-caused NO_X signals over North America seen in GOME during spring [Choi *et al*., 2005, 2007a]. The model produces 3.0×10^{26} NO molecules per flash of intracloud and cloud-to-ground flashes.

4.4 Results and Discussion

4.4.1 OMI-MLS Tropospheric O_3

Figure 4.1 Monthly mean tropospheric O₃ columns from April to August 2005 derived from OMI-MLS satellite measurements (first column), REAM simulations (second column), O₃ produced due to lightning NO production (third column), and O₃ produced due to surface emissions (last column).

Figure 4.1 shows the monthly mean tropospheric column O_3 derived from OMI-MLS satellite measurements and the corresponding model simulations from April to August 2005. The model-simulated O_3 concentrations are added to the level that located on the tropopause level from NCEP reanalysis data. OMI-MLS column shows high O_3 over the eastern United States and the western North Atlantic. Despite large surface emissions of O_3 precursors over North America, O_3 enhancements over the western North Atlantic are as high as they are over the eastern United States. In fact, in April and May, O_3 enhancements (> 45 DU) over the ocean regions are higher than they are over land. As the season progresses from spring to summer, the high O_3 regions over the western North Atlantic move northward from the coast off Florida to New England. In comparison, over the eastern United States, little O_3 enhancement occurs in April. The O_3 enhancement first reaches the southeastern United States in May, and by June, it covers the entire eastern United States. Photochemistry and O_3 production slow in April, so the O_3 enhancements are further downwind from the source regions than they are during the summer months.

Compared with the OMI-MLS measurements, REAM-simulated tropospheric O_3 columns tend to be lower in June but higher in August. Overall, the model reproduces the aforementioned features in the OMI-MLS measurements. The measurements indicate that some of the enhancements over Canada and its coast in April and May are probably related to ozone from the stratosphere, but they are not captured by the model. A detailed comparison with MOZAIC aircraft O_3 measurements and ozonesondes by Choi *et al*. shows that REAM exhibits a tendency of underpredicting upper tropospheric ozone (<

Figure 4.2 Tropospheric O$_3$ columns measured by ozonesondes, derived from OMI-MLS and simulated by REAM at Wallops Island from April to August 2005. Coincidence criteria for OMI-MLS-derived column ozone are at ±3° longitude, ±2.5° latitude on the same day as the ozonesonde measurements. Ozonesonde data are obtained from the World Ozone and Ultraviolet Data Center (WOUDC).

350 hPa) due to the low bias in the prescribed upper boundary condition of O_3 from GEOS-CHEM simulations. Yang *et al.* [2007] has conducted comprehensive comparisons of the OMI-MLS tropospheric O_3 columns with ozonesonde measurements. As an illustration, we show the comparison of OMI-MLS tropospheric O_3 columns with ozonesonde measurements at Wallops Island (38°N, 75°W) in April-August, 2005 (Figure 4.2). The tropopause levels for ozonesonde column calculations are also taken from the NCEP reanalysis data. We also show the corresponding REAM simulation results. Compared with ozonesondes, both OMI-MLS and REAM underestimate tropospheric O_3 columns, the mean biases being -3 and -4 DU for OMI-MLS and REAM, respectively, and the correlation coefficients 0.81 and 0.82, respectively. The more extensive evaluation with 8 ozonesonde stations by Yang *et al*. [2007] shows a bias (-4.7 DU) at 35-60°N in summer. The OMI-MLS biases do not affect the results of this study.

4.4.2 OMI Tropospheric Column NO_2

NOx is a major precursor for tropospheric O_3 production. Figure 4.3 shows the average tropospheric NO_2 columns retrieved from OMI and simulated by REAM in the summer of 2005. Overall, the model results are in reasonably good agreement with OMI retrievals. Compared with the OMI tropospheric NO_2 column, REAM overestimates NO_2 columns by ~1 × 10^{15} molecules cm^{-2} over the Ohio Valley, where power plant NO_x emissions are large. Frost *et al*. [2006] and Kim *et al*. [2006] found large reductions of NO_x emissions from power plants. That reduction was not taken into account in the model. We compute the contribution of lightning to the NO_2 column by comparing the standard model results to a sensitivity simulation in which lightning NO production is

Figure 4.3 Monthly mean tropospheric NO$_2$ columns during summer 2005 from OMI satellite measurements, those from REAM simulations (second column), and those contributed by lightning production in the model (third column). Only OMI data with cloud fractions of < 40 % are used. Corresponding model results are sampled at the same time as the OMI measurements.

turned off. Results show that the contribution of lightning appears to be overestimated over northern Mexico. REAM also simulates higher NO_2 column over the ocean than OMI. Compared to GOME [Choi *et al.*, 2005, 2007a] and SCIAMACHY [Martin *et al.*, 2006], the NO_2 columns retrieved from OMI over the western North Atlantic are lower. The reasons for this finding are unclear.

4.4.3 TES UT O_3 and CO Measurements

Due to insufficient spatial coverage of TES O_3 and CO measurements over North America from April to June 2005, we use only TES observations in July and August. TES O_3 distributions are patchy due in part to measurement uncertainties. Compared with TES O_3 at 300 hPa (250-350 hPa), monthly mean REAM O_3 concentrations have a low bias of 5-6% and a correlation coefficient of 0.5. Comparisons with in situ measurements such as ozonesondes show that UT TES measurements tend to overestimate O_3 [Worden *et al.,* 2007] but the lightning-derived UT O_3 enhancements in the model are consistent with lightning-caused O_3 column peaks (Figure 4.1). Monthly mean UT O_3 enhancements due to lightning are larger than 20 ppbv over a large portion of the western North Atlantic, the southeastern and Gulf coasts, and the southern United States (Figure 4.4). These enhancements are larger than the uncertainties of monthly mean TES O_3 retrievals, which range from 5 to 20 ppbv.

Compared with TES CO at 300 hPa, REAM CO concentrations exhibit larger mean differences in July and August of -6.4% (R=0.44) and -7.4% (R=0.41), respectively (not shown), due to the approximately 30% overestimated CO emissions in the 1999 EPA NEI [Hudman *et al.*, 2007] and the UT CO underestimation of TES, as shown by Luo *et*

Figure 4.4 Monthly mean tropospheric O_3 concentrations at 300 hPa (250-350) for July and August 2005 from measurements from the TES satellite measurements (first column,), those from REAM (second), and those from the difference between REAM and the model turning off lightning NO_X production (third). Only TES O_3 data with a degree of freedom of > 3.5 are used. Corresponding model results are sampled at the same time as the TES measurements.

al. [2007] from the comparisons with MOPITT CO. UT CO enhancements due to cloud convection that occurs over the southeastern coast, the southern United States, and the western North Atlantic, are generally consistent with O_3 column peaks due to convective outflow during the summer (Figure 4.1), but the REAM CO enhancements ranging from 6 to 20 ppbv are comparable to the uncertainties of monthly mean TES CO retrievals ranging from 10 to 15 ppbv.

4.5 Conclusions

The spatial distribution of O_3 and its precursors are strongly affected by cloud outflow and lightning NO_X production. The tropospheric O_3 column by OMI and MLS, the tropospheric NO_2 column by OMI, and UT CO and O_3 by TES can be used to identify the impact of these transient factors using REAM. The OMI-MLS and TES independent satellite measurements show consistent convective outflow and lightning. Large enhancements of column and upper tropospheric O_3 comparable to those over the eastern United States are found over the western North Atlantic both in the satellite measurements and REAM simulations. The O_3 column peak region moves from the southern to northern North Atlantic due to convective outflow and lightning during spring to summer. Results of the model indicate large UT O_3 and CO enhancements due to lightning and cloud convection during the summer, suggesting that high-altitude aircraft campaigns will provide pivotal observations for evaluating model simulations and validating satellite observations. However, satellite uncertainties are still too large, so that model sensitivity is still critical to examine the underlying the detail mechanism of the factors. This study also provide opportunities for the future study of the impact of spatial

perturbations in the amount of O_3, aerosols, and their precursors driven by cloud convection, lightning, and photochemistry on global climate change.

CHAPTER V

LATE-SPRING INCREASE OF TRANS-PACIFIC POLLUTION TRANSPORT IN THE UPPER TROPOSPHERE

5.1 Introduction

Researchers have been concerned about the trans-Pacific transport of pollutants to North America [e.g., Andreae *et al.,* 1988; Merrill *et al.,* 1989; Kritz *et al.,* 1990; Parrish *et al.,* 1992]. They have been most concerned about the increase of pollution from Asia, particularly China, which has recently undergone dramatic economic growth, due to the resulting O_3 concentrations and their impact on the United States [e.g., Jacob *et al.,* 1999; Berntsen *et al.,* 1999]. For example, subsidence caused by high O_3 transported from Asia and produced catalytically by NO_x ($NO+NO_2$) during the oxidation of CO in addition to volatile organic compounds (VOCs) could significantly exceed standards set by the National Ambient Air Quality Standard at California mountain sites [Hudman *et al.,* 2004].

Previous analyses of the effects of trans-Pacific transport have focused on measurements of low-altitude O_3, CO, and peroxyacetyl nitrate (PAN) [Jaffe *et al.,* 1999; Lin *et al.,* 2000; Jaffe *et al*[4]*.,* 2003]. However, this study will focus on two unexplored issues and evaluate current methods of simulating these observed features. One is to ascertain the differences between the characteristics of upper tropospheric trans-Pacific transport and those at lower altitudes; and the other is to determine the effects over North America of trans-Pacific transport on O_3 and its most critical precursor, NO_x. To our

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[4]This chapter is for "Late-spring increase of trans-Pacific pollution transport in the upper troposphere," published at *Geophysical Research Letter* (*33*, L01811, doi:10.1029/2005GL024975). Authors are Y. Wang, Y. Choi, T. Zeng, B. Ridley, N. Blake, D. Blake, and F. Flocke.

knowledge, no one has examined the impact of trans-Pacific transport on North American NO_x.

This study will analyze the data from the Tropospheric Ozone Production about the Spring Equinox (TOPSE) experiment between February and May of 2000 [Atlas *et al.*, 2003]. The experiment, comprised of thirty-eight science flights in seven deployments (one to two weeks apart), took place in a region that spanned from Colorado to north of Thule, Greenland. The purpose of the experiment was to measure a comprehensive suite of chemical species relating to tropospheric O_3 chemistry from the surface up to 8 km.

This research will analyze the measurements of the TOPSE experiment using REAM [Choi *et al.*, 2005] and the global GEOS-CHEM model [Bey *et al.*, 2001]. Within the continental United States and Canada, the REAM model domain covers a horizontal resolution of 70x70 km^2 and 21 layers up to 100 hPa in the vertical [Choi *et al.*, 2005]. To simulate the meteorological fields, this study employed the National Center for Atmospheric Research/Penn State MM5 using four-dimensional data assimilation along with the National Center for Environmental Prediction reanalysis, surface, and rawinsonde observations. Initial and hourly boundary conditions for trace gases were provided by the spring 2000 simulations that used the global GEOS-CHEM model (version 7.2.4 with a horizontal resolution of 2°x2.5° and 30 layers up to 0.01 hPa, GEOS-3 meteorological fields). REAM shares the chemistry and deposition modules of GEOS-CHEM. More importantly, convective transport and lightning NO_x production schemes in the REAM are implemented [Choi *et al.*, 2005].

5.2 Results and Discussion

Results of the analysis of TOPSE 2000 showed that upper tropospheric reactive nitrogen NO_x and PAN increased the most during the late spring [Y. Wang *et al., 2003a*]. Based on observed and simulated NO_x mixing ratios from March to May TOPSE aircraft observations, an initial investigation identified large increases of NO_x concentrations above 5 km, shown in Figure 5.1. The REAM is in reasonable agreement with the low concentrations in the upper troposphere observed in February (not shown) and March. However, since it simulates some enhancements in April, but none in May, it underestimates NO_x concentrations to a great extent. April REAM enhancements, which were not simulated in the global GEOS-CHEM model, are the result of localized convective transport and lightning NO_x production.

Because of the presence of a high-pressure ridge system residing over the western United States in May, neither the REAM nor the CEOS-CHEM model shows significant lightning and convective activity over the region, but measurements in each flight during this time (not shown) reveal four enhancements, which reach 200 km horizontally and 2 km vertically, with NO_x mixing ratios of >50 pptv at altitude >6 km. However, these measurements are often restricted by sampling. Two of the enhancements (not shown) were discernable but underestimated by the corresponding model simulations. Previous NO_x simulations that used differing regional (HANK [Hess *et al.,* 2000]) and global (MOZART-2 [Horowitz *et al.,* 2003]) CTMs also found model underestimations of 50% to 60% with several data points of simulated NO_x mixing ratios >50 pptv above 5 km [Emmons *et al.,* 2003]. Nevertheless, these researchers did not provide reasons for such significant underestimation.

Figure 5.1 Observed and REAM-simulated monthly mean distributions of NO_x from March to May 2000. The REAM data were sampled along the TOPSE flight tracks.

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

Figure 5.2 shows a comparison of observed and simulated CO, PAN, and O_3 concentrations in May. The REAM has distributions similar to GEOS-CHEM but with more localized enhancements. Hence, only the former is shown. Carbon monoxide is a good tracer for anthropogenic emissions, and peroxyacetyl nitrate is the reaction product of NO_2 and peroxyacetyl radicals formed during the oxidation of VOC's. Therefore, it is a good tracer for tropospheric chemical activity of O_3 precursors. While in reasonable agreement below 6 km, the simulated CO, PAN, and O_3 concentrations are much lower than those from the observations at higher altitudes. The observed upper tropospheric enhancements of CO, PAN, and O_3 tend to be collocated with those of NO_x (Figure 5.1).

Figure 5.2 The same as Fig. 5.1, but for CO, PAN, and O₃ in May. To filter out the effect of stratospheric O₃ when constructing the observed O₃ distribution, we did not include measurements with mixing ratios >110 ppbv.

A close inspection of the simulated O_3 concentrations reveals slight enhancements in the upper tropospheric regions where high O_3 was observed. The enhancements, which correspond to those in the GEOS-CHEM-simulated western boundary conditions, are not caused by photochemical production in the regional model, suggesting that the global model has some capability of simulating trans-Pacific transport [e.g., Hudman *et al.,* 2004]; however, the simulated magnitudes are too small.

The discrepancies between simulated and observed CO and PAN concentrations are much larger in May than they are in the three previous months (not shown). At lower altitudes (<6 km), the model reproduces the observed rapid decrease of CO well from April to May, but the decrease reflects more active photochemical oxidation towards summer. While the observations show a large increase of CO at higher altitudes (>6 km), the simulated concentrations are lower in May than April. The simulated PAN concentrations in May are similar to those in April at high altitudes, while the observations also show a large increase. The observed O_3 mixing ratios at high altitudes show a clear increase from 50-60 ppbv in February to >80 ppbv in May (Figure 5.2) [Browell *et al.*, 2003]; the model does not reproduce the large increase.

We previously attributed 60% and 80% of the observed springtime O_3 increase to photochemical production at mid and high latitudes, respectively [Y. Wang *et al.,* 2003b]. Thus, the upper tropospheric O_3 problem in the model may be attributed to the large underestimation of NO_x. In addition, a direct observational evidence for the importance of photochemical O_3 production catalyzed by NO_x can be seen in Figure 5.3, which shows the observed correlation between NO_x and O_3 above 4 km in May. By examining the deviation from a normal mode in the CO cumulative probability distribution in May,

we identify two distinct data groups, CO <110 ppbv (lower 10th percentile) and CO >135 ppbv (upper 30th percentile). Low CO mixing ratios reflect a strong influence by either stratospheric or clean marine boundary layer air, while high CO mixing ratios indicate polluted air masses. The low CO data points show high O_3 mixing ratios of 150-220 ppbv with NO_x of 80-110 pptv, reflecting the influence of stratospheric air since O_3 mixing ratios in the clean marine boundary layer are low.

The high CO data points show that O_3 mixing ratios increase to 120 ppbv while NO_x mixing ratios reach 250 pptv. These high O_3 concentrations mainly reflect photochemical production of O_3 in polluted tropospheric air masses. Lightning affects the concentrations of CO or O_3 negligibly. Fresh local convection tends to produce higher CO and NO_x concentrations through transport but relatively low O_3 concentrations and PAN/NO_x ratios due in part to the time required for photochemical processing. Both the high PAN/NO_x ratios of 5-40 (not shown) and >80 ppbv of O_3 with a moderate amount of NO_x (~150 pptv) suggests that the air masses are photochemically aged and not significantly affected by local lightning or convective transport. Furthermore, inspection of back trajectories [Y. Wang *et al.*, 2003b] for data points with NO_x >50 pptv in Figure 5.3 reveals that they are driven by trans-Pacific transport, not Pacific recirculation of pollutants emitted from the West Coast.

Our hypothesis that the observed large enhancements of upper tropospheric NO_x, CO, PAN, and O_3 are due to trans-Pacific transport is also supported by the measurements of CFCs and Halon-1211 and back trajectory calculations. The production of CFCs and Halon-121 was phased out in developed countries in 1995 and will be

Figure 5.3 Observed correlations between O_3 and NO_x, grouped by CO mixing ratios (ppbv) in May. Only coincidental measurements of all three species above 4 km are included.

phased out in developing countries by 2010. Therefore, they are good tracers for air masses from East Asia. Observed CFCs and Halon-1211 exhibit similar features. Figure 5.4 shows the distribution of CFC-12 in May. The large enhancements at high altitudes (> 6 km) tend to be consistent with those of NO_x, CO, PAN, and O_3. A close inspection of the measurements, which correspond to the enhancements of NO_x and CFC-12 observed at 45-50° N at high altitudes, reveals a general association of high NO_x concentrations with high CFC-12. However, the point-to-point correspondence is poor for two possible reasons. First, CFC-12 was sampled at a much lower frequency than NO_x. Secondly, the surface sources of NO_x and CFCs are not necessarily collocated, and NO_x concentrations are also affected by lightning production.

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

Figure 5.4 Observed monthly mean distribution of CFC-12 in May.

It is possible that trans-Pacific pollutant transport surges in May due to a significant increase in convection and lightning over East Asia or the western Pacific (not simulated in the models). This possibility must be explored in a detailed analysis of other field measurements.

5.3 Conclusions

TOPSE observations show large enhancements of NO_x, PAN, CO, O_3, and CFCs at an altitude of >6 km in May. We hypothesize that these enhancements are due to trans-Pacific transport. This hypothesis is supported by our analysis of the observations and model result. First, we find that these chemical tracers show consistent enhancement patterns at high altitudes. Both CFC enhancements and back trajectory calculations imply trans-Pacific transport from East Asia. In addition, we find that the NO_x-O_3 correlation for high CO data points indicates significant tropospheric photochemical production. We also find that the relatively high PAN/NO_x ratios of >5 indicate photochemically-aged air masses. Finally, we show that separate regional/global chemical transport models using different meteorological fields and chemical formulations consistently underestimate the enhancements of NO_x, PAN, and CO. The contribution by North American surface emissions is limited in these simulations because the high-pressure ridge system over the western United States suppresses convection and lightning in May.

Our results indicate that the rapid late-spring increase of reactive nitrogen NO_x and PAN in the northern mid-latitude upper troposphere during TOPSE is most likely due to enhancements of these species by trans-Pacific transport. Such enhancements result in significant increases in photochemical oxidation and O_3 production. The trace gas

enhancements, including those of CO, continue to increase in May. This phenomenon is very different from trans-Pacific transport-driven CO enhancements at low altitudes, which peaks in March and April [e.g., Weiss-Penzias *et al.,* 2004]. The current global CTMs do not capture this rapid seasonal transition, which results in a significant underestimation of the photochemical production of O_3 in the models. The problem raises concerns about our capability to assess the effects of intercontinental transport on regional air quality.

CHAPTER VI

ASSESSING THE PHOTOCHEMICAL IMPACT OF SNOW NO$_X$ EMISSIONS OVER ANTARCTICA DURING ANTCI 2003

6.1 Introduction

In late November and December of 2003, the Antarctic Tropospheric Chemistry Investigation (ANTCI) took place [Esiele *et al.,* 2007]. Unlike the ISCAT 1998 and 2000 studies, both the tethered balloon observations at SP [Helmig *et al.,* 2007] and the Twin Otter aircraft plateau measurements gathered the critical spatial information about NO over Antarctica [Davis *et al.*, 2007]. We examined these measurements along with SP surface measurements by employing the 1-D and regional REAM models. On the basis of SP measurements, the 1-D model is to co ^{5} nstruct a snowpack NO$_x$ emission parameterization and then run 1-D model simulations to analyze the effects of vertical transport on reactive nitrogen. On the basis of balloon and Twin Otter measurements, the snowpack NO$_x$ emission parameterization is implemented in REAM to examine the effects of transport by advection and the spatial heterogeneity of snowpack NO$_x$ emissions. The focus of this modeling analysis is the plateau region, where NO$_x$ emission rates are expected to be the highest. Section 6.2 describes the models ; Section 6.3 presents a 3-D model construct of a snow NO$_x$ emission parameterization, and then Section 6.4 evaluates the 1-D and REAM simulations with surface measurements of reactive nitrogen. Finally, Section 6.5 presents a comparison of the 1-D and REAM model simulations with the balloon and Twin Otter measurements and then assesses the

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[5]This chapter is for "Assessing the photochemical impact of snow NOx emissions over Antarctica during ANTCI 2003," accepted in *Atmospheric Environment* in 2007. Authors are Y. Wang, Y. Choi, T. Zeng, D. Davis, M. Buhr, G. Huey, and W. Neff.

impact of snow NO_x emissions on the reactive nitrogen budget and photochemistry over Antarctica. Finally, Section 6.6 concludes.

6.2 3-D Model Descriptions and the 1-D Model Setup

The regional 3-D modeling system has two components, the polar version of the Penn State/National Center for Atmospheric Research mesoscale model MM5 and a regional chemistry and transport model. The models have a horizontal spatial resolution of 80×80 km^2. There are 27 vertical layers up to 10 hPa, 13 of which are placed in the lowest 1 km in order to simulate the vertical distribution of trace gases in the boundary layer. In our simulations, the MM5 simulation domain is five grid boxes larger on each side than the chemical transport simulation domain such that any dynamic anomaly near the boundary does not affect transport in the chemical model.

We use the polar version of MM5 [Bromwich *et al.,* 2001; Cassano *et al.,* 2001], which provides better meteorological simulations in comparison to regular MM5 or other similar models because the model has specific physical parameterizations for polar regions. In our simulations over Antarctica, we use four-dimensional data assimilation conducted using the ECMWF reanalysis, rawinsondes, and surface observations. Most meteorological data are archived every 30 minutes. We archive turbulence statistics every 2.5 minutes in order to resolve turbulent transport in the boundary layer. We use the ETA Mellor-Yamada-Janjic (MYJ) 2.5-order closure scheme [Black, 1994] for the turbulence calculation.

The regional chemical transport model [Zeng *et al.*, 2003, 2006; Choi *et al.,* 2005, 2007a, 2007b; Y. Wang *et al.,* 2006; Jing *et al.,* 2006] adopts the photochemical and dry

and wet deposition modules from the GEOS-CHEM model [Bey *et al.*, 2001]. The model includes a detailed photochemical mechanism with about 200 reactions and 120 concentration-varying chemical species; 24 tracers (family or species) are transported to describe O_3-NO_x-hydrocarbon chemistry. Recent kinetics data on HNO_4 photolysis and thermal decomposition [Roehl *et al.,* 2002; Gierczak *et al.*, 2005] are used in this work. The transport scheme is that by Walcek [2000]. We apply the simulation results of the global GEOS-CHEM model to specify the initial and daily boundary conditions of trace gas concentrations in the regional model. GEOS-CHEM (version 5.02 4° latitude by 5° longitude resolution) is driven by GEOS-4 assimilated fields for 2003 by the NASA Global Modeling and Assimilation Office.

A 1-D model derived from the 3-D model with vertical transport only by turbulence is used to analyze the interaction of snow NO_x emissions, photochemistry, dry deposition, and turbulent transport in the boundary layer at SP. Therefore, the 1-D and 3-D models share the same vertical structure and meteorological fields (for SP in the 3-D model). GEOS-CHEM results are used for initial and upper chemical boundary conditions at 1 km in 1-D simulations, which is well above the shallow atmospheric boundary layer at SP [Neff *et al.,* 2007]. One objective of the 1-D simulations is to construct, on the basis of SP measurements, a parameterization of snow NO_x emissions that can be used in the 3-D model for Antarctica. We use the 1-D model for this purpose because the iterative 1-D NO_x flux analysis detailed in the next section cannot be executed within the 3-D model. We chose not to include the snow emissions of H_2O_2 and CH_2O [Hutterli *et al.*, 2004] in this work for three reasons. First, measurements of H_2O_2 at the SP show magnitudes (~270 pptv) similar to those in 2000 reported by Hutterli *et al.*

111

[2004]. However, CH_2O mixing ratios (20-60 ppbv) are lower than the values in 2000 (50-150 ppbv). Model simulations for ANTCI 2003, constrained by observed concentrations of O_3, NO, hydrocarbons, and water vapor and photolysis rates of $J(O^1D)$ and $J(NO_2)$, show CH_2O values in the range of the 2000 measurements (50-120 ppbv) but higher than the 2003 measurements, implying a photochemical sink for CH_2O in snow rather than a source during ANTCI 2003. Second, measurements of H_2O_2 in 2003 are fairly constant (~200 ppbv higher than the model results). We are unable to parameterize the diagnosed emissions as functions of other variables as we did with snow NO_x emissions. Without H_2O_2 measurements in other regions, we cannot extend the emissions to other regions of Antarctica in the 3-D model. Finally, as discussed in Chen *et al.* [2004], the photochemical model (without snow emissions of H_2O_2) overestimates OH measurements. Similar discrepancies were found in the 2003 experiment. Inclusion of snow H_2O_2 emissions will further increase model overestimates. Thus, more targeted measurements will be needed to resolve the disagreement between simulated and measured OH [Chen *et al.,* 2004]. We will take this uncertainty into consideration when analyzing the results of the 3-D model, but we will not further discuss the model-measurement comparisons with regard to HO_x chemistry, which would largely be a duplication of work by Chen *et al.* [2004].

6.3 Snow NO_x Emission Flux Parameterization

We apply the 1-D model to estimate the snow NO_x emissions based on trace gas measurements at SP. We assume that the emissions are in the form of NO_2 [Jones *et al.,* 2000]. Davis *et al.* [2004], however, showed that NO and NO_2 are in photochemical

equilibrium at the surface, based on measurements taken at -20 cm to the surface. Whether the emissions are in the form of NO or NO_2 does not change the simulation results because these species reach photochemical equilibrium in minutes in the plateau atmosphere with the amount of O_3 present. We first compare simulated meteorological variables to the measurements at SP.

6.3.1 Effects of Turbulence on Boundary Layer Height and Surface Temperature and Wind Speed

A key measurement pertinent to the model flux estimation is that of boundary layer height, estimated using the Sound Detection and Ranging (SODAR) instrument. Based on the backscattered signals (due to boundary layer turbulence structures), an automatic algorithm [Neff *et al.*, 2007] that identifies the boundary layer height was applied. The maximum range of the instrument, as configured for the ANTCI 2003 study, was 180 m. The simulated diffusion coefficient drops rapidly to a minimum value at the top of the boundary layer. Therefore, we define the boundary layer height in the model as the altitude at which the turbulence diffusion coefficient drops to a value equivalent to 10 times the minimum value specified in the model. Based on this approach, the polar MM5 simulation using the original ETA MYJ 2.5-order closure scheme clearly underestimates SODAR measurements since the boundary layer only occasionally extends beyond the first model layer (Figure 6.1). Further analysis reveals a problematic assumption in the MM5 MYJ turbulence scheme implementation, i.e., the default minimum diffusion coefficient is set at 0.09 m^2 s^{-1}. While a reasonable minimum value for mid-latitude North America, it is too high over the polar region, where the surface roughness of snow is very

Figure 6.1 Observed and simulated daily boundary layer heights at SP during ANTCI 2003. Simulation results using the original and modified ETA MYJ turbulence scheme are shown. The vertical bar shows the daily standard deviation. The maximum altitude measurable by SODAR is 180 m.

Figure 6.2 The same as Figure 6.1, but for temperature and wind speed. "T" denotes temperature and "V" denotes wind speed.

low. Thus, we decreased the minimum value to 0.001 m^2 s^{-1}. With this adjustment, the simulated boundary layer height is much higher and in reasonable agreement with the SODAR measurements, particularly in light of the model's vertical resolution and the uncertainty in the SODAR boundary layer height detection algorithm [Neff *et al.,* 2007]. The correlation coefficient of observed and simulated boundary layer heights improves from 0.44 to 0.73.

Simulated surface wind speed and temperature at SP are not strongly affected by the modification of the turbulence scheme (Figure 6.2). However, some improvement in temperature simulations can be observed. Polar MM5 has a warm bias in late November. When the minimum diffusion coefficient is reduced to 0.001 m^2 s^{-1}, the warm bias is reduced (but not eliminated). Model-simulated friction velocity (u_*) values are in good agreement with sonic anemometer measurements in the second half of December (not shown). The surface stress simulation is not significantly affected by changing the minimum diffusion coefficient in the model. Additional evidence was found in our recent model analysis of (halogen-driven) ozone depletion events in Alert, Canada, in which the model simulations of surface ozone in Alert were much improved in May when the minimum diffusion coefficient decreased from 0.09 to 0.001 m^2 s^{-1} [Zeng *et al.,* 2006]. Thus, we adjusted the minimum diffusion coefficient to the lower value for our simulations.

6.3.2 Snow NO_x Emission Flux Estimation and Parameterization

We constrain the 1-D model with observed concentrations of O_3, hydrocarbons, water vapor, and the photolysis rates of $J(O^1D)$ and $J(NO_2)$. Trace gas measurements

were made on the second floor of the Atmospheric Research Observatory (ARO), approximately 10 m above the snow surface. The presence of the ARO building induces local-scale mixing; thus, we consider these measurements as averages for the lowest model layer (0-10 m). All measurements have higher measurement frequencies than hour^{-1}; hourly averages are used in the model analyses. The surface NO_x concentrations in the model are determined by an influx from the snow pack, an outflux to higher altitudes, and chemical production and loss. Other than the snow emission flux, all other terms are calculated in the 1-D model. With measurements of NO, we can therefore derive snow NO_x emission fluxes using the model. Our initial guess of the snow emission is 3.9×10^8 molec cm^{-2} s^{-1} [Oncley *et al.*, 2004]. This emission flux is adjusted iteratively until model-simulated surface NO concentrations match the measurements (to <1% each hour) or if the flux is reduced to 0. The derived daily snow NO_x flux is shown in Figure 6.3. The average emission flux derived from the 1-D model is 3.2×10^8 molec cm^{-2} s^{-1}, which is 20% lower than the mean flux of 3.9×10^8 molec cm^{-2} s^{-1} estimated by Oncley *et al.* [2004] using sonic anemometer/thermometers and NO measurements in late November/early December of the ISCAT 2000 study. The reasonable agreement found between NO_x flux estimates for ISCAT 2000 and ANTCI 2003 could be fortuitous. However, additional flux measurements/model analyses are needed to provide more substantial constraints on the year-to-year variability of snow emissions at the site.

Superimposed on the NO_x flux are observed and simulated temperature and wind speed in Figure 6.3. The derived flux appears to show anti-correlations with temperature and to some extent with wind speed. Other variables, such as surface pressure and humidity, do not significantly correlate or anti-correlate with the derived NO_x flux. Here,

Figure 6.3 1-D model derived daily snow NO_X emissions, and observed and simulated temperature and wind speed at SP. The black line shows model-derived snow NO_X emissions. "T" denotes temperature (K) and "V" denotes wind speed (m s⁻¹).

Figure 6.4 Parameterized snow pack NO$_x$ emission flux as a function of temperature (K) at a wind speed of 5 m s^{-1} and as a function of wind speed (m s^{-1}) at a temperature of 250 K.

the emission flux was parameterized on a daily basis as polynomials of simulated wind speed and temperature up to the 2nd order and obtained

$$\text{NO}_x \text{ flux} = -1009 + 8.38T - 0.0173T^2 + 2.008v + 0.0689v^2 - 0.011vT, \qquad (1)$$

where the flux is in 10^8 molec m^{-2} s^{-1}, temperature T in K, and wind speed v in m s^{-1}.

Figure 6.4 shows the parameterized flux as a function of temperature at a wind speed of 5 m s^{-1} and as a function of wind speed at a temperature of 245 K. We see that the derived snow NO$_x$ emission tends to increase as the temperature decreases; but the rate of change increases as the temperature increases at the high end. By comparison, the flux dependence on wind speed is relatively weak and nonlinear. Generally speaking, the derived snow emission rate tends to increase as wind speed decreases at the low end, but tends to increase as wind increases at the high end. The flux variation with wind speed is relatively small.

The ranges in temperature and wind speed in the parameterization are limited by the measurements at SP (a temperature from 238 to 252 K and a wind speed from 2 to 9 m/s). When applied in the 3-D model, both the temperature and the wind speed can exceed these ranges. We linearly extrapolate the parameterization for temperatures up to 260 K when flux is >0. The flux dependence on wind speed is weak; we do not use any extrapolation, i.e., out-of-bound wind speeds are replaced by the respective bound values. We did not find significant correlations of the derived snow NO$_x$ emission flux with ozone column density, solar zenith angle, or values of J(O^{1}D) or J(NO$_2$). It appears that the lack of any correlation is due in part to the relatively small range of values for these photochemical parameters at SP. Emissions of NO$_x$ from the snow pack are allowed only during daylight conditions in the 3-D simulations.

An empirical emission parameterization is constructed here to sidestep the lack of fundamental and quantitative knowledge of the snow NO_x emission process such that measurements from ANTCI 2003 can be analyzed via the model simulations to improve our understanding of photochemical processes over Antarctica. As a result, use of the emission parameterization in other periods may lead to significant errors. A more process-based parameterization of the snow pack NO_x emission rate should consider, for example, nitrate concentrations in snow [Simpson *et al.,* 2002; Wolff *et al.* 2002]. However, available snow nitrate measurements over Antarctica are currently very limited in space and time [e.g., Kreutz and Mayewski, 1999] and we do not have the necessary measurements to test the structure of snow nitrate distribution as simulated by Wolff *et al.* [2002]. Interestingly, model estimated snow pack NO_x emissions at SP by Wolff *et al.* [2002] are a factor of 3-4 lower than the measurement by Oncley *et al.* [2004] during ISCAT 2000 or the derived average flux from this study. The discrepancy underscores the need for additional laboratory and field measurements that constrain the process-based snow pack emission models.

6.4 Evaluations with Surface Reactive Nitrogen Measurements at SP

We apply the derived snow pack NO_x emission parameterization in the 1-D and 3-D models. We compare 1-D and 3-D model-simulated NO mixing ratios with the observations at SP in Figure 6.5a. Additional input to the 1-D model consisted of surface measurements of O_3, hydrocarbon concentrations, water vapor, and the photolysis rates for $J(O^1D)$ and $J(NO_2)$. However, these measurement constraints could not be applied to the 3-D simulations. In the 1-D simulation, snow NO_x parameterization as a function of

Figure 6.5a Observed and 1-D and REAM model simulated near-surface NO mixing ratios at SP. In the second 3-D simulation, parameterized snow NO_X emissions increase by 30%.

Figure 6.5b Simulated surface NO_X mixing ratios (pptv) and wind at 1200 UT on November 25 and 30, 2003.

temperature and wind speed is used. In the first 3-D simulation, the original model-derived daytime snow emission parameterization is applied over the entire Antarctic continent. In the second 3-D simulation, the parameterized snow emissions are increased by 30%.

The observed high NO episodes on November 25, 30, and December 8, 23 are generally reproduced by the model simulations. Sensitivity results indicate that stable and shallow boundary layers during those periods are main drivers for the developments of high surface NO_x concentrations [Davis *et al.*, 2004]. The correlation coefficient between observed and 1-D simulated surface NO concentrations is 0.79. In the 3-D simulation with the original snow NO_x emission parameterization, the model has a tendency to underpredict the observed values; the correlation coefficient is slightly lower at 0.74. Sensitivity analysis indicates that downward advection of lower NO_x concentrations from above in general and horizontal advection of low NO_x air on occasion are key factors in reducing surface NO_x concentrations at SP in the 3-D model compared to the 1-D model. The assumption of zero mean vertical and horizontal advection used in eddy correlation measurements and in the 1-D model could be in error because of large-scale downslope katabatic flow over Antarctica. The 3-D model results are improved by increasing snow NO_x emissions by 30%. The increase in NO_x during high NO_x episodes is higher than 30%, partly because of the nonlinear relationship between NO_x lifetime and its mixing ratio [Davis *et al.,* 2004]. The difference between the 1-D and 3-D models indicates the the eddy correlation method tends to underestimate snow NO_x emissions, as it does not account for advection. Therefore, all the 3-D model results presented hereafter are taken from the simulation with a 30% increase in snow NO_x emissions.

The 3-D model was able to simulate low NO_x concentrations around December 2, not captured by the 1-D model. However, the 3-D model clearly underestimates the NO_x episode around November 30 while reproducing the earlier episode around November 25. Horizontal gradients and transport appear to play important roles. Figure 6.5b compares surface NO_x concentrations and wind transport over Antarctica between November 25 and 30 (1200 UT). The model predicts more extensive high surface NO_x concentrations on November 25 than on November 30. While the high NO_x distribution is nearly homogeneous around SP on November 25, a large spatial gradient is simulated around SP on November 30. Simulated surface winds are in good agreement with ANTCI measurements on November 25 and with Automatic Weather Station (AWS) measurements on November 30. We use AWS data for the latter day, when ANTCI wind measurements were unavailable. Along the 0° meridian, prevailing transport on November 25 is from the high-elevation plateau, where NO_x emissions are high; prevailing transport on November 30 is from a northern low-elevation region, where NO_x emissions are low. Low-NO_x transport is important for the creation of the spatial NO gradient around SP on November 30 in the 3-D model. Thus, the underestimation in the 3-D model, but not in the 1-D model, suggests that this low-NO_x transport is exaggerated in the 3-D model; possible reasons for these findings are errors in the snow NO_x emission distribution or wind transport and coarse model spatial resolution.

Figure 6.6 shows compares observed and simulated surface HNO_3 at SP. Since HNO_3 concentrations strongly depend on NO_x concentrations, model errors in NO will propagate into HNO_3 simulations. To eliminate this error, we added another 1-D simulation in which surface NO concentrations are specified as observed, so snow NO_x

Figure 6.6 The same as Figure 6.5a, but for HNO_3. In the first 1-D simulation, surface NO is specified as observed. In the second 1-D simulation, snow NO_X emission parameterization is used. In the 3-D simulation, parameterized snow NO_X emissions (Eq, (6.1)) are increased by 30%. The measurement accuracy of HNO_3 is 20% [Huey *et al.*, 2004].

emission parameterization is not used in this simulation. The dry deposition velocity in the models is calculated with the resistance-in-series scheme by Wesely [1989]. The aerodynamic resistance is computed based on ETA MYJ turbulence output. The snow surface resistance of HNO_3 also follows Wesely [1989]. The calculated average deposition velocity during ANTCI 2003 is 0.15 cm s^{-1}. The model result shows reasonable agreement with the measurements, revealing low HNO_3 concentrations between December 3 and 20 and high concentrations between December 21 and 24. The correlation coefficients are 0.85 and 0.77 for the 1-D and 3-D models, respectively. Both models tend to overestimate HNO_3 concentrations at low HNO_3 values. However, the positive bias of the 3-D model is considerably larger; after presenting the results for HNO_4, we will discuss the reasons for the bias.

In the HNO_4 simulations, we assume that dry deposition of HNO_4 to snow is as fast as it is of HNO_3 [Slusher *et al.*, 2002]. Therefore, the average of calculated dry deposition velocities for HNO_4 is 0.15 cm s^{-1}. Figure 6.7a, in which observed and simulated HNO_4 at SP are compared, the 1-D simulations generally show agreement of the measurements, except for low bias before December 9. However, the observed variability is severely underestimated. The correlation coefficients are 0.63.

In the 1-D model, near-surface HNO_4 is determined by chemical production and loss, turbulent diffusion transport, and dry deposition. We examine each term to investigate which of these factors is likely the major contributor to the high-frequency variations in the measurements. Figure 6.7b shows the time series of each term in December. In this simulation, surface NO is specified as observed. The magnitudes of the four terms are comparable. Chemical production is generally larger than chemical loss,

Figure 6.7a Same as Figure 6.6, but for HNO_4. The measurement accuracy of HNO_4 is

30%.

Figure 6.7b Simulated chemical production, loss, turbulent diffusion transport, and dry deposition rates for HNO_4 near the surface (0-10 m) in the 1-D model.

and dry deposition loss is generally larger than turbulent influx from above. During the episode on December 21-24, both turbulent transport and dry deposition are low because of the establishment of a shallow stable boundary layer (Figure 6.1). Neither thermal deposition nor photolysis exhibits high-frequency variations, nor does the simulated aerodynamic resistance vary in high frequency. Major portions of high-frequency variations in chemical loss and dry deposition rates are driven by variability in the simulated HNO_4 concentration. The chemical production rate does exhibit large high-frequency variations, particularly between December 12 and 19. However, the high-frequency variation is modulated by turbulent transport. The initial large pulse of HNO_4 production is compensated by a decrease in turbulent transport from above. If high HNO_4 production driven by snow NO_x emissions continues, the production of HNO_4 in the layers above also increases as NO_x is transported upward by turbulence, resulting in an accumulation of HNO_4 and an increase in turbulent influx of HNO_4 to the surface layer. The slower response of the 1-D model-simulated HNO_4 to NO variation may indicate that turbulent transport between the lower model layers is overestimated. The correlation coefficient between 3-D model-simulated and observed HNO_4 is 0.61. The 3-D model simulation is considerably lower than 1-D simulated and measured HNO_4 during the high-concentration episode on December 21-24. Increasing the snow resistance to HNO_4 deposition decreases dry deposition and increases HNO_4 concentrations. A 50% increase in snow resistance pushes the HNO_4 mixing ratios to the upper bound of observed values prior to December 20, but the model still underestimates the values on December 21-24 since aerodynamic resistance during this period is high, reducing the dry deposition velocity by a factor of 4 from the earlier period. An inspection of the 3-D

128

model results reveals that advection of low HNO_4 to SP on December 21-24 contributes significantly to the low bias in the model.

To further clarify the model results, we compare the 1-D and 3-D simulated mean vertical profiles of NO, HNO_3, HNO_4 during ANTCI 2003 (Figure 6.8). The 1-D simulation with surface NO concentrations specified to the measurements are similar to that with parameterized snow NO_x emissions. Despite 30% higher emissions, the simulated NO profiles in the 3-D model are very similar to the 1-D profiles. A clear drop off in the NO profiles is evident at about 50 m, the altitude at which the boundary layer top generally resides under stable conditions. The difference between the 1-D and 3-D model vertical profiles is much larger for HNO_3 and HNO_4. Both gases show higher values at 50 m than at the surface, suggesting that vertical mixing together with advection might represent an effective loss process for reactive nitrogen from the plateau. It is also noteworthy that the estimated concentrations of both gases over the altitude range of 50-500 m when calculated using the 3-D are higher than they are using the 1-D model. These higher concentrations in the 3-D model are driven in part by advection from high plateau regions, a process not simulated in the 1-D model. While not affecting surface HNO_4 concentrations significantly, the accumulation extends to the surface for HNO_3 because HNO_3 has a longer chemical lifetime than HNO_4. Although model-calculated dry deposition is adequate in the 1-D simulations, the overestimates of HNO_3 in the 3-D model indicate a need for lower snow resistance and thus higher HNO_3 deposition. The slightly lower HNO_4 concentration at 0-50 m in the 3-D than that in the 1-D model is due in part to underestimation during the episode on December 21-24.

Figure 6.8 1-D and 3-D model-simulated mean vertical profiles of NO, HNO_3, and HNO_4 during ANTCI 2003. In the first 1-D simulation, surface NO is specified as observed. In the second simulation, snow NO_X emission parameterization is used.

Using a box model analysis of ISCAT 2000 measurements, Slusher *et al.* [2002] estimated that the lifetimes of HNO_3 and HNO_4 against deposition are 3.5 hours. With ANTCI data, a similar calculation results in a dry deposition lifetime of 10 hours. Slower dry deposition during ANTCI likely reflects a meteorological environment different from that of ISCAT 2000. Scaling a boundary layer depth to 50-100 m with a deposition velocity of 0.15 cm s^{-1} yields a lifetime in the range of 9 to 18 hours. We note that a simple scaling of the boundary layer height with dry deposition velocity underestimates the deposition lifetime of HNO_4 because its concentrations increase by a factor of 2 in the boundary layer (Figure 6.8). Estimating dry deposition lifetimes using a box model is reasonable in a well-mixing boundary layer, but it is problematic over Antarctica because the boundary layer is frequently stable. The large vertical gradients of HNO_4 and NO_x, which exhibit opposite trends, cannot be taken into account properly in a box model. Furthermore, Figure 6.7b shows that diffusion influx is as important as chemical production or deposition loss. In a shallow box near the surface, a box-model calculation would overestimate the loss by dry deposition because it accounts for both dry deposition and diffusion influx. However, the finding by Slusher *et al.* [2002] that HNO_4 deposition accounts for a significant portion of nitrogen deposition to snow is still valid in our results since the deposition flux is the product of deposition velocity and trace gas concentration. The deposition velocities are the same for HNO_3 and HNO_4, and their concentrations are in comparable ranges.

6.5 Comparison with Balloon and Aircraft NO Measurements and Assessments of Plateau Reactive Nitrogen Budget and Photochemical Impact Over Antarctica

We extend the comparison of model-simulated reactive nitrogen with surface measurements to include the vertical distributions of NO as recorded by the tethered balloon platform at SP [Helmig *et al.*, 2007] and the Twin Otter data recorded within 400 km of SP but still over the plateau [Davis *et al.*, 2007]. For this purpose, the construction of a rather crude empirical daytime snow NO_x emission parameterization (Section 3.2), without which it would be difficult to simulate the spatial variability of surface NO_x over Antarctica, is critically important.

The tethered balloon was used to measure NO vertical distributions at SP on December 17-28. High NO_x concentrations were measured near the surface on December 21 and 23 (Figure 6.5a); we separate these data from the periods of December 17-20 and 25-28. During the high-NO_x period of December 21 and 23 (no balloon measurements were made on December 24), simulated median values at low altitudes are lower than the measurements because of the model underestimation on December 21 (Figure 6.5a). The observed and simulated means are closer. The observed decrease in NO with altitude is simulated by the models. During the low-NO_x periods, the simulated median values are too low; although low bias is still evident above 60 m, the agreements among the mean values are better. The concentrations in the 3-D model are higher than those in the 1-D model due in part to the 30% higher emissions, and they are in better agreement with those in the observations.

The spatial distribution of the NO mixing ratios measured by the Twin Otter at 20-60 m above the surface on December 4-6 is shown in Figure 6.10a. From here, it can be seen that the observed NO concentrations tend to be higher at higher elevations. Such

Figure 6.9 Balloon measurements of NO profiles on December 17-28 and the corresponding model results. The horizontal bar shows the standard deviation. There are 6 profiles for December 21-23 and 21 profiles for December 17-20 and 25-28.

Figure 6.10a Twin Otter observed- and model-simulated NO mixing ratios (pptv) at 20-60 m above the surface on December 4-6. Model results are sampled along flight tracks at the time of the measurements.

Figure 6.10b Twin Otter observed- and model-simulated vertical distributions of NO on December 4-6.

a spatial distribution is captured by the model simulation. However, the model has a clear low bias, which is also shown in the vertical distribution (Figure 6.10b). While the measurements show NO mixing ratios up to 550 pptv, the model results reach only 350 pptv. Surface measurements of 100-200 pptv at SP on December 4-6 are also underestimated by the 3-D model, but to a lesser extent (Figure 6.5a). Because the model-simulated variability is driven mostly by temperature (Figure 6.4), the colder temperatures at higher elevations lead to more NO_x emissions and thus to higher NO concentrations. The resulting spatial gradient/variability is, however, underestimated by the model. Several important factors that contribute significantly to the spatial variability of snow NO_x emissions might not be accounted for in the parameterization. An adequate evaluation of this issue necessitates more extensive spatial and temporal aircraft measurements that improve on their "representativeness" as well as detailed laboratory studies of the nitrate photochemical mechanisms.

The comparison of model simulations with the measurements from the ANTCI 2003 experiment demonstrates that the 3-D model can capture some of the essential features of airborne data. Given this level of agreement, we applied the 3-D model to explore the reactive nitrogen budget over the plateau and the photochemical impact of snow NO_x emissions over the entire Antarctic continent. In general, the simulated low-altitude NO_x concentrations have low bias at SP during low-NO_x periods of balloon measurements and over the plateau regions sampled by Twin Otter, implying that the simulated nitrogen source and photochemical impact (in terms of OH concentrations) may have low bias.

Using the 3-D model results, we construct the nitrogen budget for the plateau region (elevation above 2.5 km). For December 2003, we estimate emissions of 0.25 kg N km^{-2} month^{-1}. The reactive nitrogen deposition flux is 0.13 kg N km^{-2} month^{-1}. Depositions of HNO_3 and HNO_4 account for 73% and 21%, respectively, and the rest is largely deposition of NO_2. The net outflux of reactive nitrogen is 0.12 kg N km^{-2} month^{-1}. About 90% of the outflux takes place within 1 km above the surface. Outfluxes of HNO_3 and NO_x account for 61% and 26%, respectively, and the rest is mostly HNO_4. Figure 6.11 shows the near-surface fluxes of HNO_3. As indicated in the figure, most of the transport is over eastern Antarctica. The implications of the outflux on plateau nitrogen chemistry are discussed by Davis *et al.* [2007].

Figure 6.12 shows model-simulated surface NO_x and OH concentrations over Antarctica during the ANTCI 2003 period. The emission parameterization predicts higher NO_x emissions and thus concentrations over the eastern Antarctic plateau. The concentration of OH does not maximize in regions with the highest NO_x concentrations because of the nonlinearity of HO_x chemistry [Chen *et al.,* 2001, 2004, Davis *et al.,* 2004]. Thus, the model predicts some of the highest OH levels in the downslope drainage areas of eastern Antarctica. Predicted mean surface OH concentrations exceed 2×10^6 molec cm^{-3} over most of the Antarctic continent. Using a box model having as its input the Twin Otter plateau NO data set, Davis *et al.* [2007] showed a strong vertical gradient in OH with estimated concentrations reaching as high as 4×10^6 molec cm^{-3}. Based on these results, the authors hypothesized that upon consideration of the vertical NO structure across the larger plateau, it is likely that NO_x snow emissions likely lead to an oxidizing canopy that enshrouds the entire plateau. Showing a shallow canopy of high OH concentrations above

——→0.004 moles m^{-2}day^{-1}

Figure 6.11 Simulated monthly mean near-surface HNO$_3$ fluxes for December 2003.

Figure 6.12 Simulated mean surface NO$_X$ and OH concentrations during ANTCI 2003.

Figure 6.13a Simulated cross section of OH concentrations (10^6 molec cm^{-3}) along the 90°W - 90°E meridian during ANTCI 2003.

Figure 6.13b Simulated depth (m) of the oxidizing canopy over Antarctica ([OH] > 3×10^6 molec cm^{-3}) during ANTCI 2003.

the Antarctic plateau driven by snow NO_x emissions, a model-simulated cross-section of the OH concentration level along the 90°W-90°E meridian (Figure 6.13a) supports their hypothesis, Figure 6.13b shows the simulated distribution of the oxidizing canopy thickness over Antarctica. For illustrative purposes, we define the highly active oxidizing canopy as the region with $[OH] \geq 3x10^6$ molec cm^{-3}, the highest median value found in the marine boundary layer over the tropical Pacific [Y. Wang *et al.*, 2001]. The simulated OH canopy is deeper, generally in the range of 50-150 m, over the eastern Antarctic plateau than it is over other regions. The spatial distribution of the canopy depth reflects a combination of surface NO_x emissions, boundary layer height, and transport.

6.6 Conclusions

We apply 1-D chemistry-diffusion and 3-D chemical transport models to analyze surface, balloon, and aircraft measurements of reactive nitrogen during ANTCI 2003. The emphasis of the model analysis is on high NO_x-emitting plateau regions. We simulate the meteorological fields using the polar version of MM5. The default ETA MYJ 2.5-order closure scheme predicts much lower boundary layer heights than SODAR measurements at SP. We decrease the minimum eddy diffusion coefficient from a default value of 0.09 to 0.001 m^2 s^{-1} and obtain reasonable simulations of SP boundary layer heights.

Using the 1-D chemistry-diffusion model and surface measurements at SP, we derive the necessary snow NO_x emission fluxes that explain the observed NO concentrations. The average emission flux of $3.2x10^8$ molec cm^{-2} s^{-1} is 20% lower than the mean flux of $3.9x10^8$ molec cm^{-2} s^{-1} estimated by Oncley *et al.* (2004) using sonic anemometers, temperature sensors, and high-speed NO measurements during ISCAT

2000. We parameterize the derived daytime snow emissions as a function of temperature and wind speed. The empirical parameterization is essential for simulating the spatial variability of observed NO concentrations by Twin Otter. Vertical advection, not accounted for in the 1-D model, decreases surface NO concentrations at SP; daytime snow emissions increased 30% in the 3-D model to an average of 4.2×10^8 molec cm^{-2} s^{-1} at SP in order to reproduce the observed NO concentrations. We calculate an average dry deposition velocity of 0.15 cm s^{-1} for HNO$_3$ and HNO$_4$ at SP. We find reasonable agreement between observed and simulated HNO$_3$ and HNO$_4$ at SP.

To our knowledge, this is first 3-D chemical transport model analysis of reactive nitrogen at SP or over Antarctica in general. Meteorological fields, snow NO$_x$ emission parameterization, and HO$_x$ photochemistry [Chen *et al.*, 2004] all contribute to the overall uncertainties in the simulations. In particular, simulated NO concentrations are too low compared with those of the Twin Otter measurements during December 4-6. However, a longer measurement period is needed to assess whether the bias is representative. Quantifying each of these uncertainties will require much larger datasets than those currently available during ANTCI 2003, and new laboratory studies of the snow nitrate photochemical process. Below, we focus the discussion on two major implications from the model results.

First, inefficient turbulence transport in the relatively stable Antarctic boundary layer leads to large gradients in NO (> a factor of 2 change within the lowest 50 m, Figure 6.8), which implies that the vertical structure needs to be simulated if photochemistry in the region is to be understood. For the oxidation products HNO$_3$ and HNO$_4$, extensive mixing up to 500 m is simulated. These 1-D vertical profiles are further

modified by 3-D transport. The vertical distribution of HNO_3 is affected most. The much longer lifetime of HNO_3 than NO_x or HNO_4 allows for large accumulations of this species in the upper portion of the boundary layer, resulting in HNO_3 concentrations near the surface that are significantly higher in the 3-D model than in the 1-D model. In order to reduce the "excess" HNO_3, the dry deposition velocity of HNO_3 needs to be increased in the 3-D model. Diagnostics using 1-D models will tend to underestimate HNO_3 deposition velocity. While the shape of the NO_x vertical profile is not affected by 3-D transport, snow emissions need to be increased by 30% in the 3-D model compared to 1-D model. The vertical distribution of HNO_4 is also affected by 3-D transport. By definition, the flux measurements of snow emissions or deposition by the eddy correlation technique assume zero mean advection of trace gases, which is inconsistent with the prevailing downslope circulation driven by katabatic flow over Antarctica. As a result, the effect of advection needs to be taken into account in the interpretation of any eddy-correlation flux measurements.

Second, the empirical daytime snow NO_x emission parameterization based on temperature and wind speed is obviously an oversimplification of the snow emission process. A more sophisticated process-based emission model that can be coupled with 1-D and 3-D chemical transport models will require additional detailed laboratory studies and more extensive field measurements (particularly by aircraft). Despite the above-cited simplifications, the 3-D model has shown that it can capture the observed spatial variability of near-surface NO recorded on the Twin Otter even though the magnitudes are underestimated. These model results suggest that the Antarctic plateau is a major source region for NO_x and that snow NO_x production takes place through a common

mechanism. For December 2003, the model estimates an average NO_x emission flux of 0.25 kg N km^{-2} $month^{-1}$ over the plateau (elevation above 2.5 km). About 50% of reactive nitrogen is lost by deposition and the other 50% by transport. HNO_3 and HNO_4 are major deposition species (73% and 21%, respectively); nitrogen outflux is largely in the form of HNO_3 and NO_x (61% and 26%, respectively). At the simulated NO_x levels, most of the Antarctic continent during ANTCI 2003 has near-surface mean OH concentrations of $> 2x10^6$ molec cm^{-3}. The depth of the layer with $[OH] > 3x10^6$ molec cm^{-3} is estimated to be 50-150 m over the plateau. This result shows a highly photochemically active oxidizing canopy enshrouding the entire Antarctic plateau, which was previously hypothesized by Davis *et al.* [2004].

CHAPTER VII

CONCLUSIONS

Column observations of NO_2 by GOME and CO by MOPITT over North America and surrounding oceans for April 2000 are analyzed using the Regional chEmical trAnsport Model (REAM). Transient enhancements in these measurements due to lightning NO_X production or convective transport are examined. The analyses produce clear evidence for lightning enhancements of NO_2 over the continent and western North Atlantic and for convective transport enhancements of CO over the ocean. Two independent satellite measurements show consistent enhancements related to convective events. Results of the model suggest that the enhancements are particularly large in the lower troposphere due to convective downdrafts of lightning NO_X and shallow convection of CO, implying that low-altitude aircraft in situ observations are potentially critical for evaluating the model simulations and validating the satellite observations of these transient features.

The 3-D REAM is used to simulate trace gas from February to May 2000 over North America. Once applied, the simulations result in an analysis of surface, aircraft, and satellite measurements that explain the springtime transitions of key trace gas concentrations and export. The global GEOS-CHEM model is used to provide chemical initial and boundary conditions. Surface observations from EPA AIRNow and SEARCH networks, aircraft observations from the TOPSE and MOZAIC experiments, ozonesondes, and remote sensing measurements from GOME, MOPITT, TOMS and SAGE II are then analyzed. Generally, the model results are in good agreement with the observations in the

troposphere. REAM is also used to simulate decreases in surface CO and NO_x concentrations and MOPITT CO columns from spring to summer. Results show that the seasonal change of the GOME NO_2 tropospheric column is not as large as that of the CO column because of increasing lightning and soil NO_x emissions. Differences between simulated and GOME NO_2 columns on a monthly mean basis are averaged over the four-month period. Results show that the total NOx emissions derived from the inversion of the GOME NO_2 column are in good agreement with those of the model a priori inventory. In addition, although REAM has a low bias (above 350 hPa) due to specified upper boundary concentrations, REAM-simulated surface ozone concentrations are in good agreement with AIRNow measurements. By comparison, GEOS-CHEM-simulated surface ozone concentrations show a much faster increasing trend. We find that the simulated boundary layer structure is a key process that differentiates the REAM results from GEOS-CHEM. The MM5-simulated mixing layer heights used in REAM are lower than those used in GEOS-CHEM. As a result, the activation of photochemistry in the boundary layer is much faster in GEOS-CHEM than it is in REAM. REAM results also indicate that the main contributor of the significant increase in the tropospheric ozone column over the western North Atlantic is lightning NO_x production. The impact of lightning is also evident in model-simulated pollutant exports.

The tropospheric O_3 column retrieved from OMI and MLS measurements, the NO_2 column from OMI measurements, and the upper tropospheric O_3 and CO concentrations from TES over North America and the western North Atlantic from April to August 2005 are analyzed using REAM. The satellite measurements and REAM simulations showed large enhancements of column and upper tropospheric O_3 over the

western North Atlantic comparable to those over the eastern United States. These measurements show that the O_3 enhancement region migrates northward from spring to summer. An analysis of the model indicates that the northward shift is driven by O_3 in the stratospheric flux, convective outflow and production from lightning NO_X. As their uncertainties improve, the satellite measurements of O_3 and its precursors will provide more quantitative constraints on pollutant outflow from the continents.

The observations during the TOPSE experiment show large enhancements of NO_x, PAN, O_3, CO, CFCs, and Halon-1211 in the upper troposphere over North America in the late spring. Analyses of these observations and model results indicate that the enhancements are most likely driven by a surge of trans-Pacific pollutant transport during the late spring. The rapid seasonal transition is particularly striking for upper tropospheric NO_x, resulting in large increases in photochemical oxidation and O_3 production during the period. The transition occurs later in the season than that of low-altitude trans-Pacific transport, which peaks in March and April. The current generation of global chemical transport models clearly underestimates this long-range transport of pollutants, implying that the model-projected impact on regional air quality over North America has been underestimated (through subsidence).

The results of surface and aircraft measurements reveal a large amount of reactive nitrogen tracers over the Antarctic plateau in the summer. These measurements are then subjected to the 1-D CTM and REAM for the purpose of assessing the photochemical impact of snow NO_x emissions. Then, after slightly modifying the ETA turbulence scheme, we simulated the boundary layer heights, measured by SODAR at SP, reasonably well with the polar version of MM5. Results show that the average level of

model-derived snow NO_x emissions (3.2-4.2×10^8 molec cm^{-2} s^{-1}) at SP is similar to the measured flux of 3.9×10^8 molec cm^{-2} s^{-1} during ISCAT 2000. Daytime snow NO_x emissions are parameterized as a function of temperature and wind speed. Surface measurements of NO, HNO_3, and HNO_4, and balloon measurements of NO at the South Pole are reasonably simulated by 1-D CTM and REAM. Compared with the Twin Otter measurements of NO over the plateau regions, REAM-simulated NO concentrations are at the low end, which indicates that either the parameterization based on surface measurements at SP underestimates emissions at higher-elevation plateau regions or the limited aircraft database may not totally represent the season of the year sampled. However, the model captures the spatial variability of near-surface NO measured by aircraft to a large extent, indicating that snow NO_x emissions are produced through a common mechanism. An average emission flux of 0.25 kg N km^{-2} month^{-1} is calculated for December 2003 over the plateau (with an elevation above 2.5 km). Deposition is responsible for the loss of about half of reactive nitrogen, and scavenging by transport the other half. The REAM results show that snow NO_x emissions are responsible for a shallow but highly photochemically active oxidizing "canopy" enshrouding the entire Antarctic plateau.

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