Tropospheric Ozone Over The Middle East And Its Interannual Variability: An Integrated Analysis With Satellite Observations And A Global Chemical Transport Model

by

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy

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Abstract

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Tropospheric ozone is a major atmospheric pollutant and a greenhouse gas. Nevertheless, many processes influencing its spatio-temporal distribution are still poorly understood, mainly due to the lack of adequate observations. One such region is the Middle East, where ozone measurements are scant. In this study, the GEOS-Chem chemical transport model is used to interpret newly available tropospheric ozone data from the Tropospheric Emission Spectrometer (TES) satellite instrument. TES reveals elevated ozone in the mid-troposphere (500-300 hPa) over the Middle East in summer 2005.

This study demonstrates that the Arabian anticyclone in the mid-troposphere over the Middle East plays a critical role in facilitating the buildup of ozone. Additionally, the South Asian High in the upper troposphere helps transport ozone from the Asian monsoon region. Transport from Asia and local production are predominantly responsible for the ozone buildup, each contributing 30-35% to the ozone abundance in the region. Ozone transported from the boundary layer accounts for about 25% of local production. TES retrievals of water vapour and
deuterated water are used for the first time to provide an independent assessment of the ozone transport pathways.

Using a GEOS-Chem simulation from 1987 to 2006, it is found that this ozone buildup fluctuates interannually by about ±7% (or ±6 ppbv). The major contributors, ozone transported from Asia and ozone produced locally, vary by ±30% (±7 ppbv) and ±15% (±3 ppbv), respectively. The variations of Asian and local sources are related to the strengths of the South Asian High and the Arabian anticyclone, respectively. It is found that in years when the Asian influence is weaker in the region, transport from other areas, such as North America, is enhanced. This tradeoff between transport from Asia and other regions is found to be linked to the position and strength of the subtropical westerly jet over central Asia. These results suggest that climate-related changes in the general circulation of the atmosphere will have implications for the transport of pollution into the Middle East. Such changes in pollution in the region could have feedbacks on the climate through changes in the radiative forcing associated with tropospheric ozone.
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Tibet Plateau, the Zagros and Atlas mountain regions are indicated in black (adapted from Park et al. [2009] and Lawrence [2006]).
Acronyms, Abbreviations, and Chemical Species

AIMR  All Indian Monsoon Rainfall
AIRS  Atmospheric Infrared Sounder
APDRC  Asia-Pacific Data-Research Center
CGT  circumglobal teleconnection
CH$_4$  methane
CO  carbon monoxide
CO$_2$  carbon dioxide
CTMs  Chemical Transport Models
DOFS  degrees of freedom for signal
DJF  boreal winter months including December, January, and February
EDGAR  Emission Database for Global Atmospheric Research
ENSO  Niño-Southern Oscillation
EOS  Earth Observing System
EPA  Environmental Protection Agency
GCM  general circulation model
GEIA  Global Emissions Inventory Activity
GEOS  Goddard Earth Observing System
GEOS-4  Goddard Earth Observing System, version 4
GFED  Global Fire Emission Database
GHGs greenhouse gases

GMAO Global Modeling and Assimilation Office

GOME Global Ozone Monitoring Experiment

HDF Hierarchical Data Format

HDO/H₂O deuterated water vapour

H₂O water vapour

IASI Infrared Atmospheric Sounding Interferometer

ICARTT International Consortium on Atmospheric Transport and Transformation

IDM India Meteorological Department

IGACO Integrated Global Atmospheric Chemistry Observations

IPCC Intergovernmental Panel on Climate Change

IPRC International Pacific Research Center

IR infrared

ITCZ Intertropical Convergence Zone

JJA boreal summer months including June, July and August

LOSU level of scientific understanding

LINOZ linearized ozone parameterization scheme

LIS Lightning Imaging Sensor

MAM boreal spring months including March, April, and May

MDI Meteorological Department of Iran
MEGAN Model of Emissions of Gases and Aerosols from Nature

MLS Microwave Limb Sounder

MOZAIC Measurements of Ozone and Water Vapor by in-Service Airbus Aircraft

MOZART Model of Ozone and Related Tracers

MOPITT Measurements of Pollution In the Troposphere

NAO North Atlantic Oscillation

NASA National Aeronautics and Space Administration

NCAR National Center for Atmospheric Research

NCEP National Centers for Environmental Prediction

NEI99 National Emission Inventory 1999

NH the Northern Hemisphere

NH₃ ammonia

NO nitric oxide

N₂O nitrous oxide

NO₂ nitrogen dioxide

NO₃ nitrogen trioxide, nitrate radical

NOₓ nitrogen oxides (NO+NO₂)

O atomic oxygen

O (¹D) atomic oxygen (first exited state)

O₃ ozone
O$_x$ odd oxygen

OH hydroxyl radical

OMI Ozone Monitoring Instrument

OTD Optical Transient Detector

RF Radiative forcing

ROW rest of the world, a region in the tagged ozone simulations conducted in this study

RTE radiation transfer equation

SAH South Asian High

SAGE Stratospheric Aerosol and Gas Experiment

SBUV Solar Backscattered Ultraviolet

SCIAMACHY Scanning Imaging Absorption SpectroMeter for Atmospheric ChartographY

SH the Southern Hemisphere

SCO stratospheric column ozone

SOI Southern oscillation index

SON boreal fall months including September, October, and November

STE stratosphere-troposphere exchange

SYNOZ specified ozone parameterization scheme

TCO tropospheric column ozone

TH Tibetan High

TES Tropospheric Emission Spectrometer
**TOMS** Total Ozone Mapping Spectrometer

**TOR** tropospheric ozone residual

**UTLS** the upper troposphere and lower stratosphere

**UV** ultraviolet radiation

**VMR** Volume mixing ratio

**WCBs** warm conveyer belts

**WMO** World Meteorological Organization

**WOUDC** World Ozone and Ultraviolet Radiation Data Centre
1 Introduction

1.1 Motivation and Overall Objectives

Tropospheric ozone (O₃) impacts our environment in different ways. It is a greenhouse gas in the middle and upper troposphere due to its absorption of infrared radiation. According to the Intergovernmental Panel on Climate Change (IPCC) [2007], tropospheric ozone is the third most important anthropogenic greenhouse gas, after CO₂ and CH₄, as shown by the radiative forcing (RF) estimates in Figure 1.1. In the boundary layer, ozone is a major pollutant because of its damage to human beings and other life forms through its oxidizing impact on biological tissue. Ozone in the troposphere also acts indirectly as a cleansing agent because photolysis of ozone in the presence of water vapour is the dominant source of the hydroxyl radical (OH), the primary atmospheric oxidant [Logan et al., 1981; Thompson 1992]. The lifetime of ozone in the middle and upper troposphere ranges from 10-40 days in summer and 30-150 days in winter (increasing with latitude) and this makes ozone a good tracer of transport processes [Krishnamurti et al., 1993; Liu and Ridley, 1999]. In contrast to the negative trend in stratospheric ozone abundances, ozone in the troposphere is increasing [Wang and Jacob, 1998; Prather et al., 2003; Stevenson et al., 2006]. Therefore, tropospheric ozone research has been at the forefront of atmospheric science for decades. Recently, the Integrated Global Atmospheric Chemistry Observations (IGACO) program of the World Meteorological Organization (WMO) identified four grand challenges in atmospheric chemistry: (1) tropospheric air quality, (2) the oxidation efficiency of the atmosphere, (3) stratospheric chemistry and ozone depletion, and (4) chemistry-climate interactions [IGACO, 2004]. Tropospheric ozone is closely linked to challenges (1), (2), and (4) because of its impacts on our environment as described above.

The distribution of tropospheric ozone reflects a balance between in situ photochemical sources and sinks and atmospheric transport. Figure 1.2 shows ensemble column and altitude-latitude means of tropospheric ozone for the year 2000 from 26 global models [Stevenson et al., 2006]. The ozone mixing ratio generally increases with altitude, reflecting the shorter ozone lifetime in the lower troposphere due to strong sinks in the boundary layer. In the troposphere, the ozone mixing ratio in the Northern Hemisphere (NH) is 1-2 times that in the Southern Hemisphere (SH). Also shown in Figure 1.2 is the standard deviation associated with the spread
Figure 1.1. Global average radiative forcing (RF) estimates and ranges in 2005 relative to pre-industrial conditions in the year 1750 for changes in atmospheric carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O) and other important forcing agents, together with the typical geographical extent (spatial scale) of the forcing and the assessed level of scientific understanding (LOSU). The total net anthropogenic radiative forcing and its range are also shown [after IPCC, 2007].
Figure 1.2. Modeled ozone for year 2000: (a-c) annual zonal means (AZM) (in ppbv) and (d-f) annual tropospheric columns (ATC) (in Dobson Units). Figures 1.2a and 1.2d are ensemble means from 26 global models; Figures 1.2b and 1.2e are absolute standard deviations; Figures 1.2c and 1.2f are percentage standard deviations. To calculate the ensemble values, individual model results were interpolated to a common grid (5°×5°×19 levels) and masked at the chemical tropopause (O₃ = 150 ppbv) [after Stevenson et al., 2006].
in the model simulations, which is an indicator of the model uncertainties. Indeed, many of the processes controlling atmospheric transport and ozone sources and sinks are poorly understood due to the complexity of processes involved and the lack of adequate observations of tropospheric ozone and its precursors. However, with recent satellite observations, we can now better characterize and quantify the impact of these processes on the distribution of tropospheric ozone. In the research reported in this thesis, the newly available ozone observations from the Tropospheric Emission Spectrometer (TES) satellite instrument [Beer et al., 2001] are exploited along with the use of a global chemical transport model (CTM), namely GEOS-Chem [Bey et al., 2001], to interpret the TES data for the purpose of (i) better characterizing the spatio-temporal distributions of tropospheric ozone in the Middle East region (see Section 1.3 for the uniqueness of the Middle East), (ii) improving our understanding of the underlying mechanisms controlling the ozone distribution in the region, and (iii) understanding the impact of interannual variations in long-range transport and in the local ozone production on ozone abundances in the Middle East. In the following sections, a review on the relevant issues is provided.

1.2 Sources, Sinks, and Budget of Tropospheric Ozone

Tropospheric ozone is formed and destroyed by chemical reactions involving other gas species in the atmosphere. Before the 1970s, it was assumed that ozone flux from the stratosphere was the major source of tropospheric ozone and this source was balanced with the surface sink. Since the seminal work by Levy [1971], it has been recognized that trace gases, such as carbon monoxide (CO) and hydrocarbons, can lead to the formation of ozone in the troposphere through photochemical reactions under a sufficiently high concentration of nitrogen oxides (NOx = NO+NO2) [Crutzen, 1974; Liu et al., 1980]. The chemical production is, in fact, the dominant source of tropospheric ozone [Hauglustaine et al., 1998; Wang et al., 1998a; Stevenson et al., 2006; Wu et al., 2007]. Taking CO as an example, HO2 is first produced through the oxidation of CO by OH as follows

\[ \text{OH} + \text{CO} \rightarrow \text{H} + \text{CO}_2 \] \hspace{1cm} (1.1a)

\[ \text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M} \] \hspace{1cm} (1.1b)

where \( \text{M} \) is a third body. The net effect of Equations 1.1a and 1.1b is
\[ \text{OH} + \text{CO} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CO}_2. \]

Then \( \text{HO}_2 \) reacts with \( \text{NO} \) to generate \( \text{NO}_2 \), which subsequently leads to the formation of ozone through photolysis

\[
\begin{align*}
\text{HO}_2 + \text{NO} & \rightarrow \text{OH} + \text{NO}_2 \quad (1.2a) \\
\text{NO}_2 + \text{hv} & \rightarrow \text{NO} + \text{O} \quad (1.2b) \\
\text{O} + \text{O}_2 + \text{M} & \rightarrow \text{O}_3 + \text{M} \quad (1.2c)
\end{align*}
\]

where \( \text{hv} \) denotes radiation energy at wavelengths <0.43 \( \mu \text{m} \). The net effect of Equations 1.2a to 1.2c is

\[
\text{HO}_2 + \text{O}_2 \rightarrow \text{OH} + \text{O}_3.
\]

Therefore, the net effect of Equations 1.1a to 1.2c is the production of an ozone molecule

\[
\text{CO} + 2\text{O}_2 \rightarrow \text{CO}_2 + \text{O}_3.
\]

For the ozone sink, it is suggested that chemical loss is in balance with about 90% of the chemical production in the troposphere [Müller and Brasseur, 1995; Roelofs and Lelieveld, 1995; Hauglustaine et al., 1998; Wang et al., 1998a; Stevenson et al., 2006; Wu et al., 2007].

When \( \text{NO}_x \) is not sufficiently abundant, such as in remote and unpolluted regions, \( \text{HO}_2 \) reacts with ozone rather than with \( \text{NO} \) as in Equation 1.2a

\[
\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2. \quad (1.3)
\]

Ozone loss also takes place when \( \text{O}(^1\text{D}) \), an excited oxygen atom produced by ozone photolysis, reacts with water vapour and generates \( \text{OH} \) through the following steps

\[
\begin{align*}
\text{O}_3 + \text{hv} & \rightarrow \text{O}_2 + \text{O}(^1\text{D}) \quad (1.4a) \\
\text{O}(^1\text{D}) + \text{H}_2\text{O} & \rightarrow 2\text{OH}. \quad (1.4b)
\end{align*}
\]

Dry deposition of ozone on the surface also consumes ozone in the boundary layer.
The differences in the global tropospheric ozone budget estimates are large among chemistry models [e.g., Müller and Brasseur, 1995; Roelofs and Lelieveld, 1995; Levy et al., 1997; Bernsten and Isaksen, 1997; Roelofs et al., 1997; Hauglustaine et al., 1998; Wang et al., 1998a; Stevenson et al., 2006; Wu et al., 2007]. Table 1.1 lists the tropospheric ozone budget (source, sink, and the total burden) from recent chemistry model simulations (means and the standard deviations) [Stevenson et al., 2006; Wu et al., 2007]. Also listed is a range of ozone budget estimates from different models in the 1990s [Jacob, 1999]. The global chemical production is estimated as ~5500 Tg O₃ yr⁻¹, contributing ~90% to the ozone source, while the contribution from stratospheric transport makes up the rest (~10%). Chemical processes are responsible for ~80% of the ozone sink, whereas dry deposition at the surface accounts for ~20% of the loss. Both sink and source estimates range from 3400 to 5700 Tg O₃ yr⁻¹. As noted by Wu et al. [2007], since the early 1990s, the estimated chemical source of ozone in models has increased by as much as 35%, while the global burden of ozone in the models has increased by about 10%, due to compensating changes in the ozone budget. This is an indication of the level of uncertainty in our understanding of the budget of tropospheric ozone.

In spite of recent advances, uncertainties still remain in our understanding of tropospheric ozone, its distribution, and associated controlling mechanisms. This is partly due to the complexity of the processes involved. For example, as described above, NOₓ is an important precursor of ozone, which largely controls tropospheric ozone production. However, NOₓ emission from lightning remains highly uncertain, with estimates ranging from 1 to 20 Tg N yr⁻¹ [Lee et al., 1997; Boersma et al., 2005]. Traditionally, the global NOₓ emission from lightning is estimated from the number of molecules of NO produced per flash and from the global flash rates. Both values may vary by an order of magnitude [Martin et al., 2007]. Recently, satellite observations of NO₂ added constraints to the NOₓ emission estimate from lightning in the tropics [Martin et al., 2007; Sauvage et al., 2007]. Another example of uncertainty is that associated with stratosphere-troposphere exchange (STE). Jacob [1999] suggested a wide range of STE influx from 400 to 1100 Tg O₃ yr⁻¹ (Table 1.1). In an IPCC report, Prather et al. [2001] gave a similar range of 390 to 1440 with a mean of 770 Tg O₃ yr⁻¹. This mean value likely overestimates the STE influx [Wu et al., 2007] and the recent estimate is 550 ± 170 Tg O₃ yr⁻¹, based on an ensemble of 21 global models (Table 1.1) [Stevenson et al., 2006].
Table 1.1. Global budget for tropospheric ozone in the recent model simulations.

<table>
<thead>
<tr>
<th></th>
<th>Global Total&lt;sup&gt;1&lt;/sup&gt;</th>
<th>Global Total&lt;sup&gt;2&lt;/sup&gt;</th>
<th>Range&lt;sup&gt;3&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sources, Tg O₃ yr&lt;sup&gt;⁻¹&lt;/sup&gt;</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical production</td>
<td>5110 ± 610</td>
<td>4700</td>
<td>3000-4600</td>
</tr>
<tr>
<td>From the stratosphere</td>
<td>550 ± 170</td>
<td>520</td>
<td>400-1100</td>
</tr>
<tr>
<td>Total</td>
<td>5660</td>
<td>5220</td>
<td>3400-5700</td>
</tr>
<tr>
<td><strong>Sinks, Tg O₃ yr&lt;sup&gt;⁻¹&lt;/sup&gt;</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical loss</td>
<td>4670 ± 730</td>
<td>4130</td>
<td>3000-4200</td>
</tr>
<tr>
<td>Dry deposition</td>
<td>1000 ± 200</td>
<td>1090</td>
<td>500-1500</td>
</tr>
<tr>
<td>Total</td>
<td>5670</td>
<td>5220</td>
<td>3400-5700</td>
</tr>
<tr>
<td><strong>Burden, Tg O₃</strong></td>
<td>340 ± 40</td>
<td>300</td>
<td></td>
</tr>
<tr>
<td><strong>Residence time, days</strong></td>
<td>22 ± 2</td>
<td>21</td>
<td></td>
</tr>
</tbody>
</table>

<sup>1</sup> Stevenson <em>et al.</em> [2006], mean ± standard deviation from 21 global models.

<sup>2</sup> Wu <em>et al.</em> [2007], from GEOS-Chem, version 7-02-04. It is the version used in this study.

<sup>3</sup> Jacob [1999].
Another obstacle for better quantifying the ozone budget is the lack of global observations. Tropospheric ozone is mostly measured by ground-based or balloon instruments at ozonesonde stations [IGACO, 2004; WMO, 2007] and by aircraft instruments on commercial aircraft or during field campaigns [Jacob et al., 2003; IGACO, 2004; Brenninkmeijer et al., 2005]. These observations, unfortunately, are limited spatially and temporally. Direct retrievals of tropospheric ozone profiles from satellite observations were not available until recently when TES became operational in 2004 [Beer et al., 2001]. Tropospheric ozone profile retrievals are now being performed for measurements from the Ozone Monitoring Instrument (OMI) [Levelt et al., 2006] and the Infrared Atmospheric Sounding Interferometer (IASI) [Boynard et al., 2009]. Nevertheless, in the vicinity of the Middle East, ozone measurements are scarce from any suborbital platform; therefore, much can be learned from the analysis of TES data about the behavior of tropospheric ozone over the Middle East region.

1.3 Uniqueness of the Middle East Region

The Middle East is located in a geographically unique region. In the upper troposphere, the region is strongly influenced by transport of Asian pollution associated with the extended Asian monsoon anticyclone system [Lawrence, 2004]. Previous studies [e.g., Park et al., 2004; Li et al., 2005a; Randel and Park, 2006] have shown that this anticyclone has a significant impact on the distribution of trace gases in the upper troposphere and lower stratosphere (UTLS). The influence of Asian pollution has also been observed in the middle troposphere in the eastern Mediterranean [Lelieveld et al., 2002]. Furthermore, European pollution is transported into the region at low altitudes in summer [Duncan and Bey, 2004; Duncan et al., 2008]. As a result of the combined influence of Asian and European pollution, high levels of ozone precursors such as HCHO, CH$_3$COCH$_3$, and CH$_3$OH have been observed at all levels of the troposphere over the Mediterranean [Lelieveld et al., 2002]. This has important implications for both air quality and climate in the region. The topography over the Middle East is also unique. The region is strongly influenced by the presence of the Tibetan Plateau to the east, and the Atlas Mountains of northern Algeria and the Zagros Mountains in Iran which induce anticyclonic flow in the middle and upper troposphere [Rodwell and Hoskins, 1996]. Locally, the Zagros Mountains can also
facilitate the transport of surface pollution to the free troposphere through mountain venting [Kar et al., 2006].

In a previous modeling study, Li et al. [2001] suggested the existence of a seasonal buildup of tropospheric ozone in the middle and upper troposphere over the Middle East in summer, with ozone mixing ratios of 70-80 ppbv at these altitudes. This is dubbed the “Middle East ozone maximum.” Li et al. [2001] suggested that this maximum is linked to the anticyclones and the large-scale subsidence in the middle and upper troposphere in this region. They argued that transport of pollution from Asia was responsible for the ozone feature, but they did not offer a detailed mechanistic description of the build up. Furthermore, because of the paucity of observations in the region, it was unclear if the ozone maximum was an artifact of the model. Li et al. [2001], therefore, emphasized the need for more observational evidence, especially from satellites, to confirm the presence of the ozone maximum because of its high uncertainty. Kar et al. [2002] showed that climatological observations (1985-1999, excluding 1991-1994) from the Stratospheric Aerosol and Gas Experiment (SAGE) II revealed elevated ozone mixing ratios over the Middle East at 7 km in summer. However, the SAGE II data were sparse and were biased low by 40-50% [Kar et al., 2002]. Furthermore, this ozone maximum was not found in retrieved ozone column abundances from measurements by the Global Ozone Monitoring Experiment (GOME) [Liu X. et al., 2006] or using the residual method based on ozone data from other satellite instruments [Fishman et al., 2003; Ziemke et al., 2006]. As TES is providing continuous global measurements of the vertical distribution of tropospheric ozone, it offers new information to address this issue.

Elevated ozone abundances over the Middle East would have an important implication for global climate because ozone in the middle and upper troposphere is an effective greenhouse gas [Brasseur et al., 1998a; Mickley et al., 1999, 2004; Gauss et al., 2006; IPCC, 2007; Joiner et al., 2009]. Increasing tropospheric ozone abundances since the pre-industrial period have contributed to warming. Direct radiative forcing of this change in ozone is estimated by IPCC [2007] to be about +0.35 W m⁻², with a range from 0.25 to 0.65 W m⁻² (see Figure 1.1). The estimate of the ozone radiative forcing comes with a medium level of scientific understanding (LOSU), which arises for two reasons: the spatial and temporal variability of tropospheric ozone [Stevenson et al., 2006] and the paucity of ozone measurements in the pre-industrial era [Gauss et al., 2006]. Using satellite observations of ozone and clouds from OMI and Microwave Limb
Sounder (MLS), Joiner et al. [2009] showed that the Middle East and North Africa are regions where the ozone radiative forcing is at maximum in summer (Figure 1.3). They attributed the maximum to high surface temperatures, low humidity, a low frequency of cloud, and high ozone abundance. As the distribution of tropospheric ozone reflects a balance between in situ photochemical sources and sinks and transport of ozone and its precursors, an improved understanding of the processes controlling ozone over the Middle East and North Africa is important for predicting the radiative impact of future changes on the abundance of tropospheric ozone.

Although, as discussed above, the Middle East is a nexus for transport of pollution, only a few studies have examined the influence of transport of ozone from Asia on ozone abundances over the Middle East [Li et al., 2001] and over the Mediterranean region [Lelieveld et al., 2002; Duncan et al., 2008]. There have been numerous studies based on model simulations, and aircraft and surface observations which have examined the long-range transport of ozone, but these studies mostly focused on transport between Asia, North America, and Europe [Berntsen et al., 1999; Yienger et al., 2000; Wild and Akimoto, 2001; Fiore et al., 2002; Li et al., 2002; Koumoutsaris et al., 2008]. It has been recognized that long-range transport of pollution can have a significant impact on regional budgets of tropospheric ozone. One objective of this thesis work is to better understand the impact of long-range transport of pollution on ozone abundances over the Middle East.

1.4 Interannual Variations in Long-range Transport of Tropospheric Pollutants

As long-range transport can substantially affect air quality downwind of pollution source regions, interest in long-range transport of pollutants, especially ozone, has grown quickly since the 1990s [Dickerson et al., 1995; Jaffe et al., 1999; Berntsen et al., 1999; Yienger et al., 2000; Wild and Akimoto, 2001; Fiore et al., 2002; Lelieveld et al., 2002; Li et al., 2002; Cooper and Parrish, 2004; Lawrence, 2004; Duncan and Bey, 2004]. However, only a limited number of studies have examined interannual variations in long-range transport of pollutants [Liu et al., 2003, Duncan and Bey, 2004; Liu J. et al., 2005; Liang et al., 2005], with fewer focusing on transport of ozone [Li et al., 2002; Koumoutsaris et al., 2008].
Figure 1.3. Total-sky long-wave tropospheric ozone radiative forcing (in W m\(^{-2}\)) in 2005 July [after Joiner et al., 2009].
Efforts have been made to relate long-range transport of pollution with the state of the climate system through the use of climate indices, such as the North Atlantic Oscillation (NAO) and El Niño-Southern Oscillation (ENSO). The NAO is found to be closely related to the interannual variation in pollution transport from North America to Europe [Li et al., 2002] and from Europe to other continents [Duncan and Bey, 2004]. A positive NAO phase means a strong north-south pressure gradient over the Atlantic Ocean and this condition usually enhances the transport of North American boundary layer pollutants to Europe [Li et al., 2002]. Under this condition, the export of European CO to the Arctic region tends to be higher but the export to the North Atlantic region tends to be lower [Duncan and Bey, 2004]. It was found that ENSO is linked to year-to-year variability of Asian outflow toward North America and Europe [Liu et al., 2003; Liu J. et al., 2005; Koumoutsaris et al., 2008]. Liu et al. [2003] found that the Asian outflow in spring is strong in the upper troposphere in a La Niña condition while Koumoutsaris et al. [2008] found an El Niño condition in winter favors the export of Asia pollutants toward Europe in the spring of the subsequent year. Moreover, Liu J. et al. [2005] suggested that the correlation between ENSO and Asian outflow toward North America is seasonally dependent: it is strong in winter but weak in summer with spring and fall as intermediate cases.

Most of the studies of long-range transport cited above used earlier versions of the GEOS-Chem model and were limited to a period of 5-11 years, possibly due to unavailability of gridded global data at the time. No study has specifically focused on the Middle East as a receptor or a source region. In this study, the focus is on understanding the impact of long-range transport on tropospheric ozone in the Middle East over the 1987-2006 period.

1.5 Satellite Remote Sensing of Atmospheric Ozone

In response to the concerns about atmospheric ozone, measurements of ozone have been conducted using ground, airborne, balloon-borne, and space-borne instruments. Space-borne measurements have advantages of global coverage, frequent revisit time, and long-term coverage, some of which are not available from any other platform. Both total column abundances and profiles can be retrieved. The launch of the first satellite Sputnik 1 in 1957 opened a new era for human beings to explore the mystery of atmospheric chemistry from space.
with this advanced technique. Since then, there have been numerous satellite instruments aimed at ozone measurement [IGACO, 2004], which makes ozone one of the atmospheric gases that has been most extensively measured from space.

While satellite measurements have many unique advantages, the uncertainties of the measurements can be significant. Clouds are constant obstacles to retrievals from any optical instrument. The vertical resolution is usually coarse and a measurement at one altitude is often contaminated by signals from other altitudes. Interpreting satellite data can be difficult and requires an understanding of the measurement approach and the instrument characteristics. Although the data are usually free to users, satellite instruments are expensive to build and operate. Furthermore, like any other data, satellite measurements alone are not sufficient for understanding the complex physical and chemical processes associated with atmospheric chemistry. Numerical models, such as CTMs, can simulate processes controlling atmospheric chemistry and thus can be a useful tool to help understand the underlying mechanisms. However, these models need rigorous validation with measurements from satellite and other platforms. Satellite observations can meaningfully constrain the model outputs. Therefore, integration of satellite observations with chemical transport models is a promising approach that is gaining increasing attention as it can convincingly address scientific issues related to atmospheric chemistry [e.g., Kunhikrishnan et al., 2004; Li et al., 2005a; Zhang et al., 2008; Nassar et al., 2009]. This is the approach that is adopted for further exploration in this thesis research. As more satellites are launched for atmospheric chemistry studies, it can be expected that synergistic integration of satellite observations and atmospheric models will open new opportunities for an enhanced understanding of atmospheric ozone.

In remote sensing applications, electromagnetic radiation is used mostly for conveying information about a targeted object. From radiation that the atmosphere absorbs, emits, and scatters in various spectral regions of the ultraviolet (UV), visible, infrared (IR), and microwave, scientists have derived information about atmospheric constituents. Ozone molecules absorb radiation strongly in the middle ultraviolet Hartley-Huggins bands (0.22-0.32 μm), moderately in the infrared bands (9.6 μm), and weakly in the visible Chappuis bands (0.4-0.9 μm). This provides a basis for ozone measurement, from which four methods have been developed and successfully used on satellite platforms: backscatter, occultation, emission, and limb-scatter
methods [Krueger et al., 1980; Houghton et al., 1984; Miller, 1989; Stephens, 1994; Kidder and Vonder Haar, 1995; Liou, 2002, Gottwarld et al., 2006].

Satellite observations have been used to derive a global picture of tropospheric ozone distribution. Fishman et al. [1990] developed the tropospheric ozone residual (TOR) method based on satellite observations, which derives the tropospheric column ozone (TCO) by subtracting the stratospheric column ozone (SCO) from total column abundance of ozone. They presented the first global map of TCO using satellite observations of SCO from SAGE and total column ozone from Total Ozone Mapping Spectrometer (TOMS) [Krueger et al., 1989]. The main challenge of the TOR method is to separate the relatively small tropospheric component, generally 5-15%, from the total column. This is especially difficult at mid-latitudes because of the variability in the extratropical stratosphere. This issue has been continually addressed in a number of studies using either new data processing procedures or new satellite data [Hudson and Thompson, 1998; Ziemke et al., 1998; Chandra et al., 2003; Fishman et al., 2003; Ziemke et al., 2006]. Figure 1.4 shows the climatology (1979-2000) of the seasonal distribution of TCO based on SCO from the Solar Backscattered Ultraviolet (SBUV) and total column ozone from TOMS [Fishman et al., 2003]. These seasonal maps confirm and refine the following features in the distribution of tropospheric ozone shown in earlier studies: (1) Ozone over the tropical oceans appears lower than that in higher latitudes throughout the year in both hemispheres; (2) in the Northern Hemisphere, the seasonal variation in the mid-latitudes is large, with a springtime ozone maximum; (3) the Northern Hemispheric summer is characterized by high ozone plumes downwind of North America, Europe, and Asia; (4) the strong biomass burning from September to November is responsible for high ozone in the Southern Hemisphere in that season.

Because the TOR method provides only the TCO, other approaches have been explored to get information on the vertical distribution of tropospheric ozone from satellite observations [e.g., Worden et al., 2007a]. Liu X. et al. [2005] characterized GOME’s vertical sensitivity in different latitudinal zones and found that the instrument is more sensitive to the vertical distribution of ozone in the upper troposphere than in the middle and lower troposphere in the mid-latitudes. This may partially explain why elevated ozone over the Middle East is not observed in the GOME data. On the other hand, TES measures upwelling thermal radiation and is sensitive to the ozone in the mid-troposphere [Worden et al., 2007a]. Therefore, TES ozone
Figure 1.4 Climatology of tropospheric column ozone (in Dobson units) obtained from satellite measurements of TOMS and SBUV between 1979 and 2000. The four panels correspond to Northern Hemisphere winter (DJF: December-January-February), spring (MAM: March-April-May), summer (JJA: June-July-August), and autumn (SON: September-October-November) [after Fishman et al., 2003].
data are well suited for this study because of this higher sensitivity to the ozone in the mid-troposphere than GOME or OMI.

1.6 Specific Objectives and Structure of This Thesis

This thesis work can be summarized in two parts. First, the GEOS-Chem model is used to interpret observations of tropospheric ozone over the Middle East and North Africa from the TES instrument in 2005. The goal is to develop an understanding of the mechanisms controlling the summertime ozone distribution over the Middle East. Second, the interannual variation of ozone in the Middle East is characterized and possible mechanisms for this variation are explored with a GEOS-Chem simulation from 1986 to 2006. The focus is mainly on understanding the interannual variations in ozone associated with year-to-year changes in the meteorology in the region. In the first part, the following questions are to be addressed:

- What are the characteristics of TES ozone retrievals? How can these characteristics affect our interpretation of the ozone distribution in the Middle East?

- Does the Middle East have an ozone maximum as suggested in Li et al. [2001]?

- What are the meteorological and chemical mechanisms responsible for the ozone distribution in the Middle East and North Africa?

- What are the roles that local production and long-range transport play in the seasonal variation of the ozone distribution in the Middle East and North Africa?

- Can TES water vapour and isotope data provide additional constraints for our understanding of the influence of transport on the ozone distribution, as simulated by the model?

In the second part, the following questions are to be addressed:
• What is the climatology of the ozone distribution in the Middle East? Are the features in the ozone distribution observed in the Middle East in 2005 (during the TES period) representative of the long-term ozone climatology?

• How do ozone abundances in the Middle East vary from year-to-year? How large is the interannual variation?

• How does the Asian influence on ozone abundance in the Middle East vary from year to year? What are the controlling mechanisms for the variations in long-range transport?

• How does locally produced ozone vary interannually? What are the underlying mechanisms for the variation?

• What is the relationship between patterns of long-range transport from different source regions? What controls the patterns in the Middle East region?

• How do variations in long-range transport depend on climate? Can these variations be described by some climate indices?

The remaining chapters are organized as follows. The background information on the data and the model, respectively, is provided in Chapter 2. After an introduction of the GEOS-Chem model, a description is provided of the tagged ozone simulation used in the analysis and an assessment of the consistency between the tagged ozone simulation and its corresponding full chemistry simulation. The validation of GEOS-Chem is presented for the ozonesonde stations in the Middle East and South Asia. In the section on the TES data, general information about TES data and the retrieval approach that the TES team employs is provided. TES ozone retrievals are specifically discussed in terms of the a priori, instrument vertical sensitivity, and sampling size.

The main focus of Chapter 3 is on the interpretation of the TES ozone observations in 2005 with the GEOS-Chem model. In this chapter it is first shown that TES observations reveal elevated ozone abundance in the middle troposphere (500-300 hPa) across North Africa and the Middle East in summer. The underlying mechanisms are examined in terms of the influence of local photochemical production and long-range transport of ozone into the region. Finally, TES observations of water vapour (H₂O) and the ratio of deuterated water to water vapour
(HDO/H$_2$O) are examined to assess the consistency of the model simulation with these constraints in TES data on the transport pathways over North Africa and the Middle East.

The main points in Chapter 4 consist of four parts. The first part presents a 20-year (1987-2006) climatology of ozone in the Middle East and associated interannual variations. As the results suggest that in summer, locally produced ozone and transport of Asian ozone remain the major contributors to the elevated ozone in the Middle East, interannual variations of ozone from these two origins are discussed in the second and the third parts. The emphasis is placed on understanding the mechanisms responsible for these year-to-year variations. The fourth part is about the interannual variation of trade-offs in transport from different regions to the Middle East. Possible mechanisms for the variations are proposed.

Finally, a summary and discussion are given in Chapter 5, where future work is also suggested.
2 The GEOS-Chem Model and TES Ozone Observations

2.1 GEOS-Chem Model Description, Simulations, and Validation

The GEOS-Chem global chemical transport model [Bey et al., 2001] is used to interpret TES observations and to investigate the mechanisms controlling the summer ozone distribution over the Middle East. GEOS-Chem is driven by assimilated meteorological observations from the National Aeronautics and Space Administration (NASA) Goddard Earth Observing System (GEOS) from the Global Modeling and Assimilation Office (GMAO). The model simulates detailed tropospheric O$_3$-NO$_x$-hydrocarbon chemistry, including the radiative and heterogeneous effects of aerosols.

We employ version v7-02-04 of GEOS-Chem (http://www-as.harvard.edu/chemistry/trop/geos), with meteorological fields from the GEOS-4 version of the GMAO assimilation system at 6-hour time steps (3 hours for surface variables and the mixing depth). The horizontal resolution is 4° latitude by 5° longitude, degraded from the GEOS-4 native resolution of 1° latitude by 1.25° longitude. There are 30 vertical levels, with ~15 in the troposphere from 1000 to 100 hPa. The advection, wet deposition, and dry deposition schemes are based on Lin and Rood [1996], Liu et al. [2001], and Wang et al. [1998b], respectively. For moist convection, the model treats deep and shallow convection separately following the schemes of Zhang and McFarlane [1995] and Hack [1994].

In this version of GEOS-Chem, the global ozone source and sink are 5220 Tg O$_3$ yr$^{-1}$ each [Wu et al., 2007], which are comparable to the ensemble average of ~5660 Tg O$_3$ yr$^{-1}$ reported by Stevenson et al. [2006] (see Table 1.1) from simulations from 21 global models. Anthropogenic emissions are from the Global Emissions Inventory Activity (GEIA) [Benkovitz et al., 1996], with emissions in the United States based on the Environmental Protection Agency (EPA) National Emission Inventory 1999 (NEI99) [Hudman et al., 2007]. Emissions from biofuel combustion and biomass burning are from Yevich and Logan [2003] and Duncan et al. [2003], respectively. Global NO$_x$ emissions from lightning are specified at 4.7 Tg N yr$^{-1}$, based on the parameterization of Price and Rind [1992] and with the vertical distribution of the NO$_x$ emissions imposed according to Pickering et al. [1998]. These emission inputs represented the standard configuration of v7-02-04 in 2006 when this study was initiated. In the most recent
version of GEOS-Chem, v8-02-01, the anthropogenic emission inventory from the Emission Database for Global Atmospheric Research (EDGAR) [Oliver and Berdowsi, 2001] is available as an optional input. Biomass burning emissions from the Global Fire Emission Database (GFED) [van der Werf et al., 2006] are also optional, as are biogenic emissions from the Model of Emissions of Gases and Aerosols from Nature (MEGAN) [Guenther et al., 2006]. The lightning parameterization is improved by using satellite observations of lightning flashes by Murray et al. [manuscript in preparation, 2010].

GEOS-Chem can be run in several modes. The two modes used in this study are the full chemistry simulation and the tagged ozone simulation. The former simulates the detailed tropospheric O₃-NOₓ-hydrocarbon chemistry, whereas the latter linearizes the chemistry to enable tracking of ozone to quantify the contribution of ozone from different source regions to the ozone abundance in a given receptor region. In Chapter 3, we run the full chemistry simulation with the linearized ozone (LINOZ) parameterization scheme [McLinden et al., 2000] to represent the ozone influx to the troposphere from the stratosphere. The results from this simulation are compared with TES observations. Since assimilated meteorological fields produce excessive stratosphere-troposphere exchange [e.g., Weaver et al., 1993; Tan et al., 2004], our tagged ozone simulation uses a specified ozone flux boundary condition at the tropopause (SYNOZ) [McLinden et al., 2000] to ensure that the source of ozone from the stratosphere is not overestimated. Although the SYNOZ scheme correctly reproduces the annual global source of stratospheric ozone, it may not correctly capture the variability in the magnitude of the stratospheric ozone fluxes locally. We find, however, that over the Middle East during summer 2005, the period of our analysis, the mean differences in ozone abundances in the middle troposphere simulated with the LINOZ and SYNOZ schemes are less than 3%. In Chapter 4 the analysis is based mainly on the tagged ozone simulation using the SYNOZ scheme. We also present in Chapter 4, a comparison between the simulated ozone abundances from the tagged ozone and full chemistry simulations to assess the impact of the linearization assumption on the analysis.

In our tagged ozone simulation, the tropospheric ozone chemistry is linearized using archived production and loss rates of odd oxygen (Oₓ). Odd oxygen is defined in the model as $Oₓ = O₃ + O + NO₂ + 2NO₃$ because NO₂ and NO₃ are short-lived precursors of ozone, which rapidly produce ozone once formed. Since ozone accounts for most of Oₓ, we refer to ozone
instead of \( O_x \) for clarity in this thesis. Daily odd oxygen production rates and loss frequencies are first generated and archived from a full chemistry model simulation. Then, GEOS-Chem is run again in a tagged ozone mode using the archived ozone production and loss data, with separate tracers for the ozone produced from each specified source region. The rate of change of the ozone concentration is given by

\[
\frac{\partial \left[ O_3 \right]}{\partial t} = P - \left[ O_3 \right] L - V \cdot \nabla \left[ O_3 \right]
\]  

(2.1a)

where \([O_3] \) is the ozone concentration (in molecules \( \text{cm}^{-3} \)), \( P \) is the production rate (in molecules \( \text{cm}^{-3} \text{ s}^{-1} \)), \( L \) is the loss frequency (in \( \text{s}^{-1} \)), \( V \) is the wind vector, and the last term on the right side represents the influence of transport on the ozone budget. In the tagged ozone simulation, we divide the global atmosphere into \( N \) regions and tag the ozone produced in each of these regions. Since the ozone produced in each region is chemically removed at the same frequency as ozone in Equation 2.1a, the sum of the ozone produced in each region is equal to the total ozone concentration (defined as ozone in Equation 2.1a) and we can write Equation 2.1a as

\[
\frac{\partial \left( \sum_{i=1}^{N} [O_3^i] \right)}{\partial t} = \sum_{i=1}^{N} P^i - \sum_{i=1}^{N} [O_3^i] L - V \cdot \nabla \left( \sum_{i=1}^{N} [O_3^i] \right).
\]  

(2.1b)

Here \( P^i \) are the production rates for ozone from region \( i \), which are non-zero only in region \( i \). We, therefore, have an equation analogous to Equation 2.1a for ozone from each of the \( N \) regions

\[
\frac{\partial [O_3^i]}{\partial t} = P^i - [O_3^i] L - V \cdot \nabla [O_3^i].
\]  

(2.1c)

The value of the total ozone mixing ratio in each grid box, calculated with the tagged simulation, is compared with that from a full chemistry simulation for 2005. Figure 2.1 shows such a comparison using daily ozone mixing ratios averaged over the Middle East in the mid-troposphere (434 hPa, \( \sim 6.6 \) km). The correlation coefficient between the two simulations is 0.998 (Figure 2.1a). Good agreement between the two simulations suggests that the non-linear effects are small. The monthly relative difference is less than \( \pm 1\% \) in summer and less than \( \pm 3\% \) over 2005 (Figure 2.1b). Wu et al. [2009] found weak nonlinearity in summer, which is in contrast to strong nonlinearity outside summer, possibly due to the shorter ozone lifetime in summer.

Several studies have evaluated the model’s simulation of tropospheric ozone in the context of quantifying the impact of long-range transport of pollution on the distribution of
Figure 2.1. (a) Comparison of daily mean ozone mixing ratios in the Middle East between a full chemistry run and a tagged ozone run in 2005 at 434 hPa (~6.6 km). The correlation coefficient and the p-value in the Student’s t-test are indicated by $r$ and $p$, respectively. (b) The monthly mean percentage difference between the two datasets ($=(O_3$ from the tagged ozone run - $O_3$ from the full chemistry run)/$O_3$ from the full chemistry run). The bars indicate one standard deviation.
tropospheric ozone [e.g., Bey et al., 2001; Martin et al., 2002; Jaeglé et al., 2003; Hudman et al., 2007; Li et al., 2005a; Zhang et al., 2006, 2008; Sauvage et al., 2007; Wu et al., 2007]. Hudman et al. [2007] compared ozone concentrations over the United States between the GEOS-Chem simulation and aircraft observations during the International Consortium on Atmospheric Transport and Transformation (ICARTT) campaign. They found that the model compared well with the aircraft data in the lower troposphere. In the upper troposphere, they had to increase NOx emission from lightning by a factor of 4 to better reproduce the aircraft data.

In Figure 2.2 we compare ozone profiles between GEOS-Chem and the ozonesonde data at a site in the Middle East (Isfahan, 32.5°N and 51.5°E) and at two sites in India (Thiruvananthapuram, 8.5°N and 76.9°E; Delhi, 28.3°N and 77.1°E) [Meteorological Department of Iran (MDI) and India Meteorological Department (IDM), 2009]. The ozonesonde data are downloaded from the World Ozone and Ultraviolet Radiation Data Centre (Woudc) (www.woudc.org/index_e.html) for Isfahan in 2005-2006 and for Delhi and Thiruvananthapuram in 2006 because 2005 data are not available at the two sites. The ozone profiles from GEOS-Chem are sampled within 2 hours of measurements in the grid boxes containing these sites. At the Isfahan site (Figures 2.2a and 2.2d), the ozone profiles from GEOS-Chem are in good agreement with the ozonesonde data, both showing distinct differences between winter and summer. The ozone peak in the mid-troposphere in JJA is consistent with the Measurements of Ozone and Water Vapor by in-Service Airbus Aircraft (MOZAIC) measurements at Dubai and Teheran in the Middle East [Li et al., 2001]. The peak disappears in winter in both GEOS-Chem and the ozonesonde profiles. For the Indian sites, the shapes of vertical profiles from GEOS-Chem at Thiruvananthapuram agree reasonably well with those from ozonesonde observations in both seasons but the magnitude in winter is ~20 ppbv larger than the ozonesonde data (Figures 2.2b and 2.2e). At Delhi, the shapes of vertical profiles in summer from both datasets are similar, although GEOS-Chem overestimates the ozone mixing ratios by ~20 ppbv (Figure 2.2c). In addition, in winter GEOS-Chem increases ozone mixing ratio above 400 hPa in comparison with the ozonesonde data (Figure 2.2f). Overall, GEOS-Chem does reproduce the seasonal variations in the ozone profiles at these geographically different sites, but the model generally overestimates ozone in the upper troposphere over South Asia. This overestimate is likely due to an overestimate of ozone production from lightning [Sauvage et al., 2007] and will be discussed in Sections 3.4 and 3.5.
Figure 2.2. Seasonal ozone profiles (top row for JJA and bottom row for DJF) from GEOS-Chem (in green) and ozonesonde data (in red) at a Middle Eastern site: Isfahan (32.5°N, 51.5°E) in 2005-2006 and at two Indian sites: Thiruvananthapuram (8.5°N, 76.9°E) and Delhi (28.3°N, 77.1°E) in 2006. Dashed red lines denote one standard deviation for the ozonesonde profiles. The number of profiles for each mean profile is indicated by $n$. 
2.2 TES Satellite Data

2.2.1 The TES Instrument

TES is a Fourier transform spectrometer [Beer et al., 2001] onboard the NASA Earth Observing System (EOS) Aura spacecraft which was launched on 15th July 2004. The Aura satellite is in a sun-synchronous orbit at an altitude of 705 km with an inclination of 98.2° and an orbit repeat cycle of 16 days. It can map the globe in 16 orbits (~26 hours). TES was designed to look at the atmosphere in the nadir and limb views (but the limb measurements were stopped in April 2005). The nadir measurement has a footprint on the surface of 5.3 km by 8.5 km. The instrument operates in a global survey mode, in which the nadir observations are spaced about 2° along the orbit track, and in a step-and-stare mode, in which the observations are made every 40 km along the orbit. The global survey was reduced to cover only latitudes between 50°S-70°N after July 2008 to extend the lifetime of TES because the interferometer scan mechanism was showing signs of increasing friction.

TES is one of the first satellite instruments to provide measurements from which vertical profiles of tropospheric ozone are retrieved. Tropospheric ozone is much more difficult to monitor from satellites than stratospheric ozone because of the presence of clouds and aerosols, the complexity of the interaction between the surface and the atmosphere, and the small ratio of tropospheric ozone to the total column abundance of ozone (~5-10%). TES records the Earth’s spectral radiance in the wavelengths ranging from 3.1-15.4 μm (650-3250 cm\(^{-1}\)) [Osterman et al., 2006], which includes 9.6 μm where ozone absorbs infrared radiation moderately. The TES ozone retrievals, following the optimal estimation method [Rodgers, 2000], are discussed in Bowman et al. [2002, 2006], Worden et al. [2004], and Kulawik et al. [2006].

The nadir ozone data in version V002 is used in this study. The quality of this version of the data is significantly enhanced over previous versions owing to an improved radiance calibration [Osterman et al., 2006]. The ozone profiles in this version were validated by Nassar et al. [2008] using ozonesonde measurements. They reported a positive bias of 3-11 ppbv in the upper troposphere and of 4-9 ppbv in the lower troposphere. However, only one station (Isfahan) is located in the Middle East and North Africa and there are only two profiles of good quality at this station that coincide (spatially and temporally) with TES measurements between October
2004 and October 2006. Therefore, in the study of Nassar et al. [2008], no definitive comparison could be made between TES and the ozonesonde profiles for this region [Ray Nassar, personal communication, 2008]. In support of the analysis presented in Chapter 3, Worden et al. [2009] compared three years of V002 TES ozone data with 10-year climatologies from the MOZAIC program [Marenco et al., 1998] at two Middle Eastern sites, Dubai (25°N, 55°E) and Teheran (35°N, 51°E), and an Asian site, Delhi (28°N, 77°E). Their results are shown in Figure 2.3. The TES ozone values in Figure 2.3 were reduced by 12% to account for the bias suggested by Nassar et al. [2008] and then vertically averaged between 700-300 hPa. In most cases, TES ozone values are in agreement with the MOZAIC values within the standard error of the mean. TES ozone also shows similar monthly variations in summer except at Teheran in June.

Worden et al. [2009] developed an innovative approach to assess TES ozone observations by assimilating TES data into the GEOS-Chem model and comparing the results with an independent ozone dataset, which was generated by assimilating ozone data from the MLS and the OMI instruments into the GMAO assimilation system, using the GEOS-4 general circulation model (GCM). They found that differences between the two datasets were reduced after assimilation of TES ozone into GEOS-Chem. Figure 2.4 shows ozone distribution at 7-8 km from the GEOS-4 GCM assimilation (Figure 2.4a) in comparison to the GEOS-Chem simulation without TES assimilation (Figure 2.4b) and with TES assimilation (Figure 2.4c) in August 2006. As shown in Figure 2.4d, the distribution in the difference between GEOS-Chem and the combined OMI and MLS (OMI+MLS) assimilation becomes narrower and the average bias is reduced from 6.8 ppbv to 1.4 ppbv over an area of 20°N-50°N and 0-120°E after assimilation of TES ozone data into GEOS-Chem. The improvement in the agreement between GEOS-Chem with the TES assimilation and the OMI+MLS assimilation is further illustrated in Figure 2.5, which shows the vertical distribution of ozone across the Middle East along 45°E. Comparison of Figure 2.5c with Figure 2.5b shows that although both GEOS-Chem simulations produce an ozone enhancement in the mid-troposphere, similar to the OMI+MLS assimilation (Figure 2.5a), the standard GEOS-Chem simulation overestimates the ozone enhancement in the mid and upper troposphere (Figure 2.5c). Assimilation of TES ozone into GEOS-Chem reduces the maximum and produces an ozone distribution closer in agreement with that from the OMI+MLS assimilation (Figure 2.5b). The close agreement between the two assimilated products implies consistency between TES and OMI + MLS in terms of the information that they provide on
Figure 2.3. Comparison between 10-year climatologies derived from MOZAIC ozone measurements and a 3-year climatology derived from TES ozone observations. The error bars are the standard error on the mean in time for the TES ozone measurements. The TES ozone values have been decreased by 12% to account for the 10-15% TES bias. The precision of the MOZAIC ozone data is 2 ppbv. The error estimates for MOAZIC data are unavailable to us in this study [after Worden et al., 2009].
Figure 2.4. Mean August 2006 ozone distribution at 7-8 km produced by (a) assimilation of OMI and MLS data into the GMAO GEOS-4 GCM, (b) the GEOS-Chem model, and (c) the GEOS-Chem model after assimilation of bias-corrected TES data following Nassar et al. [2008]. (d) Histogram of the differences in ozone between the GMAO ozone assimilation and the GEOS-Chem model with (red line) and without (black dashed line) assimilation of TES data. The y-axis is the number of samplings based on daily modeled fields at 0 GMT in the boxed area in Figure 2.4a [after Worden et al., 2009].
Figure 2.5. Monthly mean latitude-altitude cross sections of modeled ozone in August 2006 along 45°E for (a) the GEOS-4 GCM with assimilated observations from OMI and MLS, (b) the GEOS-Chem with assimilated data from TES, and (c) the GEOS-Chem without assimilation of TES data [after Worden et al., 2009].
ozone, and offers an indirect validation of the TES data over the Middle East region.

In addition to ozone, TES also provides data of other atmospheric trace gases such as CO, CO₂, CH₄, and NH₃ (see http://tes.jpl.nasa.gov/data/products/). Two of particular interest to this study are water vapour (H₂O) and the ratio of deuterated water vapour (HDO) to H₂O. Shephard et al. [2008] compared H₂O measurements from TES with nighttime radiosonde data from the National Centers for Environmental Prediction (NCEP). They found that the mean difference between the two datasets is less than 5% in the lower troposphere (at pressures greater than 600 hPa), increasing to a maximum of ~15% in the upper troposphere (300-200 hPa), with the radiosonde data being drier. Worden et al. [2006] characterized the error of the TES HDO/H₂O ratio and reported a precision of 1-2% in the ratio and a possible bias of 5% due to the HDO spectroscopic line strengths. The TES retrieval of the HDO/H₂O ratio is most sensitive near 700 hPa and has the smallest uncertainty in the tropics and the largest uncertainty at higher latitudes.

The TES data are available in a Hierarchical Data Format (HDF) from NASA Langley Atmospheric Science Data Center at http://eosweb.larc.nasa.gov/PRODOCS/tes/table_tes.html. In our analysis, daily ozone data in 2005 are taken along the satellite tracks and are gridded horizontally into the GEOS-Chem cells of 4° latitude by 5° longitude. Figure 2.6 shows an example of the number of TES observations per grid box in July 2005 at 464 hPa. For the Middle East region (20°N-40°N and 30°E-60°E), the number of observation ranges between 3-10 counts per grid box in this month. The mean and the standard deviation of the number of observations in the Middle East are 6.6 and 1.7 counts per grid box, respectively. Monthly composites are taken for most analyses in Chapters 3 and 4. Note the Middle East region is defined as 20°N-40°N and 30°E-60°E for statistical analysis in this thesis unless it is indicated otherwise. In the tagged ozone simulations, the Middle East region is defined slightly differently (see Sections 3.5.2 and 4.2.1).

2.2.2 General Retrieval Theory for the Emission Method

An accurate interpretation of TES data requires an understanding of the underlying retrieval theory, which is based on the radiative transfer equation (RTE). Ignoring scattering, the radiancex_

I_\lambda measured by a satellite instrument at wavelength \lambda can be expressed as [Liou, 2002]
Figure 2.6. The number of TES observations per grid box (4° latitude by 5° longitude) for July 2005 at 464 hPa.
\[ I_\lambda = B_\lambda(T_s) \tau_\lambda(p_s) + \int_0^T B_\lambda(T(p)) \frac{\partial \tau_\lambda}{\partial p} dp \]  \hspace{1cm} (2.2)

where \( B \) is the Planck blackbody function, \( T \) is temperature, \( \tau \) is transmittance, and \( p \) is pressure. Subscript \( s \) indicates the surface. The challenge is to obtain the ozone concentrations from the measured radiance by inverting this RTE. Two possible methods used for infrared measurements from instruments such as TES or the Atmospheric Infrared Sounder (AIRS) are the optimal estimation method [Rodgers, 2000] and the iterative method [Chahine, 1990; Smith, 1993]. The iterative method starts with a guessed gas profile and adjusts the profile iteratively using the measured radiance. This method is simple and requires no limiting assumptions, but can fail to converge or converge to wrong solutions. Hence, the optimal estimation method is used more widely and it is the method that was adopted for TES [Bowman et al., 2002]. The following illustrates the optimal inverse method as employed by the TES team, which follows the approach of Rodgers [2000].

Given a state vector \( x \) for an ozone profile and a radiance observation vector \( y \), \( y \) can be related to \( x \) by a forward model \( F(x) \). If the forward model is linear, then,

\[ y = F(x) + \varepsilon = Kx + \varepsilon \]  \hspace{1cm} (2.3)

where \( \varepsilon \) is a vector of errors, and \( K \) is the Jacobian matrix (or the weighting function). \( K \) represents the sensitivity of the observation vector to the state vector, i.e., \( K = \frac{\partial y}{\partial x} \).

The inversion question is: how to achieve an optimal estimate of \( x \), denoted by \( \hat{x} \), provided that we can characterize the errors of the observation \( y \) and the \emph{a priori} \( x_a \). The goal is to find an optimal estimate that minimizes the analysis error. For Gaussian error statistics for \( y \) and \( x \), this is equivalent to minimizing the cost function \( J(x) \)

\[ J(x) = (y - Kx_a)^T S_y^{-1} (y - Kx_a) + (x - x_a)^T S_a^{-1} (x - x_a) \]  \hspace{1cm} (2.4)
where \( S_y \) and \( S_a \) are the observation error covariance matrix and the \textit{a priori} error covariance matrix, respectively. This gives an optimal estimate

\[
\hat{x} = x_a + G(y - Kx_a)
\]  

(2.5)

where \( G \) is the gain matrix

\[
G = (K^T S_y^{-1} K + S_a^{-1})^{-1} K^T S_y^{-1}.
\]  

(2.6)

Note: \( G = \frac{\partial \hat{x}}{\partial y} \). Using the Bayesian theorem, with the assumption of Gaussian error statistics, minimizing Equation 2.4 also gives the maximum \textit{a posteriori} estimate.

Based on Equations 2.5 and 2.6, the estimated ozone profile \( \hat{x} \) can be retrieved. This method requires an \textit{a priori} profile because the problem is ill-posed. Accurately developing \( F(x) \), and defining \( K, S_y \) and \( S_a \) are key steps in the inversion.

Furthermore, if ignoring the error term, Equation 2.5, combined with Equation 2.3, can be expressed as

\[
\hat{x} = x_a + A(x - x_a)
\]  

(2.7a)

or

\[
\hat{x} = Ax + (I - A)x_a
\]  

(2.7b)

where \( A \) is the averaging kernel matrix and \( A = \frac{\partial \hat{x}}{\partial x} \). \( I \) is the identity matrix, and \( x \) is the true profile. \( A \) is a measure of the vertical sensitivity of an instrument, indicating the sensitivity of the retrieved ozone profile to the true ozone profile at all retrieval levels. In the ideal case, \( A \) would be equal to \( I \), which means that the retrieved profiles would represent the true profiles. In the worst case, \( A \) would be zero and the retrieved ozone profiles are equal to the \textit{a priori}, meaning the variation from the \textit{a priori} cannot be captured by the instrument. \( A \) is a function of \( K, S_y \) and \( S_a \) as \( A = GK \). Another important measure of the vertical sensitivity of an instrument is the degrees of freedom for signal (DOFS) [Rodgers, 2000]. DOFS gives the number of independent
pieces of information available vertically in the measurements and it is the sum of the diagonal elements of the averaging kernel matrix.

2.2.3 TES Ozone Retrievals

In the TES retrieval, the \( a \) priori profile \( (x_a) \) and the \( a \) priori error covariance \( (S_a) \) are based on the simulations from the Model of Ozone and Related Tracers (MOZART) model [Brasseur et al., 1998b]. The \( a \) priori profile is averaged on spatial scales of 10° latitude × 60° longitude monthly. Figure 2.7 shows the TES \( a \) priori in July over the mid-troposphere, in which the ozone mixing ratios are also high over the Middle East region. To demonstrate that the enhanced ozone in the TES retrievals over the Middle East is not just a reflection of the \( a \) priori, we modify the TES retrieval using a globally uniform \( a \) priori [Zhang et al., 2006; Kulawik et al., 2008; Worden et al., 2009]. From Equation 2.7b, the TES retrieval \( \hat{x}^{\text{TES}} \) with the \( a \) priori \( x_a^{\text{TES}} \) can be expressed as

\[
\hat{x}^{\text{TES}} = Ax + (I - A)x_a^{\text{TES}} \quad (2.8)
\]

where \( Ax \) is the contribution from the atmosphere (the true state) and \( (I - A)x_a^{\text{TES}} \) is the contribution from the \( a \) priori. For a uniform \( a \) priori \( x_a^{\text{U}} \), a retrieval \( \hat{x}^{\text{U}} \) becomes

\[
\hat{x}^{\text{U}} = Ax + (I - A)x_a^{\text{U}} . \quad (2.9)
\]

Therefore, a TES ozone profile with a uniform \( a \) priori can be retrieved by Equation 2.9 minus Equation 2.8

\[
\hat{x}^{\text{U}} = \hat{x}^{\text{TES}} + (I - A)(x_a^{\text{U}} - x_a^{\text{TES}}) . \quad (2.10)
\]

In the TES retrieval, the state vector \( x \) is expressed in terms of the natural logarithm of the volume mixing ratio (VMR).

We selected the \( a \) priori profile from a TES retrieval over the Pacific Ocean at approximately 30°N and 180°W as the global uniform \( a \) priori profile \( x_a^{\text{U}} \). As shown in Figure 2.7, the ozone mixing ratio is low over the central subtropical Pacific. With the \( a \) priori from this
Figure 2.7. TES ozone \textit{a priori} mixing ratios (ppbv) at 464 hPa. The \textit{a priori} values are sampled at the locations where TES took measurement in July 2005 and then gridded into the GEOS-Chem cells of 4° latitude by 5° longitude. This causes some structures in the TES ozone \textit{a priori} blocks of 10° latitude by 60° longitude in this plot.
retrieval used uniformly in all the TES retrievals, any spatial features in the distribution of $\hat{x}^U$ would signify information in the TES measurement that is independent of the a priori. The resulting horizontal ozone distribution at 464 hPa is shown in Chapter 3 (Section 3.2). Even with the globally uniform low a priori ozone abundances, the overall spatial distribution of ozone in the Middle East does not change significantly from the original TES retrievals, suggesting that the a priori does not significantly bias the TES retrievals over this region.

TES ozone retrievals are reported on 67 levels from the surface to 0.1 hPa. However, the vertical resolution of the profiles is about 6 km, with at most 4 DOFS in the whole profile [Bowman et al. 2002; Worden et al., 2004]. Figure 2.8a shows an example of the global DOFS distribution on 31 July 2005. The total DOFS is typically less than 4 with at most 1-1.5 in the troposphere. The DOFS is higher in the tropics than at the poles and is greater in the mid-latitudes of the Northern Hemisphere (the summer hemisphere) than in the Southern Hemisphere, mainly because the thermal contrast between the surface and the atmosphere tends to be high in low latitudes (especially over land), which enhances the DOFS. An example of the TES averaging kernels in the Middle East (24.8°N, 49.5°E) on 31 July 2005 is shown in Figure 2.8b, where the averaging kernels are grouped into four altitude bands: 1000-500 hPa (in light blue), 500-300 hPa (in red), 300-150 hPa (in green), and 150-50 hPa (in blue). We are mostly interested in the middle troposphere (500-300 hPa, in red). The averaging kernels for these altitudes indeed peak between 500-250 hPa, suggesting that TES retrievals between 500-300 hPa are mostly sensitive to ozone in the mid-troposphere around 400 hPa. For altitudes between 300 and 150 hPa (in green), the averaging kernels peak around 270 hPa. The averaging kernels for the lower troposphere (1000-500 hPa) also peak in the middle troposphere, suggesting that ozone in the lower troposphere is not well constrained by the retrieval in this region.

TES ozone profiles averaged over the Middle East show an ozone buildup in July between 500-300 hPa (red, solid line in Figure 2.9a). However, the buildup is not present in October (red, solid line in Figure 2.9d). This seasonality is generally in agreement with the GEOS-Chem simulation and will be discussed in detail in Chapter 3 (Section 3.4). In July (Figure 2.9a), the ozone buildup is more pronounced in the TES retrievals (red, solid line) than that in TES a priori (red, dashed line), suggesting that TES really captures signals that are independent from the a priori. To further demonstrate that the ozone buildup near 400 hPa in
Figure 2.8. (a) The TES DOFS for both the full (black crosses) and tropospheric (red crosses) ozone profiles on 31 July 2005. (b) An example of TES averaging kernels at a Middle East location (24.8°N and 49.5°E) on the same day, for the lower troposphere (cyan), the mid-troposphere (red), the upper troposphere (green), and lower stratosphere (blue). The surface pressure for this profile is 996 hPa.
Figure 2.9. Vertical ozone profiles averaged over the Middle East from the TES retrievals with a vertical uniform \textit{a priori} (in blue, solid line) in comparison with the original TES retrievals (in red, solid line) for (a) July, (b) August, (c) September, and (d) October 2005. Dashed lines indicate the uniform \textit{a priori} ($x_a^U = 63$ ppbv below 200 hPa, in blue) and TES \textit{a priori} ($x_a^{TES}$, in red).
July is not due to the \textit{a priori}, we substitute a vertically uniform \textit{a priori} into the retrievals using Equation 2.10. The \textit{a priori} was constructed by specifying a constant value of 63 ppbv below 200 hPa, which is an average of the 51 ppbv at 464 hPa in July over the Pacific Ocean at 30°N and 180°W and the 75 ppbv at 34°N and 65°E (east of the Middle East). With this vertically uniform \textit{a priori} (blue, dashed line in Figure 2.9a), the retrieved ozone profile (blue, solid line in Figure 2.9a) still shows an ozone maximum around 400 hPa in July. The peak around 400 hPa gradually decreases in August and September (blue, solid line in Figures 2.9b and 2.9c). By October, the retrieved ozone profile (blue, solid line in Figure 2.9d) is close to the vertically uniform \textit{a priori} (blue, dashed line in Figure 2.9d). This suggests that although TES generally has at most 1-1.5 DOFS in the troposphere, it has sufficient vertical sensitivity to the ozone in the mid-troposphere to capture the seasonal build up of ozone over the Middle East.

2.3 Conclusions

The performance of the GEOS-Chem model was examined in this study using ozonesonde data from a Middle Eastern site and two Indian sites for summer and winter. The observed seasonal variations in the ozone profiles are reproduced by GEOS-Chem at these geographically different sites. However, the model overestimates ozone in the India sites by 10-30 ppbv relative to the ozonesonde observations. The impact of the assumed linearity in the chemistry in the tagged ozone simulation was also assessed by comparing this simulation with a full chemistry run. The ozone mixing ratios between the two simulations are highly correlated ($r > 0.99$) in the mid-troposphere over the Middle East. The monthly difference is within 5% of the full chemistry simulation. These evaluations provide us with confidence in the fidelity of the ozone simulation in the model for the analysis in the thesis.

TES ozone observations are the primary dataset used in this study. TES was the first satellite instrument from which tropospheric ozone profile data were directly retrieved. Although direct comparisons between TES and ozonesonde observations is not possible over the Middle East due to limited ozonesonde observations, Worden \textit{et al.} [2009], in support of the analysis in the thesis, compared TES ozone values averaged between 700-300 hPa with observations from the MOZAIC aircraft program at two Middle Eastern sites and at a South Asian site. They found
that ozone values in the two datasets agree within the TES standard errors, if the TES ozone values are corrected to remove the bias estimated by Nassar et al. [2008]. Worden et al. [2009] showed that when the TES ozone data are assimilated into the GEOS-Chem model, there is close agreement between the assimilation ozone field and that obtained by assimilation of OMI and MLS data into the GEOS-4 data assimilation system at GMAO. The agreement between the two assimilated ozone fields over the Middle East implies consistency between TES and OMI+MLS observations in terms of the information that they provide on tropospheric ozone over Eurasia.

The TES retrievals use a maximum a posteriori retrieval approach, which employs an a priori ozone profile. Although the TES averaging kernels indicate peak sensitivity of the instrument to ozone in the middle troposphere, between 500-300 hPa, the ozone maximum in the middle troposphere could reflect a bias associated with the a priori profile. To assess the impact of the a priori on the TES retrievals, the standard TES a priori profile was replaced with a vertically uniform a priori profile using Equation 2.10. Even with a vertically uniform a priori, the TES retrievals still showed enhanced ozone in the mid-troposphere in July, which vanishes in October. This suggests that although the DOFS of the TES retrievals is less than 1.5 in the troposphere, the measurements can capture the seasonal build up of ozone over the Middle East.
3 Summertime Buildup of Tropospheric Ozone Over the Middle East and North Africa

3.1 Introduction

In this chapter, we examine the mechanisms contributing to the summertime ozone buildup over the Middle East in the context of the new observations from TES. We focus on the year 2005 because it is the first summer that TES data became available. We use the GEOS-Chem CTM to better understand the processes responsible for the high concentrations of ozone observed by TES across the Middle East and North Africa. We first present, in Section 3.2, the ozone enhancement observed by TES over the Middle East and surrounding areas. In Section 3.3 we discuss the summertime meteorological conditions in the Middle East. In Section 3.4 we present the GEOS-Chem simulation of the distribution of ozone, \( \text{H}_2\text{O} \), and \( \text{CO} \) and discuss the mechanism responsible for the ozone enhancement. We then examine in Section 3.5 the ozone photochemical production in the region and quantify the contribution of local chemical production and long-range transport of ozone to the ozone enhancement. In Section 3.6 we examine TES observations of \( \text{H}_2\text{O} \) and HDO/\( \text{H}_2\text{O} \) to assess the consistency of the model simulation with the constraints provided by the TES data on the transport pathways over North Africa and the Middle East. Finally, in Section 3.7 we summarize our results.

3.2 Comparison of Modeled Ozone With TES Observations

The monthly mean ozone mixing ratio retrieved from the TES instrument at 464 hPa in July 2005 is shown in Figure 3.1a. Enhanced ozone abundance is observed over a broad region extending from North Africa to the Middle East (approximately 20°N-40°N, 20°E-60°E). The spatial distribution of the observations is compared to that predicted by the GEOS-Chem model (Figure 3.1b). Each GEOS-Chem ozone profile has been smoothed by applying the TES averaging kernels and \textit{a priori} constraint vector [e.g., Jones \textit{et al.}, 2003] for the co-located retrieved TES profile to account for the bias introduced by the averaging kernels and the \textit{a priori} profile. This transformation is given by the following expression, which is analogous to Equation 2.7a

\[
\hat{x}^{\text{GCS}} = x^{\text{TES}} + A(x^{\text{GC}} - x^{\text{TES}}) \quad (3.1)
\]
Figure 3.1. Monthly mean ozone mixing ratio (in ppbv) in July 2005 at 464 hPa from (a) TES, (b) GEOS-Chem, smoothed with the local TES averaging kernels (see Equation 3.1). Note the maximum scale is 120 ppbv for TES data and 100 ppbv for GEOS-Chem data.
Figure 3.1. (c) Monthly mean ozone mixing ratio (in ppbv) in July 2005 at 464 hPa from TES with a global uniform *a priori*. 
where $A = \partial \hat{x}/\partial x$ is the TES averaging kernel matrix which describes the sensitivity of the TES ozone estimate to the profile of ozone, $x^{GC}$ is the nearest GEOS-Chem ozone profile, which has been mapped to the TES pressure grid, and $\hat{x}^{GC}$ is the smoothed GEOS-Chem profile. The quantity $x_{a}^{TES}$ is the TES a priori, the constraint vector, which is based on ozone simulations from the MOZART model and is averaged on spatial scales of $10^\circ$ latitude $\times 60^\circ$ longitude (see Figure 2.7). $x^{GC}$, $\hat{x}^{GC}$, and $x_{a}^{TES}$ are expressed in terms of the natural logarithm of the volume mixing ratio. The spatial distribution of the modeled mixing ratio over the Middle East (Figure 3.1b) is similar to that observed by TES (Figure 3.1a). However, the modeled ozone enhancement is more pronounced over Saudi Arabia. The observed ozone peaks at about 120 ppbv, whereas the modeled ozone peaks at about 100 ppbv. Across the extratropics of the Northern Hemisphere, the model underestimates the ozone abundances compared to the observations, which Parrington et al. [2008] attributed to an underestimate of mid-latitude NO$_x$ emissions from lightning in this version of the model. The ozone distribution is also similar to that obtained by Li et al. [2001] using an earlier version of the GEOS-Chem model.

As a result of the limited spatial sampling of the TES observations, Worden et al. [2009] reported that the uncertainty on the mean ozone values over the Middle East is about 10 ppbv in 2006. However, in their analysis of TES ozone data, Worden et al. [2009] showed that ozone abundances are enhanced in the middle troposphere over the Middle East and North Africa for the summers from 2005 through 2007, indicating that the ozone feature is robust.

We examine here the effect of the a priori bias on the spatial distribution of the TES ozone data by varying the a priori profiles used in the TES retrievals. As discussed in Chapter 2, we modify the TES ozone retrievals by substituting a globally uniform a priori profile in the TES retrievals using Equation 2.10. This a priori was taken from a retrieval over the Pacific Ocean, at approximately 30°N and 180°W, and has ozone values of 30–40 ppbv in the lower troposphere and 40–50 ppbv in the upper troposphere, representative of clean marine conditions. The resulting ozone distribution for July 2005 at 464 hPa is shown in Figure 3.1c. The overall spatial distribution remains unchanged, although the ozone abundances are reduced due to the lower ozone abundance in the uniform a priori (the ozone abundance of the uniform a priori averaged over the Middle East is 51.4 ppbv at 464 hPa compared with 84.3 ppbv for the a priori
used in the TES retrievals shown in Figure 3.1a). Figure 3.1c indicates that the *a priori* bias in the TES retrieval does not significantly affect our conclusion about the spatial distribution of ozone over the Middle East.

### 3.3 Summertime Meteorology in the Vicinity of the Middle East

During boreal summer, the circulation in the subtropical troposphere of the Northern Hemisphere is dominated by the influence of the Asian monsoon [Rodwell and Hoskins, 1996; Lelieveld *et al.*, 2002; Lawrence, 2004]. Rodwell and Hoskins [1996] showed that an upper tropospheric anticyclone, known as the South Asian High (SAH) or the Tibetan High (TH) [Yanai and Wu, 2006], associated with the Asian monsoon reflects a Rossby wave response in the atmosphere to the diabatic heating from convection in the monsoon region. The vertical motions associated with this system consist of rising motion in the convection region over Asia and descending motion in the Rossby wave response region (to the northwest of the convection region). Previous studies have shown that the anticyclone associated with this Rossby wave response has a significant influence on the distribution of trace gases such as ozone, H$_2$O, and CO in the UTLS [e.g., Rosenlof *et al.*, 1997; Kar *et al.*, 2004; Filipiak *et al.*, 2005; Li *et al.*, 2005a; Randel and Park, 2006; Park *et al.*, 2007]. Observations from MLS, for example, reveal that within the anticyclone in the UTLS, high concentrations of CO are collocated with high H$_2$O and low ozone, which is attributed to deep convection in the monsoon region [Park *et al.*, 2007].

In the middle troposphere, the descent associated with the monsoon anticyclone is localized over the eastern Mediterranean and over Central Asia (near the Caspian and Aral Seas) [Rodwell and Hoskins, 1996]. The interaction of the mean flow with the Atlas Mountains of northern Algeria and the Zagros Mountains in Iran induces anticyclonic flow in these regions, and equatorward transport of cold air on the eastern flanks of the anticyclones help localize and intensify the descent over the eastern Mediterranean and Central Asia [Rodwell and Hoskins, 1996]. The air that is transported equatorward sinks adiabatically along isentropes, which reduces its relative humidity, and thereby contributes to the aridity observed in these regions. Diabatic cooling in the descent regions further enhances the descent, enabling the air masses to descend faster than the isentropic surfaces [Rodwell and Hoskins, 1996; Eshel and Farrell, 2000].
The vertical velocity and wind vectors in the middle troposphere from the GEOS-4 meteorological fields in the GEOS-Chem model are shown in Figure 3.2. The model captures the centers of descent over the eastern Mediterranean and over Central Asia identified by Rodwell and Hoskins [1996]. Across tropical Africa, the influence of the Intertropical Convergence Zone (ITCZ) is present in the model as a band of rising air along 10°N. The anticyclones over northwestern Africa (near the Atlas Mountains, referred as the Saharan anticyclone) and over southwestern Iran (near the Zagros Mountains, referred as the Iranian high or Arabian anticyclone) [Zhou and Li, 2002; Lawrence, 2004] in GEOS-4 are also shown in Figure 3.2. The northwesterly flow on the eastern flank of the anticyclones coincides with the regions of strongest descent, as predicted by Rodwell and Hoskins [1996].

In the lower troposphere, the meteorological conditions across the Mediterranean and Middle East are characterized by a thermal low that extends from the Persian Gulf across Iraq and into Turkey, and which is capped at about 850 hPa (1400-1500 m) [Bitan and Sa’aroni, 1992] by a thermal inversion that is formed by the warming from the subsidence extending down from the middle and upper troposphere. Associated with this “Persian trough” is a northwesterly flow of cool air from Europe in the eastern Mediterranean [Ziv et al., 2004]. Because of the thermal inversion, local anthropogenic emissions from North Africa and the Middle East are not expected to provide a significant contribution to ozone production in the middle and upper troposphere. Kar et al. [2006], however, reported that observations of atmospheric CO from the Measurements of Pollution In the Troposphere (MOPITT) satellite instrument reveal a persistent enhancement in CO over the Zagros Mountains, which they argued is linked to mountain venting which transports boundary layer air into the free troposphere, suggesting that surface pollution could contribute to the ozone enhancement observed in the region.

3.4 GEOS-Chem Simulations of Ozone, CO, and H₂O

The seasonal evolution of the atmospheric circulation and the ozone distribution at 434 hPa over North Africa and the Middle East from GEOS-Chem is shown in Figure 3.3. In May 2005 (Figure 3.3a) the flow is primarily westerly, with high ozone across the mid-latitudes, reflecting the well-known mid-latitude springtime maximum in ozone [Wang et al., 1998c] (also see Figure 1.4). By June 2005 the anticyclone over the Persian Gulf forms (Figure 3.3b) and associated with
Figure 3.2. Horizontal winds (in m s$^{-1}$, arrows) overlaid with vertical velocity (dp/dt, in Pa s$^{-1}$, color) as monthly means in July 2005 at 434 hPa (~6.7 km) in GEOS-Chem (GEOS-4 fields). Red indicates descent while blue shows ascent. The double black lines delineate the Atlas and Zagros Mountains. The magnitude of the wind speed is indicated at the lower-right corner.
Figure 3.3. Ozone mixing ratio (in ppbv, color) overlaid with horizontal winds (in m s\(^{-1}\), arrows) from May to October 2005 at 434 hPa (~6.7 km) in GEOS-Chem. The magnitude of the wind speed is indicated at the lower-right corner.
it are relatively high abundances of ozone across the Middle East and Central Asia. By July and August 2005 (Figures 3.3c and 3.3d), the anticyclones over the Persian Gulf and northwestern Africa are well established in the model and the region of high ozone extends from the Middle East, across North Africa, and over the eastern subtropical Atlantic. In July, over Central Asia, on the eastern flank of the anticyclone over the Persian Gulf, the enhanced ozone extends eastward into Central Asia. This eastward extension of the region of enhanced ozone across Mongolia and southern Russia in July 2005 can also be seen in the TES observations in Figure 3.1a. After September, ozone concentrations across the region decrease dramatically as the anticyclones weaken and the region is ventilated more effectively (Figures 3.3e and 3.3f). The seasonal cycle of the ozone enhancement is also illustrated in Figure 3.4, which shows the time series of observed and modeled ozone over the Middle East at 464 hPa in 2005. For comparison, we show the original modeled ozone abundances and the modeled fields sampled along the TES orbit and transformed using the TES averaging kernels and a priori profiles. Both TES and GEOS-Chem show a similar seasonal dependence with a correlation of coefficient of $r = 0.94$.

The modeled and observed ozone abundances decrease from a maximum of about 80-90 ppbv in July and August to a minimum of about 50-60 ppbv in winter. In contrast, zonal mean mixing ratios in the mid-troposphere of the extratropics are at a maximum in April in the model (not shown, see Figure 4.3b for reference).

The vertical structure of the modeled and observed ozone, averaged over the Middle East, is shown in Figure 3.5. The ozone enhancement as observed by TES is localized in the middle troposphere around 400 hPa and is at a maximum in July (Figure 3.5a). The observed ozone enhancement peaks at about 90 ppbv in July 2005 and is much less pronounced by October 2005 (~60 ppbv) (Figure 3.5d), reflecting the weakening of the anticyclone over the Arabian Peninsula in boreal fall. The vertical structure of the enhancement is much less pronounced in the model and in the a priori than in the TES observations. The ozone abundances in the upper troposphere in the model are significantly higher than those retrieved from TES in July and August 2005. In contrast, by October 2005 the modeled vertical distribution of ozone is in better agreement with the TES observations. In summer, the model simulation overestimates ozone in the upper troposphere with both the LINOZ and SYNOZ stratospheric boundary conditions. This seasonality of the ozone profile is similar to that measured over Teheran (35°N, 51°E) and Dubai (25°N, 55°E) by the MOZAIC program [Li et al., 2001]. In the ozonesonde measurements at
Figure 3.4. Daily ozone mixing ratio (in ppbv) averaged over the Middle East at 464 hPa from TES (in red), the GEOS-Chem model (in green), and the GEOS-Chem model smoothed with the TES averaging kernels and *a priori* (in black, see Equation 3.1). Continuous TES data are available for the area from July 1 to December 31, 2005.
Figure 3.5. Monthly mean ozone vertical profiles of TES, the \textit{a priori}, GEOS-Chem, and GEOS-Chem smoothed with the local TES averaging kernels (see Equation 3.1) in the Middle East in 2005 (a) July, (b) August, (c) September, and (d) October.
Isfahan (32.5°N, 51.7°E), ozone mixing ratios near 400 hPa were over 100 ppbv on 14 August 2005 (Figure 3.6a), but were significantly lower by October 2005 (Figure 3.6b). Figure 3.6a also shows an overestimate of ozone in the upper troposphere by GEOS-Chem on 14 August 2005.

In July 2005, the well-developed anticyclones over northwestern Africa and the Persian Gulf, together with the subtropical westerly jet over the Mediterranean in the north and the ITCZ to the south, isolate northeastern Africa and the Middle Eastern middle troposphere. In this region, enhanced ozone in the middle troposphere in the model is strongly correlated with low specific humidity and low atmospheric CO spatially (Figure 3.7). The low specific humidity in the model is consistent with strong descent from the upper troposphere over the region. In the middle troposphere (6-8 km) over the Middle East (15°N-35°N, 30°E-60°E), the spatial correlation between ozone and CO is $r = -0.70$ and the correlation between ozone and H$_2$O is $r = -0.71$. For North Africa (15°N-35°N, 0-30°E), the correlation is $r = -0.87$ between ozone and CO and $r = -0.80$ between ozone and H$_2$O. The ozone-CO correlations suggest three distinct regions across North Africa and the Middle East: high ozone and high CO north of the westerly jet, high ozone and low CO south of the jet, and low ozone and high CO in the vicinity of the ITCZ over central Africa. North of the westerly jet, both high ozone and CO reflect the influence of anthropogenic emissions on the distribution of ozone and CO, whereas over tropical Africa, the high CO and low ozone is due to the influence of rapid convective transport of surface emissions of CO. Similarly, over central Africa and Asia, high abundances of H$_2$O coincide with low ozone due to the influence of convective transport within the ITCZ.

The high ozone, low CO, and low specific humidity that characterizes the Middle East in the middle troposphere is in contrast to the conditions in the UTLS region, where, as discussed above, the large scale extension of the Asian monsoon anticyclone is associated with high CO, high specific humidity and low ozone. The GEOS-Chem simulation of ozone, CO, and specific humidity in the upper troposphere are shown in Figure 3.8. In the upper troposphere, the model simulates a broad maximum in CO extending from East Africa to Asia, similar to previous studies on westward outflow of Asian pollution in summer [e.g., Lawrence et al., 2003; Kar et al., 2004]. Although the modeled ozone abundances are low in the UTLS over the Indian Ocean and Asia, the modeled ozone distribution does not exhibit a minimum within the anticyclone region as previously observed [e.g., Park et al., 2007]. This bias may be related to the overestimate of ozone in the model, relative to TES observations, in the UTLS over the Middle
Figure 3.6. Ozone profiles at Isfahan (32.5°N, 51.7°E) from ozonesonde measurements and GEOS-Chem simulations on (a) 14 August 2005 and (b) 19 October 2005.
Figure 3.7. GEOS-Chem simulated: (a) ozone mixing ratio (in ppbv), (b) CO mixing ratio (in ppbv), and (c) specific humidity (in g kg\(^{-1}\)) at 434 hPa (~ 6.7 km) in July 2005. All are overlaid with the winds at this altitude.
Figure 3.8. GEOS-Chem simulated (a) ozone mixing ratio (in ppbv), (b) CO mixing ratio (in ppbv), and (c) specific humidity (in g kg\(^{-1}\)) at 139 hPa (~14 km) in July 2005. All are overlaid with the winds at this altitude.
East, as shown in Figure 3.5a and in Worden et al. [2009], or due to discrepancies in the strength of deep convection over Asia in the model.

3.5 Sources of Ozone Over the Middle East and North Africa

3.5.1 Ozone Photochemical Production

Photochemistry provides a net source of ozone in the upper troposphere in summer [e.g., Wang et al., 1998a; von Kuhlmann et al., 2003], whereas it is generally a net sink for ozone in the lower troposphere, in the absence of anthropogenic emissions, because of the high ozone loss rates in the boundary layer. Over continental regions, however, due to anthropogenic emissions, photochemical production can provide a net source of ozone in the boundary layer. The net photochemical production rate of ozone as a function of longitude and altitude in the subtropics (20°N-30°N) is shown in Figure 3.9a. In the subtropical middle and upper troposphere in July, the net photochemical production of ozone is at a maximum over South Asia (60°E-90°E), East Asia (90°E-120°E), and over southern North America (60°W-120°W). Li et al. [2001] found that emissions of NOx from lightning provided an important source of ozone over the Middle East. The maxima in the ozone production rates shown in Figure 3.9a are co-located with regions of strong emissions of NOx from lightning (Figure 3.9b), with South Asia providing the dominant source of lightning NOx in the subtropics between 20°N-30°N in the model. The maxima in the ozone production rates also are co-located with high concentrations of atmospheric OH (not shown), which are associated with high concentrations of ozone precursors such as CO and acetone (not shown). The enhanced abundance of OH, CO, and acetone is due to the convective transport of anthropogenic emissions of ozone precursors from the South Asian boundary layer to the middle and upper troposphere.

As the upper troposphere in the Middle East is strongly influenced by transport of pollution from Asia [Li et al. 2001; Lawrence 2004], accurately reproducing the horizontal and vertical distribution of ozone over the Middle East will depend on correctly capturing the magnitude and spatial distribution of the lightning NOx source over South Asia. Although GEOS-Chem does capture the ozone production over the Asian monsoon region, the production seems to be overestimated in the upper troposphere (as discussed in Section 2.1). Sauvage et al.
Figure 3.9. GEOS-Chem simulated (a) net ozone production rate (in molec. cm\(^{-3}\) s\(^{-1}\)) and (b) NO\(_x\) produced from lightning (in molec. cm\(^{2}\) s\(^{-1}\)) for 2005 July averaged over 20°N-30°N. The altitude for the elevated ozone in Figure 3.1 is around 6-8 km.
[2007] modified the lightning NOx source in a version of the GEOS-Chem model, using data from the Optical Transient Detector (OTD) and Lightning Imaging Sensor (LIS). They found that lightning NOx emissions were lower in summer over the Asian monsoon region in the model than the original version. Consequently, the overestimate of ozone relative to ozonesonde measurements over a Middle Eastern station, Dubai, was reduced in the middle and upper troposphere in the model.

As shown in Figure 3.9a, across North Africa (0-30°E) the net rate of production of ozone is relatively uniform. At 8 km the mean net production rate for ozone is about $2 \times 10^5$ molec. cm$^{-3}$ s$^{-1}$, which is about 2 ppbv day$^{-1}$. The ozone enhancement is confined to the middle and upper troposphere because of the strong photochemical sink of ozone in the lower troposphere. The lifetime of ozone over northeastern Africa decreases from about 50 days at 9 km to less than 10 days at 4 km. Confinement of the region due to the presence of the Arabian anticyclone and weak winds over northeastern Africa are therefore critical for enabling the buildup of ozone. Ozone that is produced in the middle and upper troposphere over North Africa and the Middle East is rapidly destroyed in the lower troposphere as a result of the descent in the region. Accurately reproducing the ozone distribution across North Africa and the Middle East will depend on correctly capturing the descent in the region and the relative strengths of the anticyclones over the Persian Gulf and northwestern Africa. These meteorological conditions are prescribed by GEOS-4.

3.5.2 Tagged Ozone Simulation

We conduct a tagged ozone simulation using the GEOS-Chem model to quantify the contribution of local production and long-range transport of ozone to the ozone enhancement over the Middle East and North Africa. In our analysis, we focus on two receptor regions where the ozone abundance is high: the Middle East (15°N-35°N, 30°E-60°E) and North Africa (15°N-35°N, 0°E-30°E). The source regions include Asia (0°-35°N, 60°E-145°E), North America (15°N-70°N, 125°W-65°W), equatorial Africa (20°S-15°N, 25°W-55°E), and Europe (40°N-70°N, 15°W-40°E) (Figure 3.10a). Each region is further divided into three layers in altitude: an upper tropospheric layer (300 hPa to the tropopause), a middle tropospheric layer (700 - 300 hPa), and
Figure 3.10. Definition of domains in the tagged ozone simulations (a) for 2005 in Chapter 3 and (b) for multiple years in Chapter 4. In Figure 3.10a, each domain is further divided into three layers: the upper troposphere (300 hPa–tropopause), the middle troposphere (700–300 hPa), and the boundary layer (>700 hPa). Two additional regions are the stratosphere and the rest of the world in the troposphere (ROW), which includes all the troposphere outside all the boxed regions.
the boundary layer (pressures greater than 700 hPa). Two additional source regions are the rest of the world (ROW), which includes all the troposphere outside the above-defined regions, and the stratosphere. In our analysis, we use "ozone" or "total ozone" to represent ozone (or ozone mixing ratio) for a given grid box or region. "Asian ozone" refers to ozone (or ozone mixing ratio) in a grid box or region that is originated in Asia. This also applies for other source regions. "Locally produced ozone" or "local ozone" refers to ozone (or ozone mixing ratio) that is produced in a receptor region.

Figure 3.11 shows the seasonal variation of the fractional contribution of ozone from the different source regions to the ozone abundances at about 434 hPa over the Middle East and North Africa. Over the Middle East (Figure 3.11a), both local production and transport of ozone from Asia are the major sources of ozone in the middle troposphere in July and August (contributing about 30-40% each). In contrast, the influences of the other regions are at a minimum (5-10% each) (Figure 3.11b), reflecting the isolation of the region due to the presence of the summertime Arabian anticyclone. Over North Africa (Figure 3.11c) the contribution from local production and transport from Asia in summer is reduced to ~20% and ~15%, respectively, while the contribution from transport from other source regions becomes larger, especially from North America (~10%) and the rest of the world (~20%). Table 3.1 provide a summary of the fractional contribution of the different source regions to the ozone budget in July at 434 hPa, partitioning the contribution from each region into components from the upper troposphere, the middle troposphere and the boundary layer. Over the Middle East, for example, the contribution of ozone transported from the upper troposphere, the middle troposphere, and the boundary layer of Asia are estimated to be 13%, 10%, and 8%, respectively. For the local source of ozone in the Middle East, the dominant contribution is from ozone produced in the middle troposphere (16%), although ozone produced in the upper troposphere and in the boundary layer each contributed about 8%. A recent study by Lelieveld et al. [2009] revealed high surface ozone concentrations in the Middle East during summer, partly due to anthropogenic surface emission.

Figure 3.12 shows examples of the distinct spatial patterns of the ozone abundances at 434 hPa in July 2005, which are attributed to ozone produced in the middle troposphere of the Middle East (Figure 3.12a), the upper troposphere of Asia (Figure 3.12b), the North American boundary layer (Figure 3.12c), and the stratosphere (Figure 3.12d). As noted above, local
Table 3.1. Fractional contribution (in %) to the ozone abundance in the Middle East and North Africa at 434 hPa in 2005 July from a GEOS-Chem tagged ozone simulation.

<table>
<thead>
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<th>Receptor Region</th>
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<th>UT¹</th>
<th>MT¹</th>
<th>BL¹</th>
<th>Total</th>
</tr>
</thead>
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<td>10</td>
<td>8</td>
<td>31</td>
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<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
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<td>8</td>
</tr>
<tr>
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<td>North Africa</td>
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<td>3</td>
<td>1</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>The Middle East²</td>
<td>8</td>
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</table>

¹UT denotes the upper troposphere (300 hPa to the tropopause); MT is the middle troposphere (700 – 300 hPa); and BL is the boundary layer (>700 hPa). ²This is the local ozone production.
Figure 3.11. The fractional contribution (in %) from different source regions to the ozone abundance in (a, b) the Middle East and (c, d) North Africa at 434 hPa in 2005. The left panels show the contribution from local production (in red) and from ozone transported from Asia (in blue). The right panels show the fractional contribution from the other source regions (see regional domains in Section 3.5.2). The European influence is small and thus is excluded in the figure.
Figure 3.12. GEOS-Chem simulated ozone mixing ratios (in ppbv) in July 2005 at 434 hPa that is attributed to ozone production in (a) the Middle Eastern middle troposphere, (b) the Asian upper troposphere, (c) the North American boundary layer, and (d) the stratosphere.
production in the middle troposphere of the Middle East and ozone transported from the Asian upper troposphere are the two dominant contributions to ozone abundances in the Middle East.

The ozone produced in the mid-troposphere in the Middle East is confined over Saudi Arabia (Figure 3.12a), largely due to the presence of the Arabian anticyclone over the Persian Gulf around this altitude (see Figure 3.3c). The ozone from the Asian upper troposphere is transported westward between 20°N-35°N and descends to the mid-troposphere most strongly over the Middle East and Central Asia (Figure 3.12b). This is consistent with the discussion of the meteorological and chemical contexts in Sections 3.3 and 3.5.1. The contributions of ozone from the North American boundary layer and from the stratosphere (Figures 3.12c and 3.12d) are relatively small, less than 5% to the ozone abundance over the Middle East. The stratospheric ozone contribution is largest in the regions of strong descent, such as over northeastern Africa and Central Asia, whereas the North American source is transported from the west and is dominant over the eastern Mediterranean.

The different pathways for transport of ozone over North Africa and the Middle East are shown in the plots of the zonal flux of ozone in Figure 3.13. In the northern region of the domain (Figure 3.13a), transport is primarily westerly, in the vicinity of the westerly jet, whereas in the south (Figure 3.13c) transport is easterly, capturing the outflow from the Asian monsoon region. Furthermore, Figure 3.13 reveals that downward transport of ozone is localized in the eastern Mediterranean region in the model and that there is significant upward transport of ozone from the boundary layer into the middle troposphere in the Middle East. This upward transport is strongly influenced by the orography of the region. Over the Zagros Mountains (between 50°E-70°E in Figures 3.13a and 3.13b), there is significant upward transport of ozone extending into the middle troposphere in the model. There is also strong upward transport of ozone over western Saudi Arabia and Yemen, between 40°E-50°E in Figure 3.13c. This region of upward transport extends along the Asir and Hijaz mountain ranges, along the Red Sea coast of western Saudi Arabia. In fact, the greatest upward flux of ozone in the lower troposphere in the Middle East in the model is located in this region. As shown in Table 3.1, our tagged ozone analysis indicates that transport of ozone from the boundary layer in the Middle East domain accounts for a large fraction (about 25%) of the locally produced ozone.
Figure 3.13. GEOS-Chem simulated ozone flux (in kg s\(^{-1}\)) along (a) 30°N, (b) 26°N, and (c) 15°N -20°N in July 2005.
Recently, Tangborn et al. [2009] showed that the simulation of CO in the GEOS-4 general circulation model at GMAO, with surface emissions and the atmospheric chemistry of CO specified from the GEOS-Chem model, significantly underestimates CO abundances over the Arabian Peninsula compared to observations from Scanning Imaging Absorption Spectrometer for Atmospheric CHartographY (SCIAMACHY) and MOZAIC. Since CO serves as a proxy for the hydrocarbon and combustion-related precursor emissions of ozone, this bias could indicate a significant underestimate of the impact of surface emissions in the Middle East on ozone abundances in the middle troposphere as a result of the strong upward transport shown in Figure 3.13.

3.6 Constraints From TES H₂O and HDO/H₂O on the Transport Mechanisms

We examine in this section TES observations of H₂O and HDO to assess the consistency of the model simulation with the constraints from the TES data on the transport pathways over North Africa and the Middle East. Observations of HDO/H₂O are particularly valuable in this context as the isotopic composition of water vapor can be used as an indicator of the source of the vapor, and therefore provides information on the transport pathways of air masses [Worden et al., 2007b]. Water vapor becomes more depleted in HDO/H₂O as it undergoes condensation, and as such, the most depleted vapor is that at high latitudes and altitudes in the troposphere or of stratospheric origin. In the case of the latter, water in the lower stratosphere is dominated by a tropospheric source which has undergone an extensive history of condensation as it crosses the tropopause. On the other hand, vapor that has not undergone a history of condensation will appear as relatively enriched in HDO relative to H₂O and indicate an air mass source (either from evaporation from the ocean or from continental evapotranspiration) near the surface.

Monthly mean TES observations of H₂O for July 2005 are shown in Figure 3.14a. Low abundances of H₂O are observed across North Africa and the Middle East as expected given the aridity of these regions. The dipole structure in the distribution of H₂O, with high H₂O over Asia and low H₂O across North Africa and the Middle East, reflects the influence of convective transport over Asia and subsidence over North Africa and the Middle East [e.g., Stone et al., 2000]. Note, there are gaps in the H₂O and HDO/H₂O maps shown in Figure 3.14 due to the low
Figure 3.14. TES observations of (a) H$_2$O (in VMR) and (b) $\delta D$ (in per mil) for July 2005, averaged over 850-450 hPa. White areas are missing data.
density of reliable H₂O and HDO retrievals. The number of observations per grid box for July 2005 ranges from 2-8 over the Middle East and North Africa.

Figure 3.14b shows monthly mean TES observations of HDO/H₂O, defined as δD [Worden et al., 2007b]

\[ \delta D = 1000 \left( \frac{R}{R_{VSMOW}} - 1 \right) \]  (3.2)

where \( R \) is the measured isotope ratio (=HDO/H₂O, both HDO and H₂O are expressed in volume mixing ratios) and \( R_{VSMOW} \) is the isotope ratio of Vienna Standard Mean Ocean Water reference (=3.11×10⁻⁴). Figure 3.14b reveals a spatial distribution different from that of H₂O. Values of δD are high across much of the region, except over northeastern Africa. The high δD values over northwestern Africa (near Morocco) and the Middle East, in contrast to the lower δD over northeastern Africa (near Egypt), indicates that the origin of the air in these regions is different from that over northeastern Africa. Over the Arabian Peninsula and Central Asia, where δD is high, one would expect a strong evapotranspiration source at the surface. As shown in Figure 3.13, there is significant upward transport of ozone in these regions, associated with the Zagros Mountains in southern Iran and the Asir and Hijaz mountain ranges on the Arabian Peninsula. This upward transport would also provide a source of surface air with high δD to the middle troposphere. Similarly, the high δD values over northwestern Africa are consistent with convection and orographic lifting over the Atlas Mountains, which has been reported by Knippertz et al. [2003]. This region of convection and orographic lifting in the GEOS-Chem fields is shown in Figure 3.2 as a region of upward motion extending from Morocco to southern Spain (near 0°E, 35°N), and coincides with region of high δD inferred from the TES data (Figure 3.14b). This region of upward motion in GEOS-Chem also coincides with low abundances of ozone simulated over northwestern Africa, as shown in Figure 3.7a.

The region of low δD values over northeastern Africa is coincident with the strong descent over North Africa and the downward transport of ozone shown in Figures 3.13b. Figure 3.14b suggests that subsidence from the upper troposphere is responsible for the depleted HDO/H₂O. Since the downward transport is equatorward along the isentropes, the air over eastern North Africa will originate mainly in the extratropical upper troposphere. Indeed, back trajectory analyses conducted using the GEOS-4 meteorological fields (not shown) indicate that
air masses over eastern North Africa originate over North America and the western Atlantic and are transported across the northern Atlantic Ocean and up to the high latitude upper troposphere, followed by equatorward descent over Europe down to the Mediterranean region, accounting for the low δD observed over North Africa by TES. Furthermore, as shown above in our tagged ozone analysis, it is over this region that the contribution of ozone from North America is at a maximum.

3.7 Conclusions

We used the GEOS-Chem chemical transport model to interpret observations of tropospheric ozone from the TES satellite instrument. Observations from TES reveal elevated ozone in the middle troposphere (~500-300 hPa) over the vicinity of the Middle East in summer 2005. The horizontal extent and vertical location of this enhancement is similar to the “Middle East ozone maximum” previously suggested in a model study by Li et al. [2001]. However, the modeled ozone enhancement is more pronounced over Saudi Arabia than in the observations. We have examined the mechanism responsible for this “ozone maximum” in the context of the recent TES measurements. In particular, we focused on understanding the influence of long-range transport of ozone and local chemical production on the spatial and temporal variations of tropospheric ozone over the Middle East and North Africa.

We showed that ozone abundances in the middle troposphere across the region are at a maximum in June-August and a minimum in December-February. In summer, the spatio-temporal distribution of ozone across North Africa and the Middle East reflects the influence of the Arabian and Saharan anticyclones, centered in the vicinity of the Zagros and Atlas Mountains, respectively. In the model, the eastern flanks of these anticyclones coincide with regions of descent over North Africa and Central Asia (east of the Caspian Sea), as described by Rodwell and Hoskins [1996]. In the observations and in the model, we found high concentrations of ozone extending from the Arabian anticyclone region to the coast of northwestern Africa, near the southeastern flank of the Saharan anticyclone, bounded by the ITCZ to the south and the subtropical westerly jet to the north. We showed that in the model, over the Middle East, high ozone abundances in the middle troposphere are correlated with low specific humidity and low
atmospheric CO. This is in contrast to conditions in the outflow region of the Asian monsoon in the UTLS where low ozone is correlated with high specific humidity and high CO.

We conducted a tagged ozone simulation using the GEOS-Chem model to quantify the contribution of local production of ozone and transport of ozone to the ozone enhancement. We found that local production and transport from Asia provided comparable contributions of 30-35% to the ozone over the Middle East in July 2005. Over North Africa, the contribution to the ozone in the middle troposphere from local production was dominant (at about 20%), with transport from Asia, North America, and equatorial Africa each contributing about 10-15% of the aggregate ozone. Over both North Africa and the Middle East, the contribution of European emissions to the ozone enhancement was less than 2%, reflecting the confinement of European pollution to the lower troposphere. We found that the North American influence was at a maximum over North Africa, in the region of strong descent.

Although the lower troposphere in the Middle East in summer is capped by a thermal inversion, we found that ozone produced in the boundary layer of the Middle East accounted for about 25% of the local Middle Eastern contribution to the ozone enhancement in the middle troposphere. We showed that this transport of boundary layer air to the middle troposphere is consistent with the distribution of HDO retrieved from the observations from TES. Examination of TES H₂O and HDO/H₂O showed that although H₂O is low across North Africa and the Middle East, high δD values over the Middle East and Central Asia indicate significant isotopic enrichment of H₂O in these regions which we argued is due to the transport of boundary layer air into the middle troposphere by orographic lifting over the Zagros Mountains in Iran and along the Asir and Hijaz mountain ranges in Saudi Arabia.

Our analysis showed that the model overestimates ozone in the middle and upper troposphere over the Middle East. This bias may be due to an overestimate of local production of ozone in the middle and upper troposphere over the Middle East or to discrepancies in the description of the outflow of ozone precursors from the Asian monsoon region in the model. Accurately simulating the magnitude and spatial distribution of the ozone enhancement will require properly reproducing ozone production rates in the middle and upper troposphere and characterizing the atmospheric circulation response in the Middle East to the Asian monsoon. Our results also suggested that although the focus on the ozone enhancement in the Middle East
has been primarily in the context of long-range transport, further work is needed to better quantify the influence of surface emissions on the ozone budget over North Africa and the Middle East. High-resolution regional chemical transport models would be especially useful, as they should more accurately capture the impact of orography on the atmospheric circulation over this region.
4 Interannual Variations in Tropospheric Ozone in the Middle East

4.1 Introduction

Tropospheric ozone varies on a range of temporal and spatial scales. To date, most studies on tropospheric ozone have focused on its short-term variations and less attention has been paid to the processes driving interannual variations in ozone. It has been recognized that changes in emissions and meteorology, including STE, are key factors driving interannual variations in tropospheric ozone [Chandra et al., 1998; Ziemke and Chandra, 1999; Karlsdottir et al., 2000; Thompson et al., 2001; Fusco and Logan, 2003; Stohl et al., 2003; Zhou et al., 2003; Duncan and Bey, 2004; Zeng and Pyle, 2005; Wild and Palmer, 2008; Voulgaraki et al., 2009]. However, challenges remain in characterizing the interannual variations in tropospheric ozone on global and regional scales, understanding the underlying mechanisms, and quantifying the relative contributions of the different factors.

In this chapter, we investigate how the ozone distribution in the Middle East, examined in Chapter 3 for 2005, varies from year to year. We focus on how the variations are influenced by changes in meteorology using a 20-year (1987-2006) simulation of the GEOS-Chem model. Improved understanding of this meteorological influence is important for predicting the impacts of climate-related changes in the general circulation of the atmosphere on the ozone distribution in the Middle East and for understanding how changes in ozone in this region will feedback on the climate system.

We first describe the GEOS-Chem tagged ozone simulation and the statistical analysis methods in Section 4.2. Then, we discuss the meteorological conditions that influence the ozone distribution in the Middle East in Section 4.3. The mean ozone abundance in the region and its variation over the 20 years are reviewed in Section 4.4. This is followed in Section 4.5 with a discussion of the year-to-year variations in Asian ozone and locally produced ozone, which are the two major contributors to the ozone enhancement in summer over the Middle East. In this section, trade-offs in transport among different source regions are also presented and their underlying mechanisms are proposed. In Section 4.6 we examine the impact of changes in the ozone chemistry on our interpretation of the variability in ozone induced by the meteorology. Finally, conclusions are drawn in Section 4.7.
4.2 Model Simulations and Data Analyses

4.2.1 Tagged Ozone Simulations

To investigate the interannual variations in ozone in the Middle East, a tagged ozone simulation is run from January 1986 to December 2006, using 1986 for model spin-up. Since the focus is on the impact of the meteorology on ozone, we allow the meteorological fields to vary from year to year, but keep the ozone chemical production and loss rates constant. For this purpose, we run the tagged ozone simulation from 1986 to 2006 using archived daily ozone production and loss data for 2005. To test the robustness of the simulation results, we repeat the 20-year simulation with chemical rates appropriate for 1990 and 1995. Years 1990 and 1995 were randomly selected years for comparison. Ozone production/loss rates in 1990, 1995, and 2005 represent different ranges of chemical conditions. The comparison of the three 20-year time series will be shown in Section 4.6. We take the 20-year time series generated using the 2005 ozone production/loss rates as the primary dataset for analysis so that the results are comparable to those in Chapter 3. All analyses in this chapter are based on the time series with 2005 chemistry input unless it is stated otherwise.

The regional definitions in Chapter 3 are retained but modifications are made for Asia, Europe, North Africa, South Africa, and North America, in order to cover a larger area for each of these continents (see Figure 3.10b). We also include ozone from South America and Australia. These regions are defined as: the Middle East (15°N-35°N, 30°E-60°E), Asia (5°N-60°N, 60°E-145°E), North America (15°N-70°N, 170°W-65°W), South America (55°S-15°N, 90°W-30°W), North Africa (15°N-35°N, 20°W-30°E), South Africa (35°S-15°N, 20°W-55°E), Europe (35°N-70°N, 15°W-60°E), and Australia (45°S-5°N, 90°E-160°E). Two additional regions are the stratosphere and the rest of the world (ROW), which includes all the troposphere outside the above-defined areas. We focus here mainly on the Middle East as a receptor region.

4.2.2 Statistical Analysis: Anomalies, Covariance, and Significance Test

Our statistical analysis is generally based on monthly composites. Monthly means for the ozone mixing ratio are calculated from the GEOS-Chem fields, which were archived every six hours.
The anomaly of a variable in a given month for a year (e.g., anomaly of ozone mixing ratio or anomaly of wind speed) is calculated from the difference between the monthly mean of the variable in that year and the long-term mean of the variable in that month.

For variables $x$ and $y$, their covariance can be estimated from

$$\sigma_{xy} \approx \sum_{i=1}^{n} (x_i - X)(y_i - Y)/(n - 1) \quad (4.1)$$

where $X$ and $Y$ are the long-term mean of $x$ and $y$, respectively. $n$ is the number of years (20 years for this study). $x_i$ and $y_i$ are monthly mean of $x$ and $y$ for year $i$, respectively. Therefore, $\sigma_x^2$ and $\sigma_y^2$, the variance of $x$ and $y$, respectively, can also be obtained from Equation 4.1 using $x$ or $y$ only for the two variables. Furthermore, the correlation coefficient $r$ between $x$ and $y$ is calculated from

$$r = \frac{\sigma_{xy}}{\sigma_x \sigma_y} \quad (4.2)$$

where $\sigma_x$ and $\sigma_y$ are the standard deviations of $x$ and $y$, respectively. In our analysis, we usually normalize variable $x$ first by

$$\tilde{x} = \frac{x - X}{\sigma_x} \quad (4.3)$$

Consequently, $\sigma_x = 1$ and thus the resultant covariance $\sigma_{xy}$ has the same magnitude as $\sigma_y$ since $|r| \leq 1$. It also has the same unit as $\sigma_y$ because $\tilde{x}$ is dimensionless. For a three-dimensional domain, all the equations apply to each grid box.

A significance level test is critical in climate statistical analyses as the test provides an objective criterion for rejecting or accepting a hypothesis [Storch and Zwiers, 1999]. Throughout this thesis, we use the Student’s t-test to assess statistical significance of covariance or correlation coefficient between variables of interest [Storch and Zwiers, 1999]. The test is conducted using the null hypothesis $H_0$: there is no correlation between the two variables of interest. The probability of falsely rejecting $H_0$ when it is true is the power of the test, which is
indicated by the $p$ value and is usually taken as 1-10%. If the null hypothesis is rejected, the probability of the result arising from chance is less than 1-10%. This also can be interpreted as that the two variables are positively or negatively correlated at the 90-99% significance level.

4.3 Meteorological Conditions

The meteorological conditions in the vicinity of the Middle East were discussed in Sections 3.3 and 3.4, with a focus on summer 2005. The primary features remain similar in the 20-year mean. As stated in Section 3.3, the Asian summer monsoon imposes a predominant influence on the circulation in the subtropical troposphere of the Northern Hemisphere. The Asian monsoon is caused by the large amplitude of the seasonal cycle of thermal contrast between land and nearby oceans, with the Tibetan Plateau acting as a strong heat source because of its size, height, and latitudinal position [Ye and Wu, 1998]. Randel and Park [2006] illustrated a warm core over the Tibetan Plateau between $20^\circ N$ and $40^\circ N$ and between 500 and 150 hPa (~7-12 km), a feature also pointed out by Hoskins and Wang [2006]. The heating of the air over the Plateau plays an important role in maintaining the Asian summer monsoon [Tao and Chen, 1987; Ye and Wu, 1998; Yanai and Wu, 2006]. Intense convection transports large amounts of sensible heat and moisture, as well as air pollutants from the surface to the upper troposphere [Ye and Wu, 1998; Lawrence et al., 2003; Kar et al., 2004; Park et al., 2007]. In response to the heating and persistent deep convection, an anticyclone, the SAH, forms in the upper troposphere. The SAH is found to have a great impact on the atmospheric circulation in the Northern Hemisphere and on the weather and climate in eastern Asia [Krishnamurti et al., 1973; Ye and Wu, 1998; Qian et al., 2002; Zhang et al., 2005]. Figure 4.1a shows the climatological distributions of the geopotential height and stream lines associated with the anticyclone from NCEP, National Center for Atmospheric Research (NCAR). The tropical easterly jet extends from 100$^\circ E$ to 20$^\circ E$ along the southern edge of the SAH and transports ozone and other pollutants from Asia westward (to be discussed in Section 4.5).

In the mid-troposphere (Figure 4.1b), a key feature is the Arabian anticyclone (or the Iranian High) over the Middle East [Zhou and Li, 2002; Ziv et al., 2004]. In Chapter 3, we
Figure 4.1. The mean geopotential height (in dynamic m) overlaid with stream lines for July (1987-2006) at (a) 150 hPa, (b) 400 hPa, and (c) 1000 hPa (topography is not shown). Data source: NCEP/NCAR reanalysis [Kalnay et al., 1996].
illustrated its important role in trapping ozone at these altitudes. Its contribution to interannual variations in ozone in the Middle East will be further explored in Section 4.5.

Near the surface (Figure 4.1c), there is a low pressure system over the Indian subcontinent and central Asia where the air flow converges, as illustrated by the stream lines. Moist air from the Indian Ocean in the Southern Hemisphere is transported to the Indian subcontinent by the Somali jet through the Arabian Sea and the Bay of Bengal. This low pressure facilitates deep convection and production of ozone from lightning. In contrast to summer conditions, the surface in winter is under the influence of a high pressure system.

In this chapter, the meteorological data are based on GEOS-4 unless it is stated otherwise. The geopotential heights are from NCEP/NCAR reanalysis data [Kalnay et al., 1996] because the geopotential heights were not archived in the GEOS-4 product available for GEOS-Chem.

4.4 The 20-year Climatology of the Tropospheric Ozone Distribution in the Middle East

Figure 4.2 shows the GEOS-Chem simulated ozone mixing ratio at 400 hPa in July averaged from 1987 to 2006. The spatial pattern in this 20-year mean is similar to that for 2005 (shown in Figure 3.1b); ozone mixing ratios are low over the tropical oceans, whereas they are high over the Northern Hemisphere, over the biomass burning regions in the Southern Hemisphere, and across the Atlantic and the Indian oceans. Ozone mixing ratios are also high over eastern North America and over Eurasia. The high ozone abundances (around 80-100 ppbv) over the Middle East and North Africa still stand out in this 20-year mean.

The seasonal variation of the 20-year mean ozone mixing ratios in the mid-troposphere over the Middle East shows a maximum in summer (Figure 4.3a), similar to that shown in Figure 3.4 for 2005. In contrast, the zonal mean ozone mixing ratios in the same latitudes (15°N-35°N) exhibit a different seasonality, with a maximum in spring and a minimum in summer (Figure 4.3b). As discussed in Chapter 3, given the long lifetime of ozone in the middle and upper troposphere (30 days at 6 km), the differences in the seasonality of ozone over the Middle East and the zonal mean are attributable to atmospheric dynamics. On a timescale of a week, transport by the zonal winds would produce an ozone distribution that is well mixed zonally. It is the
Figure 4.2. GEOS-Chem simulated mean ozone mixing ratios (in ppbv) in July averaged from 1987 to 2006 at 400 hPa.
Figure 4.3. GEOS-Chem simulated seasonal variation in ozone mixing ratios (in ppbv) at 400 hPa (a) in the Middle East (15°N-35°N, 30°E-60°E) and (b) for the zonal mean in the subtropics (averaged between 15°N-35°N). The lines are for the 20-year mean and the bars indicate one standard deviation.
presence of the anticyclones that prevent this mixing and produces the localized buildup of ozone in summer over the Middle East. The ozone vertical profile in summer for the 20-year mean shown in Figure 4.4a is consistent with that in July 2005 (see Figure 3.5a). The latitude-altitude cross section along 40°E across the Middle East is shown in Figure 4.4b. The high ozone airmass displays a maximum around 25°N in the mid-troposphere over the Middle East.

The 20-year averaged ozone mixing ratio at 400 hPa over the Middle East and the ozone contributions from the different source regions are given in Table 4.1. We first examine the seasonal variation of the 20-year mean. The seasonal variations of the Asian and local ozone sources are larger than the variations in the ozone mixing ratio over the Middle East. The ratio of the summer to winter (JJA/DJF) contribution from the Asian and local ozone sources are 4.0 and 9.0, respectively, whereas the JJA/DJF ratio for the ozone mixing ratio in the region is only 1.3. This reflects the seasonal compensation between the Asian and local ozone sources and the other source regions. In the NH summer (JJA), the Asian and local ozone sources provide the dominant contribution to the ozone mixing ratios over the Middle East, about 31% and 23%, respectively (see also the fractional contributions in Figure 4.5). The next largest contributions are from North Africa and South Africa (~10% each), North America, the ROW, and the stratosphere (~6% each). The other regions contribute little. In NH winter, ozone from outside the Middle East and Asia provides the dominant contribution to the total ozone mixing ratios (Figure 4.5).

The values of the standard deviation in Table 4.1 show that the variability in the Asian source is the largest in the NH summer and fall, with a standard deviation of 3-5 ppbv, likely due to the Asian monsoon. Locally produced ozone also varies greatly in the NH summer and fall with a standard deviation of 2-3 ppbv. In JJA, the anomaly in the total ozone mixing ratio ranges by ±6 ppbv, which is about ±7% of the mean. The anomalies of the Asian and local ozone sources range ±7 ppbv (or ±30%) and ±3 ppbv (or ±15%), respectively. We will discuss in detail in Section 4.5 the factors responsible for this difference in variability. The variability in ozone from all the NH source regions and the ROW is larger in the NH summer than in winter, whereas the variability in ozone from all the SH source regions and from the stratosphere is smaller in the NH summer than in winter. As the chemistry is constrained by 2005 conditions in the simulation, interannual variations from different sources should be related to variation in meteorology.
Figure 4.4. The 20-year averaged ozone mixing ratio (in ppbv) in July. (a) Vertical profiles averaged over the Middle East. The dashed lines denote one standard deviation. (b) Ozone (color, in ppbv) along a latitude-altitude cross section at $40^\circ$E overlaid with the winds. White areas denote topography. The vertical velocity is enlarged by 100 times for illustration purposes.
Table 4.1. Seasonal variation of mean ozone mixing ratios (in ppbv) in the Middle East at 400 hPa in total and contributions from different source regions. In parentheses is the standard deviation (in ppbv).

<table>
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<th>DJF(^1)</th>
<th>MAM(^1)</th>
<th>JJA(^1)</th>
<th>SON(^1)</th>
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<td>70 (3.1)</td>
<td>77 (3.7)</td>
<td>61 (3.0)</td>
</tr>
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<td>7 (1.2)</td>
<td>24 (4.2)</td>
<td>14 (3.4)</td>
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<td>18 (2.8)</td>
<td>9 (1.9)</td>
</tr>
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<td>8 (1.3)</td>
<td>6 (1.0)</td>
</tr>
<tr>
<td>South Africa</td>
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<td>16 (3.4)</td>
<td>8 (1.3)</td>
<td>12 (2.6)</td>
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<tr>
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<td>8 (1.1)</td>
<td>5 (1.2)</td>
<td>6 (1.0)</td>
</tr>
<tr>
<td>South America</td>
<td>9 (1.5)</td>
<td>6 (1.2)</td>
<td>1 (0.3)</td>
<td>2 (0.5)</td>
</tr>
<tr>
<td>Europe</td>
<td>1 (0.2)</td>
<td>1 (0.3)</td>
<td>3 (0.8)</td>
<td>2 (0.5)</td>
</tr>
<tr>
<td>Australia</td>
<td>2 (0.3)</td>
<td>1 (0.2)</td>
<td>1 (0.1)</td>
<td>1 (0.2)</td>
</tr>
<tr>
<td>Rest of the World</td>
<td>9 (0.6)</td>
<td>9 (0.8)</td>
<td>5 (0.8)</td>
<td>6 (0.6)</td>
</tr>
<tr>
<td>Stratosphere</td>
<td>10 (1.9)</td>
<td>11 (1.9)</td>
<td>5 (0.9)</td>
<td>3 (0.5)</td>
</tr>
</tbody>
</table>

\(^1\)DJF denotes the mean of December, January, and February; MAM refers to March, April, and May; JJA refers to June, July, and August; SON refers to September, October, and November.
Figure 4.5. The 20-year mean fractional contribution to the total ozone (in %) in the Middle East at 400 hPa (a) for Asian and locally produced ozone and (b) for ozone from the other regions. Australia is excluded due to its negligible contribution to the Middle East (see Table 4.1).
4.5 Interannual Variation in Ozone and its Sources

4.5.1 Interannual Variations in Asian Ozone Over the Middle East

Figure 4.6 shows a time series of the anomalies in Asian ozone in July averaged over the Middle East at 400 hPa, as simulated by GEOS-Chem. This is based on the 20-year simulation using 2005 chemical production rates and loss frequencies for ozone (see Section 4.2). The Asian ozone anomalies fluctuate by ±7 ppbv or ±30% from the 20-year mean. The year 2005 studied in Chapter 3 is a relatively normal year with respect to the Asian influence on the Middle East. The two most extreme years are 1994 and 2002, with the largest positive and negative anomalies, respectively.

The distributions of the Asian ozone source at 400 hPa, overlaid with the horizontal winds for the two extreme years, 1994 and 2002, are shown in Figure 4.7. High ozone mixing ratios appear in two regions in Asia: one in the east over eastern China and the other in the west over South Asia. As shown in the wind field, the ozone in the eastern part is transported eastward to the Pacific ocean and then to North America, whereas the ozone in the western part, i.e., over South Asia, is transported westward to the Middle East along the tropical easterly jet (between 20°E-90°E and 15°N-25°N). The location of high ozone abundances in South Asia corresponds to the location of high ozone production shown in Figure 3.9a (see Figure 4.23, which is discussed in Section 4.6.1). Park et al. [2004] also showed a lightning-induced upper tropospheric NOx maximum over the Asian monsoon region from a MOZART simulation.

The vertical structure of the Asian ozone source (averaged 1987-2006) over Asia (along 80°E) and over the Middle East (along 40°E) is shown in Figure 4.8. The maximum ozone mixing ratios are located in the middle and upper troposphere in the Asian monsoon region in Figure 4.8a, associated with NOx production from lighting in the upward monsoon flow south of the Tibetan Plateau. This ozone is circulated around the SAH and is also transported to the west in the middle and upper troposphere and descends over the Middle East. Over the Middle East (along 40°E in Figure 4.8b), Asian ozone is confined to the middle and upper troposphere. The ozone distribution in Figure 4.8a resembles some features in the CH4 distribution in the middle and upper troposphere simulated with MOZART by Park et al. [2004]. Similarly, Xiong et al. [2009] reported an enhanced methane plume over the Asian monsoon region following a
Figure 4.6. Anomaly of Asian ozone (in % on the left y-axis and in ppbv on the right y-axis) in July from 1987 to 2006, averaged over the Middle East at 400 hPa using the 2005 chemistry input.
Figure 4.7. Asian ozone (in ppbv) overlaid with horizontal winds at 400 hPa in July for (a) 1994 and (b) 2002.
Figure 4.8. The climatology of Asian ozone (in ppbv) in July along latitude-altitude sections at 80°E (a) and 40°E (b). Both are overlaid with the climatology of winds. The vertical velocity is enlarged by 100 times for illustration purposes. White areas denote topography.
convective pathway. The deep convection mechanism during the Asian monsoon season was also described by Randel and Park [2006]. The westward transport pathway for Asian ozone is similar to that for CO proposed by Lawrence et al. [2003]. The difference is that the CO source is from the surface, whereas ozone is produced in the middle and upper troposphere (see Figures 3.9 and 4.23 later), although the ozone production from lightning seems to be overestimated in the model according to our analysis in Sections 3.4 and 3.5.

A striking difference between the ozone distributions in 1994 and 2002 shown in Figure 4.7 is the absence of significant amounts of Asian ozone over the Arabian Peninsula in 2002. A comparison of the vertical structure of the ozone distribution and the wind fields between the two years is shown in Figure 4.9. The easterly jet in the subtropics is clearly stronger in 1994 than in 2002, in particular between 400-100 hPa and 80°E-30°E. The mean wind speed averaged over an area of 15°N-30°N and 50°E-90°E at 300 hPa is -6.2 m s⁻¹ and -2.8 m s⁻¹ for 1994 and 2002, respectively. As shown in Figure 4.9, the peak in Asian ozone is further east in 2002 than in 1994, with much less ozone transported to the west, especially in the middle troposphere over the Middle East. The 20-year mean winds and the July wind anomalies at 300 hPa in 1994 and 2002 are shown in Figure 4.10. On average, easterlies prevail south of 20°N in July while westerlies dominate north of 30°N (Figure 4.10a). Between 20°N-35°N, extending from South Asia to the Middle East (80°E to 40°E), there are negative anomalies in zonal winds in 1994 (Figure 4.10b), indicating stronger than normal easterlies, whereas positive anomalies were present in the same region in 2002 (Figure 4.10c). Consequently, there is more Asian ozone transported to the Middle Eastern middle troposphere in 1994 than in 2002.

The covariance between the zonal winds and Asian ozone are shown in Figure 4.11. The Asian ozone anomalies in the Middle East are mostly correlated to zonal winds in the subtropical upper troposphere between 30°E-80°E (Figure 4.11a); the stronger the easterlies (more negative), the greater the transport of Asian ozone to the Middle East. Furthermore, the wind anomalies in Figure 4.11b show a coherent structure across Eurasia, suggesting a teleconnection associated with the SAH. We find that the tropical easterly jet is strongly correlated with geopotential heights at 150 hPa over central Asia, near 30°N-40°N and 60°E-80°E (Figure 4.11b). Higher pressures in this region are linked to stronger (more negative) easterlies in the subtropics. Hoskins and Wang [2006] described the close link between the SAH and the easterly jet. They
Figure 4.9. Longitude-altitude cross section of Asian ozone (in ppbv) along 26°N in July for (a) 1994 and (b) 2002. Both are overlaid with winds. The vertical velocity is enlarged by 100 times for illustration purposes. White areas denote topography. The altitude 400 hPa is marked with a line.
Figure 4.10. For July at 300 hPa: (a) wind climatology, (b) anomalies in 1994, and (c) anomalies in 2002. Unit: m s$^{-1}$. 
Figure 4.11. (a) Covariance (in m s\(^{-1}\)) between easterly winds and the Asian ozone anomaly in a longitude-altitude cross section along 26°N. Brown areas denote topography. (b) Covariance (in m) between the geopotential height at 150 hPa and the easterly winds averaged over a region of 20°N-30°N and 30°E-80°E from 300 to 100 hPa (the boxed area in Figure 4.11a). Filled contours are statistically significant at the 90% level using the Student’s t-test. Data source for the geopotential heights: NCEP/NCAR reanalysis [Kalnay et al., 1996].
Figure 4.11 (c) Covariance (in m) between the Asian ozone anomaly and the geopotential height at 150 hPa. Filled contours are statistically significant at the 90% level using the Student’s t-test. Data source for the geopotential heights: NCEP/NCAR reanalysis [Kalnay et al., 1996].
pointed out that the Tibetan Plateau is a major factor determining the character of both the SAH and the easterly jet.

The Asian ozone anomalies are positively correlated with the geopotential height at 150 hPa (Figure 4.11c) and the largest covariance is located over the same region in central Asia (30°N-40°N, 60°E-80°E). Examination of the geopotential height anomalies for 1994 and 2002, shown in Figure 4.12, indicates positive height anomalies (about 80 m) in central Asia in 1994 (Figure 4.12a), whereas there were negative anomalies (about 100 m) in the same region in 2002 (Figure 4.12b). Thus, our analysis suggests that variation in the strength and structure of the SAH are associated with the interannual variability of the Asian outflow of ozone to the Middle East. The core with covariance at the 90% significance level shown in Figure 4.11c coincides with a region of high variability in geopotential heights reported by Ding and Wang [2005], which, as discussed in Section 4.5.3, they suggested is part of a circumglobal teleconnection pattern linked to the Asian monsoon.

4.5.1.1 Connection Between the Asian Ozone Anomalies and the Asian Summer Monsoon

As discussed in Section 4.3, the thermal contrast between land and ocean in summer is intensified in Asia by the Tibetan Plateau due to its size, height, and longitudinal location [Ye and Wu, 1998]. The thermal contrast eventually triggers large circulations entraining rising air from the surface. Webster et al. [1998] suggested that there are three circulations associated with the monsoon: a transverse monsoon circulation to the west, a lateral monsoon circulation to the south, and the Walker circulation to the east. The ascending regions of these circulations are all collocated over South Asia [Webster et al., 1998]. Ye and Wu [1998] found that the lateral circulation extends between 55°E and 140°E according to the NCEP reanalysis data. They also suggested an additional circulation to the north between 40°N and 47°N. Ye and Wu [1998] found that the outflow of ascending air over the Plateau is separated into two branches: an eastern branch that flows eastwards and descends east of 170°E, and a western branch that flows westwards and then descends over Afghanistan, Iran and Saudi Arabia. This western branch is similar to what we have observed in this study. The transverse circulation to the west can be seen in Figure 4.9 with ascending flows around 80°E-100°E, and descending flows around 20°E-40°E.
Figure 4.12. (a) Anomaly of the geopotential height (in m) in July at 150 hPa for 1994, and (b) for 2002. Data source: NCEP/NCAR reanalysis [Kalnay et al., 1996].
The three-circulation proposal by Webster et al. [1998] suggests a close positive correlation between the westward transport of the Asian airmass and the Asian summer monsoon. When deep convection is intensified, the transverse circulation, which is related to the transport of the Asian outflow to the Middle East, is intensified. The lateral circulation, which is related to the Indian summer monsoon, is likely to be strengthened as well.

We use two independent monsoon indices to further explore the correlation between the Asian monsoon and the Asian ozone anomalies in Figure 4.6. One index is the All-India Monsoon Rainfall (AIMR) anomalies over India for JJAS (June-July-August-September), based on the measurements from 306 weather stations [Parthasarathy et al., 1987, 1995]. The rainfall data are available from the Indian Institute of Tropical Meteorology (www.tropmet.res.in). The second index is the Webster-Yang monsoon index, which is circulation-based and is defined according to the strength of the vertical shear in the zonal wind between 850 and 200 hPa averaged over the region 40°E-110°E and 0°N-20°N [Webster and Yang, 1992]. The normalized Webster-Yang monsoon index is available from the Asia-Pacific Data-Research Center (APDRC) of the International Pacific Research Center (IPRC) (iprc.soest.hawaii.edu/users/ykaji/monsoon/seasonal-monidx.html). According to both indices, 1994 is a strong monsoon year while 2002 is a weak monsoon year. Figure 4.13 shows that the Asian ozone anomaly significantly correlates with the AIMR anomalies (with a correlation coefficient $r = 0.67$, $p<0.01$) and the Webster-Yang monsoon index (with a correlation coefficient $r = 0.66$, $p<0.01$). This suggests that the circulation in favor of the Asian monsoon may also enhance the transport of Asian outflow of ozone to the Middle East. Accordingly, these summer monsoon indices can capture ~45% of the interannual variation in the transport of Asian ozone to the Middle East.

The two extreme years for transport of ozone from Asia were also associated with extreme anomalies in rainfall over India. In 1994 there was significantly greater rainfall than average, whereas in 2002 there was a drought [Chaudhari et al., 2008]. According to Chaudhari et al. [2008], July 2002 had the lowest rainfall recorded in the previous 130 years. Chaudhari et al. [2008] found that 1994 was associated with a positive outgoing longwave radiation (OLR) anomaly over South Asia, in contrast to a negative OLR anomaly in 2002, suggesting stronger than normal convection in 1994 and weaker than normal convection in 2002.
Figure 4.13. Correlation between the Asian ozone anomaly in July at 400 hPa and (a) the All Indian Monsoon Rainfall (AIMR) anomaly and (b) Webster-Yang monsoon index (see the text for the definitions and data sources). The correlation coefficient and the p-value in the Student’s t-test are indicated by $r$ and $p$, respectively. The data points for 1994 and 2002 are indicated.
Previous studies have found correlations between ENSO and long-range transport of ozone in the Northern Hemisphere [Liu et al. 2003; Liu J. et al., 2005; Koumoutsaris et al., 2008]. In this study, no close correlation could be found between ENSO (using the Southern oscillation index (SOI)) and the westward transport of Asian ozone to the Middle East in summer. This suggests that the ENSO-transport relationship may be weak for this pathway in summer. Liu J. et al. [2005] also found a weaker relationship between ENSO and the outflow of Asian pollution to North America in summer compared to other seasons.

4.5.2 Interannual Variations in Locally Produced Ozone in the Middle East

The GEOS-Chem 20-year averaged distribution of ozone produced within the Middle East in July is shown in Figure 4.14. The distribution at 400 hPa (Figure 4.14a) is similar to that in July 2005 (Figure 3.12a), with the ozone localized over the Middle East, reflecting the confinement by the anticyclone in the mid-troposphere. There is evidence of transport of ozone out to the northeast of the anticyclone by the westerlies and out to the southwest by the easterlies. Vertical cross sections in Figures 4.14b and 4.14c show a strong source of ozone in the boundary layer over the Hijaz Mountain, which is located in 25°N in Figure 4.14b and 40°E in Figure 4.14c indicated by the white areas. An upward ozone flux from the surface can be observed on the south side of the Hijaz Mountain (Figure 4.14b) and its east side (Figure 4.14c, also see Figures 3.13b and 3.14b). This is the transport of boundary layer ozone to the middle troposphere, as discussed in Chapter 3.

The anomalies in locally produced ozone are shown in Figure 4.15. We define locally produced ozone as ozone produced within the region between 15°N-35°N and 30°E-60°E. Compared with Asian ozone (Figure 4.6), locally produced ozone varies less year-to-year in the mid-troposphere in summer (Figure 4.15, also see the standard deviations in Table 4.1), with a range of variability within ±3 ppbv or ±15% from the mean. Unlike Asian ozone, the local ozone anomalies show no extrema in 1994 and 2002.

As shown in Figure 4.14a, and discussed in Chapter 3, the confinement of locally produced ozone in the mid-troposphere of the Middle East is a result of the presence of the anticyclone over the region. In Figure 4.16 we compare the mean anomalies of the geopotential
Figure 4.14. The locally produced ozone (in ppbv) as a 20-year mean in July (a) at 400 hPa, (b) along 40°E longitude, and (c) along 26°N latitude. Also shown are the 20-year mean winds. The vertical velocity is enlarged by 100 times for illustration purposes in (b) and (c). White areas denote topography.
Figure 4.15. Anomaly of locally produced ozone (in % on the left y-axis and in ppbv on the right y-axis) in July from 1987 to 2006, averaged over the Middle East at 400 hPa, using the 2005 chemistry input.
Figure 4.16. Anomaly of the geopotential height (in m) in July at 400 hPa averaged over the years with (a) positive ozone anomalies and (b) negative ozone anomalies shown in Figure 4.15. Data source: NCEP/NCAR reanalysis [Kalnay et al., 1996].
heights at 400 hPa in July for all years with positive local ozone anomalies (Figure 4.16a) to the mean geopotential height anomalies for years with negative local ozone anomalies (Figure 4.16b). The mean anomalies of the geopotential heights over the Arabian Peninsula are around +5 m and -5 m, respectively, for all years with positive and negative ozone anomalies in Figure 4.15, indicating that increased (reduced) abundances of locally produced ozone in the Middle East are associated with positive (negative) anomalies in the geopotential heights over the Arabian Peninsula. This is further supported by the covariance between locally produced ozone anomalies and the geopotential heights over the 20-year period at 400 hPa (Figure 4.17). The areas with largest covariance (~10 m) are located over the northeast of the Arabian Peninsula, within the centre of the anticyclone (shown in Figure 4.14a), where the correlation coefficient between the two variables reaches ~0.8.

4.5.3 Other Regional Contributions to the Interannual Variations in Ozone in the Middle East

Although locally produced ozone and ozone transported from Asia predominantly contribute to the total ozone mixing ratios over the Middle East in summer, we find that the interannual variations in the ozone mixing ratios in the Middle East are only partially explained by the variations of these two large sources. As shown in Figure 4.18, the correlation coefficient is 0.54 between the ozone anomalies and the sum of Asian and locally produced ozone anomalies, suggesting trade-offs among the contributions from the different regions to the ozone abundance. The variance for the total ozone mixing ratio over the 20-year in July is 5.3 ppbv², while its covariance with Asian ozone is 3.1 ppbv². The covariance between the total ozone mixing ratio and locally produced ozone is 1.6 ppbv², while it is 1.0 ppbv² with North African ozone. The covariance of the total ozone mixing ratio with the ozone ratio of Europe, North America, and ROW is negative, ranging from -0.2 to -0.5 ppbv².

Changes in transport of Asian ozone to the Middle East is mostly compensated by transport of ozone from North America and the ROW, as reflected in the striking anti-correlation between Asian ozone and ozone from North America (with $r = -0.75$) and ozone from the ROW (with $r = -0.87$) (Figure 4.19). Because of these trade-offs, the ozone mixing ratio over the Middle East varies less year-to-year than the Asian and local ozone sources (also see Table 4.1).
Figure 4.17. Covariance (in m) between the locally produced ozone anomalies (shown in Figure 4.15) and the geopotential heights at 400 hPa and. Filled contours are statistically significant at the 90% level using the Student’s t-test. Data source for the geopotential heights: NCEP/NCAR reanalysis [Kalnay et al., 1996].
Figure 4.18. Correlation between the total ozone anomaly and the sum of Asian and locally produced ozone anomalies in the Middle East in July at 400 hPa. The correlation coefficient and the p-value in the Student’s t-test are indicated by $r$ and $p$, respectively.
Figure 4.19. Correlations (a) between Asian and the North American ozone anomalies and (b) between Asian and ROW ozone anomalies in the Middle East in July at 400 hPa. The correlation coefficient and the p-value in the Student’s t-test are indicated by $r$ and $p$, respectively. The data points for 1994 and 2002 are indicated.
As shown in Section 3.5.2, ozone transported from North America to the Middle East originates mainly in the North American boundary layer. The major transport pathway for this ozone source extends from eastern North America to the western North Atlantic Ocean [Cooper and Parrish, 2004]. Along this pathway, surface ozone, together with other pollutants such as CO [Liu J. et al., 2006], is transported along warm conveyor belts (WCBs) to the upper troposphere. The WCB is the warm airstream that is ahead of the surface cold front on the eastern side of mid-latitude cyclones. It typically extends as far as thousands of kilometres from the southwest to the northeast of the cyclone and lofts boundary layer air into the free troposphere [Cooper et al., 2002; Cooper and Parrish, 2004]. After the ozone in the WCB reaches the western North Atlantic, it is then transported along the subtropical westerly jet and descends into the Middle East, near the Mediterranean. This transport pathway is illustrated in Figures 3.12c and 3.13a (also see the strong descent over the Mediterranean in Figure 3.2).

The North American ozone anomalies at 400 hPa in July for 1994 and 2002 are shown in Figure 4.20, overlaid with the horizontal winds. Over the Middle East, near 35°N there are negative anomalies of about 4 ppbv in 1994, whereas there are positive anomalies of about 4 ppbv in 2002. The North American ozone anomalies averaged over the entire Middle East region are -27.9 % and +21.6% of the 20-year mean in 1994 and 2002, respectively. When the North American ozone contribution is at a minimum (maximum), in 1994 (2002), the Asian ozone is at a maximum (minimum). The subtropical westerly jet, north of the Middle East, is shifted further north in 1994 (between 40°N-50°N) than in 2002 (when it is between 30°N-40°N). When the westerly jet shifts further south in 2002, the Arabian anticyclone circulates the North American ozone from the eastern flank of the anticyclone to the Middle East, near 30°N and 60°E, and positive ozone anomalies can be observed over this region. In contrast, when the westerly shifts further north in 1994, the jet is more zonally uniform north of the Middle East region. The horizontal wind anomalies in the two years are also noticeable in Figure 4.10 at 300 hPa. This difference is further illustrated in Figure 4.21 in a latitude-altitude cross section at 40°E (across the Middle East). The subtropical westerly jet is stronger and located further north in 1994 than in 2002.

The ROW region in the Northern Hemisphere includes the Northern Hemispheric Pacific and Atlantic Oceans (see Figure 3.10b). It is ozone produced in these regions (downwind of
Figure 4.20. North American ozone anomaly (in ppbv) in July at 400 hPa in (a) 1994 and (b) 2002. Both are overlaid with horizontal winds. The latitude of 35°N is marked with a line.
Figure 4.21. Zonal winds (in m s\(^{-1}\)) in a latitude-altitude cross section in July at 40°E in (a) 1994 and (b) 2002. The latitude of 35°N is marked with a line. Brown areas denote topography.
North America and Asia) that is transported to the Middle East though the subtropical westerlies. Little ozone in the Southern Hemisphere of the ROW is transported to the Northern Hemisphere in boreal summer (as South American and Australian ozone abundances are small in the Middle East in boreal summer as shown in Table 4.1). Similar to the case for North America, as shown in Figure 4.20, when the jet shifts to the north in 1994, less ozone from the ROW is transported through the westerly jet to the Middle East (not shown). Conversely, when the jet shifts to the south in 2002, more ozone from the ROW is transported into the Middle East (not shown). This is similar to the seasonal trade-off between transport of ozone into the region (shown in Figure 4.5); ozone from Asia and the Middle East are the main source of ozone in the region in summer, whereas ozone from outside the Middle East and Asia provides the dominant contribution in the Middle East in winter, when the westerly jet is more zonally uniform and is located across the Middle East.

The subtropical westerly jet over Asia exhibits seasonal variations in strength and latitudinal position. The core of the jet over Asia in summer is generally located near 200 hPa with wind speeds around 20-40 m s\(^{-1}\) (see Figure 4.21), compared with 50-70 m s\(^{-1}\) in winter [Zhang et al., 2006; Schiemann et al., 2009]. From winter to summer, the jet transits from south to north [Zhang et al., 2006; Schiemann et al., 2009]. Schiemann et al. [2009] found that during the northward transition, the jet intensity and its latitudinal location vary greatly from year to year.

Our analysis suggests a strong connection between the trade-off in transport from the different source regions and the meridional location and strength of the subtropical westerly jet. The Asian ozone anomalies are negatively correlated with zonal winds at 200 hPa over a region of 20°N-40°N and 30°E-90°E from South Asia to the Middle East at the 90% significance level (Figure 4.22a). This is consistent with the analysis in Section 4.5.1 (Figure 4.11), i.e., the stronger the easterlies in these latitudes, the more Asian ozone is transported to the Middle East. In contrast, over almost the same latitudes, positive correlations of 0.5-0.8 are found between zonal winds and the North American and ROW ozone anomalies (Figures 4.22b and 4.22c), although the details are slightly different. The American and ROW ozone anomalies are more sensitive to zonal wind over the Middle East (30°E-60°E), while the Asian ozone anomalies are
Figure 4.22. Correlation between zonal winds at 200 hPa and averaged ozone anomalies over the Middle East from (a) Asia, (b) North America, and (c) ROW. Filled areas are statistically significant at the 90% level using the Student’s t-test. All values are for July.
more sensitive to zonal wind from Asia to the Middle East (60°E-80°E). A more southward shift of the westerly jet brings about stronger westerly flow over the Middle East (also see Figure 4.10c) and favors the transport of ozone from North America and ROW to the region. The transport of North American ozone into the Middle East is through strong descent over North Africa and the eastern Mediterranean. When the westerly jet is displaced north, the transport of this ozone down into the Middle East is restricted.

Ding and Wang [2005] examined the connection between the westerly jet and the Asian monsoon. They identified six centers of variability in geopotential heights in the upper troposphere at 200 hPa across the Northern Hemisphere, and suggested that the six centers compose a circumglobal teleconnection (CGT) pattern in the summertime mid-latitude circulation of the Northern Hemisphere linked to the Indian summer monsoon. In the first scenario, the monsoon induces a positive geopotential anomaly to the northwest, over central Asia, which excites a teleconnection pattern downstream, across East Asia, the North Pacific, North America, the North Atlantic, and Europe. In the second scenario, instability in the westerly jet in the North Atlantic (where there is a jet exit) generates an anomalous high over western Europe, which excites a teleconnection over central Asia and influences the monsoon. They indicated the need for further research to better understand the interaction between the two mechanisms.

The relationship between the CGT and the westerly jet can be seen in Figures 4.12, 4.20 and 4.21. When the CGT center of action in central Asian is in a positive phase in 1994 (Figure 4.12a), the westerly jet is displaced further north at ~45°N (40°E-80°E) (Figures 4.20a and 4.21a), whereas in 2002 when this centre is in a negative phase (Figure 4.12b), the westerly jet stays in a more southern latitude at ~35°N (Figures 4.20b and 4.21b). In 2002, there are also positive pressure anomalies over Western Europe and East Asia (Figure 4.12a). These are the other centers of variability in Eurasia identified by Ding and Wang [2005]. As shown in Figure 4.7a, the pressure anomalies in Europe in 1994 are associated with strong anticyclonic flow and the equatorward component of the flow over Eastern Europe contributes to the stronger westerly flow in central Asia. In 2002, the anticyclonic flow over Europe is weaker (see Figure 4.7b) and it extends into Siberia, which contributes to a weaker westerly jet that is shifted further south over the Middle East.
4.6 Contribution of Changes in the Ozone Chemistry to the Interannual Variations in Ozone

All the analyses in this chapter so far are based on the tagged ozone simulation using 2005 ozone chemical rates. In this section, to assess the potential impact of the 2005 chemical rates on our analyses, we compare these analyses with ozone simulations using 1990 and 1995 chemical fields. We also examine the impact of linearizing the ozone chemistry in the tagged ozone simulation.

4.6.1 Sensitivity to the Specified Tagged Ozone Photochemical Production and Loss Rates

The distribution of ozone photochemical production rates in the mid-troposphere (~7 km) is shown in Figure 4.23a, which is an average of the GEOS-Chem simulation from 1987 to 2006 for July. In summer, ozone production is high across the subtropics and in the mid-latitudes over North America and Asia. The highest ozone production rates are over South Asia (around 80°E) and are due to NOx emissions from lightning associated with the Asian monsoon (discussed in Section 3.5). The 20-year averaged ozone production rate over the Middle East (15°N-35°N, 30°E-60°E) at ~7 km in July is $4.2 \times 10^{-20}$ kg cm$^{-3}$ s$^{-1}$, with a standard deviation of $3.6 \times 10^{-21}$ kg cm$^{-3}$ s$^{-1}$, while the mean and standard deviation are large for the South Asia monsoon region (15°N-35°N, 60°E-100°E), being $6.4 \times 10^{-20}$ kg cm$^{-3}$ s$^{-1}$ and $5.0 \times 10^{-21}$ kg cm$^{-3}$ s$^{-1}$, respectively. For comparison, the distribution of the net ozone production rates for July 2005 is shown in Figure 4.23b and the differences between the 20-year mean and 2005 are shown in Figure 4.23c. Regions with large differences appear over central Asia, eastern China, eastern USA, and biomass burning regions in Africa and South America. The differences are one order of magnitude smaller than the net ozone production rates. The differences between 2005 and 1990 and between 2005 and 1995 are also one order of magnitude smaller than the net ozone production rates (not shown).

Asian ozone anomalies produced using the 1990, 1995, and 2005 chemistry fields are compared in Figure 4.24a. Overall, the three time series show similar interannual variations in Asian ozone over the Middle East, indicating that the differences in the chemical fields have a small impact on our analysis. Over the South Asian monsoon region (15°N-35°N, 60°E-100°E), the ozone production rates in July 1990, 1995, and 2005 are 6.5, 6.8, and $6.3 \times 10^{-20}$ kg cm$^{-3}$ s$^{-1}$,
Figure 4.23. GEOS-Chem simulated net ozone production rates (in kg cm\(^{-3}\) s\(^{-1}\)) at ~7 km in July for (a) the 20-year mean (1987-2006), (b) 2005, and (c) the difference between 2005 and the 20-year mean.
respectively, at ~7 km. These differences produce variations in the Asian ozone anomalies that are smaller than the range of the year-to-year variations. For example, the Asian ozone anomalies in 1994 are 26.7% over the Middle East using the 2005 chemistry fields, while they are 29.2% and 29.5% using the 1990 and 1995 chemistry fields, respectively. In 2002, the Asian ozone anomalies are -26.6% with the 2005 chemistry input, compared with -27.6% and -27.0% using the 1990 and 1995 chemistry inputs, respectively. Li *et al.* [2001] found that there remained a Middle East ozone maximum even when both lightning and Asian anthropogenic sources are suppressed in their model simulation, although the maximum ozone values were reduced by 10-20 ppbv. Our analysis is consistent with Li *et al.* [2001] on the important role that meteorology plays in maintaining elevated ozone over the Middle East.

As shown in Figure 4.24b, the year-to-year variations in the local ozone source are also comparable in the three time series, suggesting that our analysis using the 2005 chemical fields provides a representative description of the impact of the variability in ozone. The 20-year averaged ozone production rate over the Middle East at ~7 km in July is $4.2 \times 10^{-20}$ kg cm$^{-3}$ s$^{-1}$, with a standard deviation of $3.6 \times 10^{-21}$ kg cm$^{-3}$ s$^{-1}$. The mean ozone production rate is $4.3 \times 10^{-20}$ kg cm$^{-3}$ s$^{-1}$ for 2005, comparing with $4.4 \times 10^{-20}$ kg cm$^{-3}$ s$^{-1}$ for 1990 and $4.8 \times 10^{-20}$ kg cm$^{-3}$ s$^{-1}$ for 1995. Although variations exist in a given year among the three time series, the differences are smaller than the interannual variation. For example, between the ozone anomalies using 2005 and 1990 chemical inputs, the maximum positive difference is 1.2% in 2001 and the maximum negative difference is -1.9% in 1987.

4.6.2 Impact of the Non-linearity in the Ozone Chemistry on the Ozone Variations

In the tagged ozone simulation, the ozone production rates are fixed and the loss rates are assumed to depend linearly on the ozone abundance. This facilitates tagging of the ozone contribution from different source regions. However, the ozone chemistry is inherently non-linear. To assess the impact of neglecting the non-linearity in the chemistry in our analyses, we conducted a 20-year full chemistry simulation for comparison with the tagged ozone runs. This simulation also accounts for year-to-year changes in NO$_x$ emissions due to variability in the convection. Figure 4.25a shows the correlation in the ozone anomalies over the Middle East between the simulations from the full chemistry run and the tagged ozone run (using the 2005
Figure 4.25. (a) Comparison of ozone anomalies in July at 400 hPa between a full chemistry simulation and a tagged ozone simulation using 2005 chemistry input. (b) The same comparison using 1990, 1995, and 2005 chemistry inputs. All values are means over the Middle East. The correlation coefficient and the p-value in the Student’s t-test are indicated by $r$ and $p$, respectively.
chemistry fields). Significant correlation is found between the two sets of anomalies ($r = 0.82$, $p < 0.01$). The correlation is further tested using ozone anomalies based on the 1990 and 1995 chemistry fields (Figure 4.25b). The correlation is $r = 0.82$ ($p < 0.01$) for taking all three time series together; $r = 0.79$ ($p < 0.01$) for the time series with 1990 chemistry input; and $r = 0.83$ ($p < 0.01$) for the time series with 1995 chemistry input. Overall, this suggests that the meteorology can explain over 60% of the interannual variability in the ozone mixing ratios in the Middle Eastern mid-troposphere in summer. Note that the anthropogenic emissions are unchanged from year to year in this version of the GEOS-Chem simulation. Our assessment also has not accounted for the interaction between the meteorology and chemistry since the meteorological fields are imposed and, therefore, changes in atmospheric composition do not feedback on the dynamics. Nevertheless, our analyses show the important role that meteorology plays in driving the interannual variations in tropospheric ozone. This is similar to Voulgarakis et al. [2009], who found that changes in meteorology had a stronger impact on the global ozone burden than changes in emissions in their CTM study. They found that meteorology contributed almost 80% of the interannual variations in the global tropospheric ozone burden and that the relative contribution of meteorology to the interannual variations in the ozone burden from Europe and Indonesia was 86% and 56%, respectively [Voulgarakis et al. 2009].

4.7 Conclusions

Although the processes controlling tropospheric ozone have been studied extensively, our understanding of the interannual variations in tropospheric ozone is still limited. Earlier studies suggested that changes in meteorology and emissions are the key factors that contribute to interannual variability in tropospheric ozone [Ziemke and Chandra, 1999; Thompson et al., 2001; Zhou et al., 2003; Stohl et al., 2003; Duncan and Bey, 2004; Wild and Palmer, 2008]. In this study, the interannual variations in tropospheric ozone in the Middle East are investigated for the first time through simulations from the GEOS-Chem model, driven by GEOS-4 meteorological data from 1987 to 2006. Our objective is to assess the role that changes in meteorology play in driving interannual variations in tropospheric ozone in the Middle East, with a focus on the summertime ozone distribution in the Middle Eastern mid-troposphere.

The main conclusions of this chapter are as follows.
The GEOS-Chem simulated ozone distribution averaged over 20 years in the Middle East reveals many features similar to those in 2005. The summertime ozone enhancement is still apparent as a 20-year mean over the Middle East in the mid-troposphere (~70-80 ppbv). The interannual variation of the ozone abundance, averaged over the Middle Eastern mid-troposphere, is about ±6 ppbv (or ±7%) about the mean. The climatology of Asian ozone and locally produced ozone remain predominant components, contributing ~30% and ~25%, respectively, to the total ozone mixing ratio.

Asian ozone in the Middle Eastern middle troposphere fluctuates up to ±7 ppbv (or ±30%) about the mean during the 20 years, with a maximum contribution in 1994 and a minimum in 2002. For these two extreme years, there are stronger easterlies in 1994 than in 2002. These easterlies are linked to the strength of the SAH in the upper troposphere: a stronger SAH is found in 1994 versus a weaker SAH in 2002. Our analysis suggests that the strength of the SAH is related to the interannual variability of the Asian outflow of ozone to the Middle East through its influence on the tropical easterlies. Our results suggest that the Asian ozone source is closely correlated with the Asian monsoon.

Locally produced ozone, as simulated by GEOS-Chem, varies by ±3 ppbv (or ±15%) from the mean over the 20-year period. Our analysis shows that the anticyclone in the middle troposphere traps locally produced ozone at these altitudes. Statistically, a significant correlation is found between the anomalies of locally produced ozone and the variation of intensity of the anticyclone in the middle troposphere during the 20 years.

Although being predominant components of the total ozone abundance, the Asian and local ozone sources can only partially explain the interannual variability of the total mid-tropospheric ozone abundance in the Middle East in summer. This is found to be caused by trade-offs in ozone transport to the Middle East among regions. The anti-correlation coefficients are found to be largest between Asian and North American ozone anomalies and between Asian and ROW ozone anomalies. The underlying mechanism for the variation in these trade-offs is found to be related to the meridional shift of the subtropical westerly jet: when the westerlies move further north (south), transport of Asian ozone to the Middle East increases (decreases), while at the same time, transport from North America and ROW decreases (increases).
5 Conclusions

5.1 Summary of Thesis

In this research, the focus is on understanding the processes controlling the summertime buildup of ozone over the Middle East. Recent observations by the TES satellite instrument of the vertical structure of ozone over the Middle East reveal enhanced ozone abundances in the middle troposphere in summer, similar to previous modeling predictions [Li et al., 2001].

This thesis can be summarized in two parts. First, the GEOS-Chem model was used to interpret observations of tropospheric ozone from the TES instrument in 2005. Second, the interannual variations in ozone in the Middle East were characterized and possible mechanisms for these variations were explored with a 20-year GEOS-Chem simulation.

In the first part (in Chapters 2 & 3), the focus was on elevated ozone observed by TES in the middle troposphere (500-300 hPa) across the Middle East and North Africa in summer 2005. The impact on the TES ozone retrievals of the a priori ozone profile, the vertical sensitivity of TES, and the spatial coverage of the TES data were examined. It was demonstrated that the enhanced ozone observed by TES is not biased by the a priori profile or by the sampling density of the observations in the Middle East. In a parallel study co-authored with the TES team, Worden et al. [2009], the elevated ozone was shown to be present in summer from 2005 through 2007, indicating that the feature is robust.

The TES ozone observations were compared with the GEOS-Chem model after taking into account the a priori profile and averaging kernels of TES. The modeled ozone buildup is comparable to that observed by TES (~90 ppbv in TES and ~80 ppbv in GEOS-Chem) and has the same seasonality as the observations. Horizontally, the modeled ozone enhancement is more pronounced and centralized over Saudi Arabia, reflecting the fact that the model underestimates ozone abundances across the extratropics of the Northern Hemisphere compared to the observations. Parrington et al. [2008] attributed this underestimate of mid-latitude ozone in the model to an underestimate of mid-latitude NOx emissions from lightning in this version of the model.
The mechanism responsible for this ozone buildup was examined and found to be associated with the unique conditions in the meteorology, chemistry, and topography over the Middle East and surrounding areas in summertime. In the lower troposphere, the low pressure system over the Indian subcontinent promotes deep convection that produces ozone due to NOx emissions from lightning. The SAH in the upper troposphere induces the tropical easterly jet, which, in turn, plays an important role in transporting ozone westward from the Asian monsoon region. In the middle troposphere, the Arabian and Saharan anticyclones, centered over the Zagros and Atlas Mountains, respectively, isolate the middle troposphere over northeastern Africa and the Middle East, facilitating the buildup of ozone. Seasonally, GEOS-Chem shows that ozone buildup is linked to the evolution of the Arabian and Saharan anticyclones in the middle troposphere. In spring, the air flow is primarily westerly in the middle troposphere, with high ozone across the mid-latitudes. The anticyclones are gradually established toward summer when they are strongest and thus high ozone concentrations extend from the Middle East, across North Africa. In fall, ozone concentrations across the region decrease dramatically as the anticyclones weaken and the region is ventilated more effectively.

A tagged ozone simulation using the GEOS-Chem model was conducted to isolate the influences of long-range transport and local chemical production on the ozone distribution in the Middle East. Long-range transport from Asia and local chemical production are the main sources responsible for the formation of the ozone enhancement, each contributing 30-35% to the total ozone. Over North Africa, local production is dominant (at about 20%), with transport from Asia, North America, and equatorial Africa each contributing about 10–15% to the total ozone concentration. Distinct spatial patterns of ozone abundance from different origins signify their unique transport pathways. Particularly, local production in the mid-troposphere is confined over Saudi Arabia, suggesting recirculation of air masses within the Arabian anticyclone at these altitudes. The Asian ozone from the upper troposphere is spread around the 20°N-40°N zonal band, with strong descent to the mid-troposphere over the Middle East. The stratospheric ozone contribution is largest in the regions of strong descent. The North American ozone contribution was found mostly from the North American boundary layer and transported across the North Atlantic and Europe to the Middle East. Taking into account the ozone from all sources, the spatial distribution of the ozone flux varies in three dimensions, reflecting the complexity of the system.
TES H₂O and HDO data were examined to assess the model consistency with these independent constraints. Good agreement in H₂O distribution was obtained between the model and TES observations, i.e., low H₂O over the Middle East and North Africa regions versus high H₂O over the Asian monsoon region. This agreement provided further confidence in the model performance. Additionally, high $\delta D$ values were observed over the mountain regions in the Middle East, which signals the transport of boundary layer air into the middle troposphere. This agreed with the tagged ozone analysis that suggested transport from the boundary layer accounted for about 25% of the local contribution to the ozone in the middle troposphere. This upward flux is possibly due to orographic lifting over the Zagros Mountains in Iran and along the Asir and Hijaz mountain ranges in Saudi Arabia.

The processes described above are summarized in Figure 5.1. The schematic shows the relative positions of the Arabian anticyclone and the South Asian High, together with the vertical and horizontal motions, linked to the anticyclones, which drive the summertime buildup of ozone over the Middle East. There is upward transport on the eastern flank of the South Asian High, linked with convection in the monsoon region, whereas there is downward motion on the western flank. In the middle troposphere, the Arabian anticyclone is associated with upward motion over the Persian Gulf region, and westward and downward transport from the Asian monsoon region.

The second part of the thesis (Chapter 4) examined the interannual variations in ozone in the Middle East using a 20-year GEOS-Chem model simulation from 1987 to 2006. The 20-year mean ozone distribution showed that the elevated ozone is a robust feature in summer over the Middle East with a mean ozone mixing ratios of 70-80 ppbv and a year-to-year variation up to ±6 ppbv (or about ±7%) from the mean. During the 20-year period, transport of ozone from Asia and locally produced ozone are the dominant sources driving the summertime buildup of ozone in the Middle East. Averaged over the 20 years, transport of ozone from Asia and locally produced ozone contribute ~30% and ~25%, respectively, to the summertime ozone abundance in the middle troposphere over the Middle East.

The Asian ozone contribution fluctuates by ±7 ppbv (or ±30%) from the mean during the 20 years in the GEOS-Chem simulation, with a maximum in 1994 and a minimum in 2002. Transport of Asian ozone to the Middle East depends on the strength of the SAH in the upper troposphere. It was found that positive pressure anomalies in 1994 in the western part of the
Figure 5.1. Schematic of the major weather systems and processes related to the summertime ozone buildup over the Middle Eastern mid-troposphere. A: the deep convection over the Asian monsoon region. B: the SAH at the upper troposphere and the associated circulation of the ozone which is lifted from the lower troposphere. C: the Arabian anticyclone in the mid-troposphere over the Middle East and the associated trapping of locally produced ozone. D: the subtropical westerly jet north of the SAH. E: westward transport of Asian ozone in the tropical easterlies. F: Downward transport of ozone (e. g., Asian ozone, stratospheric ozone) from the upper troposphere. G: upward transport of ozone from the boundary layer. H: downward flux from the extra-tropics (such as ozone from North America). In the background on the surface, the coast lines are denoted in blue while the Tibet Plateau, the Zagros and Atlas mountain regions are indicated in black (adapted from Park et al. [2009] and Lawrence [2006]).
SAH resulted in enhanced transport of Asian ozone, whereas negative anomalies in 2002 produced significantly less transport of Asian ozone. This research suggests that the contribution of Asian ozone source to the Middle Eastern mid-tropospheric ozone is closely correlated with the Asian monsoon.

For the locally produced ozone, GEOS-Chem simulates a year-to-year variation of ±3 ppbv (or ±15%) from the mean. It was found that this variation is associated with changes in the strength of the anticyclone in the mid-troposphere in the region. Years with positive (negative) ozone anomalies are mostly associated with positive (negative) anomalies in the intensity of the anticyclone.

In spite of their predominant roles, the Asian ozone and the local ozone sources cannot fully explain the interannual variability of the ozone abundances in the Middle Eastern mid-troposphere in summer, implying trade-offs in transport into the region from the different ozone source regions. This is confirmed by, for example, a high anti-correlation between the Asian and North American sources. It was found that the trade-off between transport from these regions is connected to the meridional shifts of the subtropical westerly jet. When the westerlies shift further north (south), the transport of Asian ozone increases (decreases), whereas the transport from North America and other regions in the Northern Hemisphere decreases (increases).

This research has made several advances in the understanding of the ozone distribution in the Middle East: (1) There are few measurements of the vertical structure of ozone across the Middle East region and TES has provided the first detailed picture of this vertical distribution of ozone from space. This thesis is focused on interpreting these new data. (2) Tropospheric ozone is a major contributor to the greenhouse effect so an improved understanding of the impact of pollution on ozone in the region is critical for reliably predicting future changes in climate associated with tropospheric ozone. This thesis provides new information to improve this understanding. (3) Aircraft campaigns have found this region to be at a cross road for pollution. However, prior to this study, there was no detailed understanding of the mechanism for long-range transport of pollution into the region. (4) The proposed new mechanisms can reasonably explain the interannual variations in local ozone production and long-range transport from different sources. (5) Focusing on the ozone budget in the Middle East as a specific receptor
region, the interannual variations in trade-offs in long-range transport among different source regions were able to be identified. (6) Although satellite observations of H₂O and HDO have been used previously for studying atmospheric dynamics, this research is the first to link these dynamical tracers with the transport of tropospheric ozone.

5.2 Implications of This Study

5.2.1 Climate-transport Interaction

This research has demonstrated the important roles that the SAH and the tropical and subtropical jets play in controlling interannual variations in transport of ozone from different regions to the Middle East. Previous GCM studies found that increasing greenhouse gases (GHGs) tends to produce a poleward and upward shift of the westerly jets in the Northern Hemisphere [Yin, 2005] and the Southern Hemisphere [Kushner et al., 2001]. Zhou et al. [2009] show a consensus by four GCMs that the SAH will become larger in summer if the sea surface temperature over the Indian Ocean and the western Pacific becomes warmer in response to global warming. This research suggests that climate-related changes in the subtropical jet and the SAH will have implications for the transport of pollution into the region. Such changes in pollution in the region could feedback on the climate system through changes in the radiative forcing associated with ozone.

5.2.2 Asian Outflow and Interhemispheric Transport

This study and earlier studies, e.g., Stohl et al. [2002], have recognized that Asian pollution in summer experiences the fastest and highest transport. Therefore, outflow of Asian ozone would significantly impact the ozone distribution not only in the Middle East but also in other regions. One of the regions of interest is the Southern Hemisphere.

The transport of pollution from industrialized nations in the Northern Hemisphere to the Southern Hemisphere has been observed from satellites and ground stations [Fishman et al., 1991]. Most studies suggested that this transport takes place in the upper troposphere [Plumb and
Mahlman, 1987; Yamazaki and Chiba, 1993]. Air parcels originating in the lower troposphere in the Northern Hemisphere are lifted by convection, and then transported aloft into the Southern Hemisphere. The transport pathway for Asian ozone can be seen in Figure 4.1a along the Equator between 50°E-140°E. With a preliminary study with GEOS-Chem, it is found that there was more Asian ozone transported to the Southern Hemisphere in 1994 than in 2002, mostly in the upper troposphere and along the downward branch of the Hadley circulation (not shown).

To date, most studies on inter-hemispheric transport of pollution focused on the transport into individual sites [e.g., Halter et al., 1988] or treated the globe in a zonally-averaged way [e.g., Plumb and Mahlman, 1987]. Our study provided a new perspective on how Asian outflow may be transported to the Southern Hemisphere from year to year. Previous studies related the interannual variation of inter-hemispheric transport to ENSO conditions [Prinn et al. 1992; Hartley and Black, 1995; Harris and Oltmans, 1997; Staudt et al., 2001]. This research shows a close correlation between the Asian summer monsoon and the westward outflow of Asian ozone, which may draw attention to the monsoon influence on the inter-hemispheric transport of air pollution from Asia.

Furthermore, the buildup of ozone over the Middle East suggests that this region could act as a reservoir for the transport of ozone to the Southern Hemisphere. Our preliminary study indicates strong interannual variations in the outflow of ozone from this region to South Africa, South American, and Australia, especially in the upper troposphere of these continents (not shown).

5.3 Uncertainties and Limitations

The interannual variations in tropospheric ozone over the Middle East have been studied with an attempt to isolate the meteorological impacts by keeping the chemistry unchanged during the 20-year period. This treatment is similar to Liu J. et al. [2005] in an 11-year simulation with MOZART and to Li et al. [2005b] for a 4-year run with GEOS-Chem. In these simulations, the importance of meteorology in re-distributing ozone in the troposphere was examined. The robustness of our analysis was also examined with three sets of chemical conditions. However, all the simulations were conducted with a long-term averaged emission inventory. Interactions
between meteorology and emissions are complicated; therefore, this study can be extended to assess the impact of changing anthropogenic emissions and dynamics on the ozone features using a coupled chemistry-climate model.

Due to lack of long-term observations of tropospheric ozone, our results from the 20-year simulation cannot be validated. Thus, the 20-year simulation can be viewed as an exploratory study that provides a basis for comparison with long-term simulations from other models and for validation by observations in different platforms as they become available.

5.4 Suggestions for Future Work

Based on this research, the following directions for future work are suggested: multiple model intercomparison and development of meteorological indices.

1. Multiple model intercomparison

Ensemble simulations of global chemistry models provide a valuable means to assess uncertainty in our understanding of atmospheric chemistry and transport at the current time. Because of this, model intercomparisons have been pursued with a number of different objectives, such as interpreting field observations, explaining front-folding events, or predicting future tropospheric ozone change [Roelofs et al., 2003; Brunner et al., 2005; Stevenson et al., 2006]. Through a model intercomparison, more confidence can be gained in our analysis. It would also help characterize uncertainties in our understanding and pinpoint sources of errors associated with how each model handles key chemical and dynamical processes. For example, this study shows that the simulated magnitude of the ozone enhancement over the Middle East depends on the model’s ozone production rate over Asia and the Middle East, as well as the strength of the anticyclones in the middle and upper troposphere. The comparison between TES and GEOS-Chem reveals overestimates of ozone by the model in the upper troposphere over the Middle East. This is likely due to an overestimate of lightning NOx, an ozone precursor, over the Asian monsoon region [Sauvage et al., 2007] or an overestimate of local ozone production in the upper troposphere over the Middle East or both. A multi-model analysis will help identify the potential impacts of errors in lightning NOx and other model errors on the ozone analysis.
2. Development of meteorological indices

In this study, the influence of the variability in the climate system on the transport of Asian ozone was assessed with climate indices, including ENSO, NAO, and monsoon indices. A close relationship was found between the transport and the Webster-Yang monsoon index. In the future, it will be possible to construct meteorological indices that provide useful frameworks for understanding the long-term variability of the processes addressed in this study, similar to what Liang et al. [2005] did for pollution transport from Asia to North America. These indices are simple but can capture most of the interannual variability of ozone transport. Therefore, developing such indices would be useful in relating the variations in transport to large scale circulations and in predicting future variations associated with climate change.

Three mechanisms were proposed in this study to explain the interannual variation of three key processes. First, the intensity of the atmospheric pressure anomalies in the upper troposphere over Asia could be a key factor relating to the interannual variability of the transport of Asian ozone to the Middle East in summer. Second, the year-to-year variation of the trapping of locally produced ozone in the Middle East is connected to the variation of the anticyclone in the region’s mid-troposphere. Thirdly, the trade-offs in transport between regions are associated with the meridional shifts of the subtropical westerly jet. Therefore, pressure-based meteorological indices may be constructed to capture the first two processes and a wind-based index for the third process. In particular, 1994 and 2002 represent two extreme phases of the variations in the pressure and wind fields, with other years varying in between. This study suggests potential value in exploring the possibility of constructing an index using pressure at 150 hPa in the western part of SAH within an area of 60°E-80°E and 25°N-45° N for the first process, and an index using winds at 200 hPa at the Middle East within an area of 30°E-60°E and 20°N-30°N for the third process.
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