ISENTROPIC OZONE TRANSPORT ACROSS THE TROPOPAUSE IN THE LOWER STRATOSPHERE AND UPPER TROPOSPHERE

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Isentropic Ozone Transport across the Tropopause in the Lower Stratosphere and Upper Troposphere
Dedication

To my parents for their love and support!
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LIST OF SYMBOLS AND ABBREVIATIONS

CAS       Contour Advection with Surgery
CTM       Chemical Transport Model
GMAO      Global Modeling and Assimilation Office
GEOS      Goddard Earth Observing System
GSFC      Goddard Space Flight Center
LS        Lower Stratosphere
MOZAIC    Measurement of Ozone and Water Vapor by Airbus In-Service Aircraft
NH        Northern Hemisphere
PV        Potential Vorticity
R_c       Cramér's correlation coefficient
RWB       Rossby Wave Breaking
SAGE      Stratospheric Aerosol and Gas Experiment
SH        Southern Hemisphere
STE       Stratosphere-Troposphere Exchange
S→T       Stratosphere-to-Troposphere
T→S       Troposphere-to-Stratosphere
UT        Upper Troposphere
θ         Potential temperature
δ         Cutoff scale in the surgery routine of contour advection
SUMMARY

This study investigates isentropic ozone exchange between the extratropical lower stratosphere and the subtropical upper troposphere. The quantification method is based on the potential vorticity (PV) mapping of Stratospheric Aerosol and Gas Experiment (SAGE) II ozone measurements and contour advection calculations using the NASA Goddard Space Flight Center Global and Modeling Assimilation Office (GMAO) analysis for 1990 and 1999. The magnitude of the annual isentropic stratosphere-to-troposphere (S→T) ozone flux is calculated to be approximately twice the flux that is directed from the troposphere into the stratosphere (T→S). The net effect is that $-92 \times 10^9$ kg yr$^{-1}$ and $-118 \times 10^9$ kg yr$^{-1}$ of ozone are transferred quasi-horizontally from the extratropical lower stratosphere into the subtropical upper troposphere between the isentropic surfaces of 330 K and 370 K in 1990 and 1999 respectively. The estimated net ozone fluxes in 1999 are approximately 45% higher in the Northern Hemisphere than in the Southern hemisphere. The inter-annual and inter-hemispheric differences of the estimated net annual ozone fluxes are caused by two factors: observed ozone mixing ratios and the quasi-horizontal area in which the isentropic cross-tropopause transport is diagnosed. The estimated monthly ozone fluxes show that the isentropic cross-tropopause ozone transport is stronger in summer/fall than in winter/spring. This is consistent with the fact that observed column ozone between 340 K and 360 K decreases in the extratropics from spring to summer and increases in early summer in the subtropics. The distributions of the estimated monthly ozone fluxes indicate that the
isentropic stratosphere-to-troposphere ozone exchange is associated with Rossby wave breaking (RWB) and occurs preferentially over the eastern Atlantic Ocean and northwest Africa in winter and over the Atlantic and Pacific Oceans in summer. The relationship between isentropic ozone transport and RWB has been analyzed over seven ozonesonde stations on 345 K and 355 K. It is found that ~50% of the identified S→T (T→S) RWB cases are associated with net S→T (T→S) isentropic ozone transport; they are shown to be better associated during summer/fall than in winter/spring; the agreement is also better for the stations above 40° latitude. This research shows that isentropic transport is important for determining ozone levels in the subtropical upper troposphere especially in summer. Remaining challenges are to gather new observational data to better estimate isentropic ozone transport, to assess the influence of isentropic transport on photochemistry in the upper troposphere, and to investigate reversibility in the cross-tropopause transport.
CHAPTER 1

INTRODUCTION

Although tropospheric ozone (O$_3$) was first measured in the late 1800s, its importance was not fully recognized until about a century later. Ozone in the troposphere is an important trace gas. First, the photolysis of ozone is a primary source of the hydroxyl free radical (OH), which is the major oxidant in the troposphere that determines the lifetimes of many chemical species. Second, tropospheric ozone is a greenhouse gas. It has a strong infrared absorption band centered at the wavelength of 9.6 μm. A recent IPCC report (2001) has ranked ozone as the third most important factor in terms of contributing to human-caused radiative forcing of the climate system. Last but not least, elevated ground-level ozone can have an adverse effect on both human health and agricultural yield. For these reasons, it is essential to understand the critical factors that control the abundance and distribution of tropospheric ozone. This will, in turn, improve our ability to understand and predict global climate change and to take economical and effective measures to ameliorate air quality.

It had been long believed that the sole source of tropospheric ozone was transport downward from the stratosphere (e.g., Junge, 1962; Danielson, 1968), because roughly 90% of global ozone is found in the stratosphere. Later, Crutzen (1973) and Chameides
and Walker (1973) proposed that in-situ photochemistry can be another significant source of tropospheric ozone. The relative importance of these two sources has been one of the most studied and debated topics since then. Since the early 1980s, the combined efforts of modeling and field observation have greatly improved our understanding of the seasonality, as well as the geographical distribution, of photochemical ozone production (e.g., Levy et al., 1985; Liu et al., 1987; Davis et al., 1996; Levy et al., 1997; Wang et al., 1998b and 1998c). Many of these studies suggested that photochemical production is a more important source of tropospheric ozone than stratospheric injection (e.g., Liu et al., 1987; Davis et al., 1996; Levy et al., 1997). However, other studies indicated that stratosphere-troposphere exchange (STE) still contributes approximately 20–50% of tropospheric ozone globally (Fellows and Austin, 1992; Roelofs and Lelieveld, 1997; Lelieveld and Dentener, 2000). And, in a recent study, Davis et al. (2003) pointed out that, from a photochemical point of view, it takes ozone to make ozone, which also implies the importance of STE. Only in rare occasions (during tropopause folding on the west side of pronounced cutoff lows or over elevated sites) can stratospheric ozone reach the surface of the earth and directly influence the air quality (Davies and Schuepbach, 1994). According to Lelieveld and Dentener (2000), zonally averaged contribution of STE to surface ozone in the Northern Hemisphere is up to 40% in the extratropics and ~15% in the tropics.

In order to correctly assess the impacts of tropospheric ozone on climate change, photochemistry, and the environment, it is necessary to have accurate estimates of the sources and sinks of tropospheric ozone. For a given location, the sources are transport of ozone from the stratosphere and from other regions in the troposphere and in situ
photochemical ozone production, while the sinks are in situ photochemical ozone destruction, transport out to the stratosphere and to other regions in the troposphere, and dry and wet deposition. However, it is hard to quantify these sources and sinks, and present modeling studies on them have large uncertainties (Table 4.12 in IPCC, 2001). In addition, it is very difficult to make direct measurements of the ozone flux. According to the IPCC (2001), the abundances of tropospheric ozone are estimated to be 193–370 Tg (1 Tg = 10^9 kg) using different global chemical transport models (CTM). However, estimates of the contribution from stratospheric transport vary widely from 391–1440 Tg/yr, and the estimated net photochemical ozone production ranges correspondingly from +507 to -810 Tg/yr. This means that correctly estimating ozone STE is not only crucial to calculating the ozone abundance in the troposphere but also to deciding the net photochemical effect on ozone is destruction or formation (IPCC, 2001).

There are two pathways for the STE of air and chemical species: the quasi-vertical diabatic transport and the quasi-horizontal isentropic transport (Holton et al., 1995). In the diabatic STE, air rises into the stratosphere at the equator, moves poleward in the stratosphere, and sinks into the troposphere at high latitudes. On the other hand, the isentropic STE moves quasi-horizontally along isentropic surfaces and crosses the tropopause at mid-latitudes, where the tropopause tilts from 380 K down to 310 K (Figure 1.1). This region has been called the ‘middle-world’ by Hoskins (1991). Diabatic flows require diabatic cooling (or warming) to transport stratospheric air (or tropospheric air) downward (or upward) across the tropopause. By contrast, isentropic flows may transfer air and chemical species adiabatically either from the stratosphere to

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Figure 1.1. Dynamical aspects of stratosphere-troposphere exchange. The tropopause is shown by the thick red line. Thin lines are isentropic surfaces labeled in Kelvin. The region where isentropic surfaces span the tropopause is the 'middle-world' (Hoskins, 1991). The wavy double-headed arrows denote meridional transport by eddy motions. The broad arrows show transport by the global-scale circulation, which is driven by the extratropical pump. (From Holton et al., 1995)
the troposphere (S→T) or from the troposphere to the stratosphere (T→S) through irreversible mixing along isentropic surfaces (Holton et al., 1995). This quasi-horizontal isentropic exchange occurs on a timescale of days to weeks, while the diabatic STE has a timescale from months to a year (Chen, 1995).

Brewer (1949) first postulated the meridional diabatic circulation to explain the sharply decreasing water vapor concentration that he observed in the stratosphere within 1 km above the tropopause. Later, Dobson (1956) noticed that the downward and poleward motion in the extratropics was consistent with the observed high ozone concentrations at mid-latitudes. This diabatic circulation is now known as Brewer-Dobson Circulation. Holton et al. (1995) explained that this diabatic circulation is driven by wave-induced forces. Waves that are generated in the troposphere and propagate into the stratosphere will deposit their westward momentum onto the westerly zonal flow in the stratosphere. Because the Coriolis force is strong in the extratropics, this westward force is associated with a poleward flow. Then, due to the mass balance, air will be 'pumped' upward in the tropics and pushed downward at high latitudes. The wave-induced forces are strongest in northern winter, because the latitudinal temperature gradient is greater in winter than in summer and the topography is less homogeneous in the northern hemisphere (NH) than in the southern hemisphere (SH). Therefore, the Brewer-Dobson Circulation has a seasonal cycle and is hemispherically asymmetric. The maximum downward flux of air mass in this circulation occurs in winter in the NH (Rosenlof, 1995). Satellite-observed, zonal-mean distributions of ozone (Wang et al., 1998a) showed that extratropical ozone concentrations are highest in spring and lowest in fall and those in the NH are higher than those in the SH by a factor of ~1.5. The
downward diabatic transport is believed to be a major contributing factor to the observed springtime ozone maxima (e.g., Levy et al., 1985; Logan, 1985; Wang et al., 1998c) in the extratropical troposphere.

While diabatic transport tends to sharpen the latitudinal ozone gradients at mid-latitudes by dumping ozone-rich air at high latitudes and pumping low concentration ozone into the tropical stratosphere, the effect of isentropic transport is to reduce this latitudinal ozone gradient by exchanging ozone quasi-horizontally between the subtropics and the extratropics. This isentropic STE is strongest in summer and weakest in winter (Dethof et al., 2000a; Dethof et al., 2000b), because the tropopause barriers at mid-latitudes are strongest in winter and are considerably weakened by monsoon circulations in summer (Haynes and Shuckburgh, 2000). Measurements taken during the Stratospheric Aerosol and Gas Experiments (SAGE II) showed a decrease of ozone in the extratropical lower stratosphere (LS) accompanied by an increasing ozone trend in the subtropical upper troposphere (UT) in summertime (Wang et al., 1998a). According to Dethof et al. (2000a), the net annual isentropic flux of air mass is from S→T and is of the same order of magnitude as the diabatic upward mass flux in the tropics. This indicates that the isentropic transport could be significant for the ozone budget in the subtropical UT by spreading the stored ozone-rich air from the extratropical LS. It is necessary to study the isentropic ozone STE separately from the diabatic ozone STE in order to understand its role in affecting ozone changes in the LS and UT.

Of the two types of STE processes, the diabatic ozone STE has been studied since the 1960s (e.g., Junge, 1962; Danielson, 1968; Gidel and Shapiro, 1980; Murphy and Fahey, 1994; Olsen et al., 2002; Olsen et al., 2003). On the other hand, the isentropic
ozone STE has not been well addressed. The relative importance of the two pathways is not clear. Recent observational evidence indicates that the isentropic STE is a potentially important process for ozone exchange between the extratropical lower stratosphere (LS) and subtropical upper troposphere (UT). For example, laminae with high ozone mixing ratios (up to 120 ppbv) were often observed in the UT over the tropical Indian Ocean during February-March 1998 (Zachariasse et al., 2000). Morgenstern and Carver (2001) showed that anomalies of ozone mixing ratios derived from the Measurement of Ozone and Water Vapor by Airbus In-Service Aircraft (MOZAIC) observations for five winters in 1995 to 1999 occurred most frequently in a belt spanning the subtropical North Atlantic and the Mediterranean, which coincided with filaments of isentropic transport, according to their model studies. However, none of these studies estimated how much ozone had been transported through those filaments of isentropic transport. The object of this study is therefore to find out how significant the isentropic ozone STE is in controlling ozone variations in the LS and UT.

Quantitatively studying the isentropic ozone STE is difficult because its spatial scale varies from large-scale (2000–3000km) to small-scale (<200km) (Appenzeller et al., 1996). Both conventional Eulerian and Lagrangian numerical methods have practical difficulties in representing the spatial complexity of the isentropic flow and at the same time keeping the computation manageable. A recently developed Lagrangian technique, contour advection, has been shown to be able to resolve the continuous generation of small-scale structures in two-dimensional isentropic flows (Norton, 1994; Waugh and Plumb, 1994; Baker and Cunnold, 2001). Numerical methods based on contour advection have been used to quantify the isentropic fluxes of air mass (Dethof et al.,
2000a) and water vapor (Dethof et al., 2000b) across the tropopause. Their results indicate that isentropic transport is an important path for the STE of air and water vapor in the LS and UT. In this study, contour advection is used following the technique of Dethof et al. (2000a) to simulate the isentropic STE of ozone.

Another challenge of estimating isentropic ozone STE is to obtain global ozone mixing ratio distributions with spatial and temporal resolutions comparable to those of the analyzed advecting wind fields. To solve this problem, this study utilizes the relationship between potential vorticity field and ozone field, which has been noticed to be tightly correlated (e.g., Danielson, 1968; Gidel and Shapiro, 1980; Danielson et al., 1987; Morgenstern and Marenco, 2000). Twelve monthly relationships between analyzed potential vorticities and ozone mixing ratios from SAGE II observations are developed on several isentropic surfaces every year. These monthly PV-O3 relationships are then used to derive daily ozone distributions from daily analyzed PV maps.

It is also important to know what triggers the occurrences of isentropic ozone STE. Studies (e.g., Norton, 1994; Holton et al., 1995; Postel and Hitchman, 1999) have acknowledged Rossby wave breaking (RWB) as an important driving force for STE processes with increasingly fine scales. Postel and Hitchman (1999) showed that RWB at 350 K occurred preferentially over the summertime oceans, downstream of the subtropical high pressure systems. During wintertime, wave breaking is centered over the eastern Atlantic and northwest Africa regions. Is the isentropic ozone STE associated with RWB?
The objective of this research is to estimate the isentropic ozone STE using contour advection and PV-O_3 mapping and to quantitatively assess its significance in controlling ozone variations in the LS and UT by answering the following questions:

(1) How much ozone is transported across the tropopause via isentropic processes in the middle-world every year?

(2) What is the seasonality of the isentropic ozone STE? How is this seasonality related to observed ozone changes?

(3) What is the geographical distribution of the isentropic ozone STE? How is it associated with occurrences of wave breaking?

(4) Are there any inter-annual or hemispheric differences in the strength and/or seasonality of the isentropic ozone STE?

The rest of the thesis is organized as follows:

- Chapter 2 describes the quantification method of estimating isentropic ozone STE and the data that are used.

- Chapter 3 assesses the accuracy of using PV-O_3 mapping to derive ozone distributions in the LS and UT.

- Chapter 4 presents the estimated isentropic ozone fluxes; investigates their seasonality, inter-hemispheric variability, inter-annual variability, and geographical distributions; and analyzes uncertainties of the estimated fluxes.

- Chapter 5 analyzes the association between isentropic ozone STE and Rossby wave breaking.

- Chapter 6 summarizes the major findings of this research and discusses future investigation plans.
CHAPTER 2

DATA AND APPROACH

2.1. Data

The meteorological data source is the Global Modeling and Assimilation Office (GMAO) at NASA's Goddard Space Flight Center. They provide Goddard Earth Observing System (GEOS) assimilated products. Their GEOS-1 datasets for the year of 1990 and GEOS-3 datasets for the year of 1999 are used in this study. The isobaric data are available 6 hourly (0000, 0600, 1200, and 1800 UTC) with a horizontal resolution of 2.0° latitude by 2.5° longitude (Schubert et al., 1993) on 18 pressure levels (1000, 950, 900, 850, 800, 700, 600, 500, 400, 300, 250, 200, 150, 100, 70, 50, 30, 20 hPa) for GEOS-1 and on 36 pressure surfaces (1000, 975, 950, 925, 900, 875, 850, 825, 800, 750, 700, 650, 600, 550, 500, 450, 400, 350, 300, 250, 200, 150, 100, 70, 50, 40, 30, 20, 10, 7, 5, 3, 2, 1, 0.4, 0.1 hPa) for GEOS-3. The isobaric data were interpolated vertically from pressure surfaces onto 11 isentropic surfaces from 320 K to 370 K at 5 K resolution using the interpolation method in Edouard et al. (1997), which is described as follows:

\[ f(\theta) = f_{\text{iso}} - \frac{\ln(\theta_{\text{iso}}/\theta)}{\ln(\theta_{\text{iso}}/\theta_{\text{ref}})} (f_{\text{ref}} - f_{\text{iso}}, \text{if } \theta_{\text{ref}} < \theta < \theta_{\text{iso}}) \]  

(2.1)
in which $\theta_k$ and $\theta_{k+1}$ ($k = 1, 2, 3,...$) are the potential temperatures on pressure levels $k$ and $k+1$ that bracket the target isentropic surface $\theta$. $f_k$ and $f_{k+1}$ are the isobaric data of any field, and $f(\theta)$ is the interpolated isentropic value of that field.

Table 2.1. Sonde data used in the analysis.

<table>
<thead>
<tr>
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<th>Period</th>
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<td>Lauder</td>
<td>-45.0</td>
<td>169.7</td>
<td>1986-2000</td>
</tr>
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</table>

The ozone data are mainly from the SAGE II measurements. SAGE II has been measuring stratospheric ozone profiles since October 1984. It has up to 15 sunrise and 15 sunset measurements every 24 hours. Version 6.1 ozone retrievals are used in this study and those with 300% measurement error bars are excluded. SAGE II V6.1 ozone mixing ratios below 20 km altitude are shown to be more accurate than previous retrievals (Wang et al., 2002). The agreement between SAGE II V6.1 and ozonesonde data in the mean is within 10% down to the tropopause. In the region between 8 km altitude and 2 km below the tropopause, the SAGE ozone is approximately 30% low compared against the ozonesonde climatology (Wang et al., 2002). The Ozonesonde data used in this study are
obtained from WUDC (World of Ozone and Ultraviolet Radiation Data Center) for two stations in Europe, Hohenpeissenberg and Payerne; four in Japan, Sapporo, Kagoshima, Tsukuba, Naha; Boulder and Wallops Island in the United States; and Lauder in New Zealand (Table 2.1).

2.2. Tropopause definition

There are two conventional ways to define the tropopause: the thermal definition based on the lapse rate criteria and the dynamical definition based on a PV threshold value. PV is used to define the tropopause in this study for two reasons: 1) the PV tropopause reflects the dynamical property differences between the stratosphere and troposphere better than the thermal tropopause; and 2) PV is conserved in isentropic frictionless flow. According to Hoerling et al. (1991), for global assimilated datasets with coarse vertical resolution, 3.5 PVU (1 PVU = 10^{-6} m^2 K s^{-1} kg^{-1}) represents an optimal value for tropopause analysis outside the tropics. As the GMAO data employed in this study has coarse vertical resolution, 3.5 PVU is chosen to represent the tropopause. The dependence of the calculated monthly isentropic ozone STE on the PV tropopause definition is discussed in Section 4.5.2.

2.3. Contour advection

Contour advection is a trajectory model that can resolve atmospheric structures over a wide range of scales. It is especially useful to study the formation of small-scale structures in tracer fields in two-dimensional isentropic flow (e.g., Norton, 1994; Waugh and Plumb, 1994).
Traditionally, material motions in a given flow are analyzed based on calculations of the trajectories of material particles in that flow. However, standard trajectory techniques cannot resolve the continual generation of new trace particles in fine-scales to maintain adequate resolution. Dritschel (1988, 1989) developed an algorithm called contour surgery to continually adjust the number and placement of trace particles along a given contour according to the curvature of this contour. The local density of particles increases where the curvature is increasing and decreases where the curvature is decreasing (Appendix).

The code of contour advection with surgery (CAS) that is used in this study was developed by Waugh and Plumb (1994). The only difference between CAS and CS is the way to determine the velocity of each tracer particle along a contour. In CS, the velocity of each particle is calculated by developing a contour integral around the contour, while in CAS calculations the velocity of each particle is determined by spatial and temporal interpolation from the assimilated gridded wind field. Comparing with CS calculations, the CAS results are accurate enough to display the fine-scales, and in practice, CAS is computationally economic and more manageable than CS (Waugh and Plumb, 1994).

The basic steps of the contour advection algorithm are: (1) represent each contour using cubic spline interpolation between particles; (2) determine the velocity at each particle from the assimilated wind field using linear interpolation; (3) advect the particles using a fourth-order Runge-Kutta scheme with a specified time step (=1 hour in this study); (4) run the surgery routine if necessary. The number and placement of particles along a contour is adjusted continually using the algorithm in contour surgery (Dritschel, 1988, 1989).
CAS (Waugh and Plumb, 1994) removes fine-scale structures by merging or disconnecting two contours with identical values and within a specified cutoff scale $\delta$. The application of the surgery routine can make the calculation more manageable and it is also justified by the fact that in the real atmosphere, dissipative processes limit the development of contours into ever-smaller scale structures (Juckes and McIntyre, 1987; Haynes and Anglade, 1997).

The results of Waugh and Plumb (1994) have shown that CAS calculations are insensitive to the spatial resolution of the advecting wind field primarily because the large-scale flows dominate the deformation field. However, the CAS calculation results are sensitive to the temporal resolution of the wind field. The more rapidly the contours evolve (e.g., during wave-breaking events), the higher the temporal resolution of the wind field required to calculate CAS accurately.

2.4. Quantification of the isentropic ozone fluxes across the tropopause

The isentropic cross-tropopause ozone fluxes are calculated for the following isentropic surfaces in the middle-world: 335, 345, 355, and 365 K. Following Dethof et al. (2000a), a control volume is consided around each of the four isentropic surfaces $\Theta$ (Figure 2.1). Its horizontal boundary is the tropopause and its vertical boundaries are $\Theta+\Delta\Theta$ and $\Theta-\Delta\Theta$ ($\Delta\Theta=5$ K). The depth of the volume is $2\Delta\Theta$ (±10 K). Therefore, the vertical bounding levels for the selected 4 isentropic surfaces are 330, 340, 350, 360, and 370 K. The rate of change of ozone in the control volume is determined by three terms: (1) the net isentropic advection of ozone across the tropopause; (2) the vertical ozone flux due to diabatic transport; and (3) the chemical formation or destruction of ozone. Dethof
et al. (2000a) used contour advection to quantify the net isentropic advection of air mass across the tropopause in the middle-world. Following their approach, an algorithm is developed to estimate the net isentropic cross-tropopause ozone flux.

![Diabatic Flow](image)

**Figure 2.1.** A schematic illustration of a control volume around the surface θ (adapted from Dethof et al., 2000a).

On each of the four isentropic surfaces, five PV contours (1.5, 2.5, 3.5, 4.5, and 5.5 PVU) are selected for the contour advection calculation. The initial locations (determined by the latitude and longitude) of these five contours on each isentropic surface are generated from GMAO analysis on Day 0, by choosing the longest continuous contours (i.e., neglecting the smaller blobs) (see Figure 2.2a). The 3.5 PVU contour on
Figure 2.2. An example of the algorithm for calculating the isentropic ozone flux across the dynamical tropopause on 345 K: (a) Initial PV field from GMAO analysis on 1 February, 1990 after neglecting smaller blobs of PV contours. The thick black contour represents the initial tropopause defined by 3.5 PVU. (b) Final PV field on 6 February, 1990 after 5-day contour advection calculation. The thick black contour is the final tropopause determined by running the surgery routine of contour advection on the 3.5 PVU contour. In both (a) and (b), 'NP' represents the North Pole and the outside circle is the Equator. The $S\rightarrow T$ transport is represented by those structures equatorward of the final tropopause with PV values $>3.5$ PVU. The $T\rightarrow S$ transport is associated with those structures pole-ward of the final tropopause with PV values $<3.5$ PVU.
Day 0 is identified as the initial dynamical tropopause, which acts as a horizontal boundary of the initial control volume.

Next, the five initial GMAO PV contours are run using contour advection without surgery for five days. The six hourly analyzed wind fields on regular grid points are linearly interpolated to determine the velocity of each particle on the PV contours. These particles are advected with a one-hour time step using a fourth-order Runge-Kutta scheme (Waugh and Plumb, 1994). The duration of a five-day calculation is long enough for the full development of the filaments (Dethof et al., 2000a) and is short enough for the PV to be considered as a quasi-conservative tracer (Andrew et al., 1987). Because the chemical lifetime of ozone in the LS and UT is about 100 days (Wang et al., 1998c), ozone can also be considered as conserved within the five-day period.

On the fifth day of each calculation on each isentropic surface, the final PV field distribution is represented by the position of the five PV contours following the contour advection. This PV field is characterized by the formation of filaments (Figure 2.2b). To determine the new position of the dynamical tropopause, a separate five-day run of the contour advection calculation is done only on the 3.5 PVU contour and this time running with surgery. The surgery routine removes those filaments on the 3.5 PVU contour by merging or disconnecting two contours with identical PV values and within a specified cutoff scale $\delta$ every 24 hours. The cutoff scale increases 0.008R (R is the radius of the Earth) every 24 hours in order to gradually isolate the small-scale structures from the main body of the tropopause contour. The final cutoff scale is 0.04R (~250 km), which is close to the grid resolution of the initial GMAO PV field. Structures below this scale have been assumed to be dissipated and irreversibly transported into the stratosphere or
stratosphere. In the end, the final dynamical tropopause is represented by the coarse-scale 3.5 PVU contour on Day 5 produced by the contour advection with surgery (Figure 2.2b).

'Overlapping' this coarse final tropopause onto the PV field from the contour advection calculations on Day 5 (Figure 2.2b) yields small-scale structures in this PV field poleward and equatorward of the tropopause. For the equatorward structures, if the PV values within them are greater than 3.5 PVU, it indicates that they are representative of stratosphere-to-troposphere (S→T) transport. On the other hand, for the poleward structures, if their PV values are smaller than 3.5 PVU, they are distinguished as troposphere-to-stratosphere transport (T→S). Gridding those fine-scale structures onto a regular 0.25° x 0.25° (latitude by longitude) grid, the mass of the ozone (M) being transported either from S→T or from T→S is calculated by summing over the grid boxes:

\[
M_{S\rightarrow T} = \sum_i \sigma_i \cdot r_i \cdot \beta_i \cdot \Delta x \cdot \Delta y \cdot 2\Delta \theta \quad \text{if } \beta_i = -1 \quad (2.2)
\]

\[
M_{T\rightarrow S} = \sum_i \sigma_i \cdot r_i \cdot \beta_i \cdot \Delta x \cdot \Delta y \cdot 2\Delta \theta \quad \text{if } \beta_i = +1 \quad (2.3)
\]

in which \( \sigma_i \) is the isentropic density of the air in grid box \( i \); \( r_i \) is the mixing ratio of ozone on the isentropic surface obtained from the PV-O3 monthly relationships; \( \beta_i \) is set to be -1 if PV in grid box \( i \) is >3.5 PVU and +1 if PV <3.5 PVU; \( \Delta x \) and \( \Delta y \) are the grid sizes; and \( 2\Delta \theta (=10 \text{ K}) \) is the isentropic depth of the grid boxes. The daily isentropic flux of ozone, either from S→T or from T→S, is obtained by dividing \( M \) by the calculation time (5 days). The net isentropic ozone flux is obtained by adding the fluxes in the two directions. New calculations are started every day. To yield the monthly and annual fluxes, the daily fluxes are summed over time.
Different from Dethof et al. (2000a), five PV contours are advected in this study rather than the tropopause contour only (i.e., 3.5 PVU). This is because we not only need to determine the final 3.5 PVU tropopause but also need to calculate the ozone mixing ratios within the filaments based on the correlation between PV and ozone. The PV field from contour advection calculation has finer spatial resolution than the analyzed PV field. According to the resolution of analyzed PV, four more PV contours (3.5±1 PVU and 3.5±2 PVU) are chosen around the 3.5 PVU tropopause contour, and the sensitivity analysis, which is described in Section 4.5.3, shows that approximately 90% of the isentropic ozone transport across this dynamically defined tropopause (i.e., 3.5 PVU) is associated with PV values between 1.5 PVU and 5.5 PVU.

The 375 K surface is not included because the 3.5 PVU contour would be close to the equator and the 3.5 PVU tropopause definition might not apply on this surface. It will be shown later in Chapter 4 (i.e., Figure 4.4) that the estimated isentropic ozone fluxes are smaller on higher isentropic surfaces. Therefore, not including the 375 K surface should not cause a significant underestimation of the isentropic ozone fluxes in the lower stratosphere and upper troposphere.
CHAPTER 3

DERIVATION OF OZONE MAPS FROM MONTHLY PV-\(O_3\) RELATIONSHIPS

A major difficulty in estimating the isentropic ozone fluxes is the lack of global ozone mixing ratio distributions with spatial and temporal resolutions comparable to the advecting wind fields. It has been noticed that the PV field and the ozone field are tightly correlated (e.g., Danielson, 1968; Gidel and Shapiro, 1980; Danielson et al., 1987; Morgenstern and Marenco, 2000; Olsen et al., 2002, 2003). This correlation is applied in this study to derive the ozone maps.

3.1. Monthly PV-\(O_3\) relationships

Twelve monthly relationships between potential vorticities and SAGE ozone mixing ratios are developed using the least squares fit on each of four isentropic surfaces (i.e., 335, 345, 355, and 365 K) for each hemisphere every year. Therefore, there are 96 scatter plots of potential vorticities and ozone mixing ratios altogether each year of 1990 and 1999. Figure 3.1 shows two scatter plots on 345 K in the NH in January 1990 using linear scaling and logarithmic scaling on the y-axis (ozone mixing ratios).
Figure 3.1. Scatter plots of PV and ozone mixing ratio on 345 K in the NH in January 1990 using linear (top) and logarithmic (bottom) scaling on the ozone mixing ratio axis. The thick lines are both the least-square fit of PV and ln(O₃).
It is found that PV and $ln(O_3)$ are better correlated than PV and $O_3$. Thus it is assumed that:

$$ln(O_3) = \beta_0 + \beta_1 |PV|$$

(3.1)

in which $ln(O_3)$ is the natural logarithm of ozone mixing ratio ($O_3$ has a unit of ppmv), $|PV|$ is the absolute value of PV (in PVU), and $\beta_0$ and $\beta_1$ are the intersection and slope of the linear regression line of PV and $ln(O_3)$. Tables 3.1-3.4 list the retrieved $\beta_0$ and $\beta_1$ values for the monthly PV-$O_3$ relations in the NH and SH in 1990 and in 1999. The monthly slopes for the four isentropic surfaces in the NH in 1990 are plotted in Figure 3.2 and they exhibit similar seasonal cycles. The low $\beta_1$ values and low correlation coefficients in summer are due to the small variation in PV. It should be noted that the large scatter in the Figure 3.1 plots, which may reflect measurement uncertainties in individual SAGE ozone and PV profiles, is not producing large uncertainties in the slopes of the regression lines shown in Figure 3.2.

The association between PV and $ln(O_3)$ reflects the different dynamical regions on each of the four isentropic surfaces. Because these four isentropic surfaces are located in the middle-world, they span both the lower stratosphere and the upper troposphere. Potential vorticities are less correlated in the upper troposphere (which has lower PV values) than in the lower stratosphere (which has higher PV values). Therefore, ozone mixing ratios increase less rapidly with respect to PV at lower PV values than at higher PV values as reflected by Equation 3.1 and Figure 3.1.

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Figure 3.2. Seasonal variation of slopes ($\Delta ln(O_3)/\Delta PV$) on four isentropic surfaces in the NH in 1990. Error bars are two standard deviations.
Table 3.1. Coefficients for the monthly PV-O3 relationships, \( \ln(O_3) = \beta_0 + \beta_1 |PV| \), in the NH for the year 1990. The correlation coefficient between \( \ln(O_3) \) and \(|PV|\) is represented by \( r \).

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Table 3.2. Coefficients for the monthly PV-O3 relationships, $ln(O_3) = \beta_0 + \beta_1 \cdot |PV|$, in the SH for the year 1990. The correlation coefficient between $ln(O_3)$ and $|PV|$ is represented by $r$.

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</tr>
<tr>
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<td>-2.63</td>
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</table>
Table 3.3. Coefficients for the monthly PV-O₃ relationships, $ln(O₃) = β₀ + β₁|PV|$, in the NH for the year 1999. The correlation coefficient between $ln(O₃)$ and $|PV|$ is represented by $r$.

<table>
<thead>
<tr>
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<th></th>
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<tr>
<td></td>
<td>$β₀$</td>
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<td>$β₀$</td>
<td>$β₁$</td>
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<tr>
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<td>0.88</td>
<td>-2.80</td>
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<td>-2.74</td>
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</tr>
<tr>
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<tr>
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<td>0.94</td>
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Table 3.4. Coefficients for the monthly PV-O3 relationships, $\ln(O3)=\beta_0+\beta_1|PV|$, in the SH for the year 1999. The correlation coefficient between $\ln(O3)$ and $|PV|$ is represented by $r$.

<table>
<thead>
<tr>
<th></th>
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<tr>
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<td>r</td>
<td>$\beta_0$</td>
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<tr>
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<td>-2.88</td>
<td>0.19</td>
<td>0.79</td>
<td>-2.87</td>
</tr>
<tr>
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<td>0.88</td>
<td>-2.64</td>
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<tr>
<td>Nov</td>
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<td>-2.80</td>
<td>0.23</td>
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<tr>
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<td>0.85</td>
<td>-2.77</td>
<td>0.17</td>
<td>0.86</td>
<td>-2.51</td>
</tr>
</tbody>
</table>

* Due to lack of data for this month, the relationships of February are used for January.
3.2. Accuracy of the PV-mapped ozone

The accuracy of the relationship between SAGE II ozone and PV on each isentropic surface is assessed by comparing the inferred ozone values against ozone mixing ratios from ozonesonde observations at Hohenpeissenberg, Boulder, Wallops, and Kagoshima in the NH and at Lauder in the SH. To make the comparisons coincident, the PV-mapped ozone mixing ratios are linearly interpolated both in space and in time to match the locations and times of the observations. The ozonesonde data are vertically interpolated onto the four isentropic surfaces using the interpolation method in Edouard et al. (1997).

The differences between PV-mapped ozone mixing ratios and ozonesonde measurements are listed in Tables 3.5 and 3.6. The median agreement is within 10% except for the 335 K surface over Hohenpeissenberg and Wallops and for 355 K and 365 K over Kagoshima. The standard deviations are within 30%. Figures 3.3-3.6 show the comparisons between the time series of PV-mapped and ozonesonde measured ozone mixing ratios on 345 K at Hohenpeissenberg, Lauder, Boulder, and Kagoshima in 1999. They demonstrate that the PV-mapped ozone mixing ratios are highly correlated with ozonesonde measurements. The correlation coefficients are greater than 0.85 for all the comparisons except for Boulder (0.80). It is also evident that the mappings have captured the magnitudes and the seasonal variations in ozone mixing ratio at mid-latitudes. In the tropics, for example at Hilo (19.7° N, 155.6° W), the median agreement between PV-mapped ozone mixing ratios and ozonesonde measurements (not shown) is still around 10%, but a smaller correlation coefficient (~0.60) and a bigger standard deviation (~50%) of the differences are exhibited. Fortunately, the uncertainties in the tropics are of little
Table 3.5. Differences between ozone mixing ratios from PV-O₃ relationships and from ozonesonde observations in 1999. N is the number of collected ozonesonde profiles; μ and σ are the median and standard deviation of their differences ([PV-mapped ozonesonde] - ozonesonde); R is the correlation coefficient of the time series of PV-mapped ozone and ozonesonde data.

<table>
<thead>
<tr>
<th></th>
<th>Hohenpeissenberg</th>
<th>Wallops</th>
<th>Lauder</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(47.5°N, 11.0°E)</td>
<td>(37.9°N, 75.5°W)</td>
<td>(45.03°S, 169.7°E)</td>
</tr>
<tr>
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<td>N = 64</td>
</tr>
<tr>
<td>θ (K)</td>
<td>μ (%)</td>
<td>σ (%)</td>
<td>R</td>
</tr>
<tr>
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</tr>
<tr>
<td>355</td>
<td>6.2</td>
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<tr>
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<tr>
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<td>-14.7</td>
<td>26.3</td>
<td>0.88</td>
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</tbody>
</table>

R

-0.9 24.2 0.89
-2.3 19.2 0.89
-11.4 27.9 0.91
-14.1 23.9 0.93

-2.9 20.5 0.92

Table 3.6. Same as Table 3.5 but for the year 1999.

<table>
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<tr>
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<th>Hohenpeissenberg</th>
<th>Boulder</th>
<th>Kagoshima</th>
<th>Lauder</th>
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</thead>
<tbody>
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<td>(40.0°N, 105.3°W)</td>
<td>(32.0°N, 131.0°E)</td>
<td>(45.03°S, 169.7°E)</td>
</tr>
<tr>
<td></td>
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<td>N = 40</td>
<td>N = 45</td>
<td>N = 52</td>
</tr>
<tr>
<td>θ (K)</td>
<td>μ (%)</td>
<td>σ (%)</td>
<td>μ (%)</td>
<td>σ (%)</td>
</tr>
<tr>
<td>365</td>
<td>6.9</td>
<td>29.4</td>
<td>3.9</td>
<td>39.5</td>
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<tr>
<td>355</td>
<td>5.2</td>
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<td>0.86</td>
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<tr>
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<td>23.7</td>
<td>0.90</td>
<td>32.8</td>
</tr>
<tr>
<td>335</td>
<td>-10.3</td>
<td>27.7</td>
<td>0.87</td>
<td>38.2</td>
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</table>

R

13.1 25.0 0.91
13.7 25.4 0.91
9.5 24.2 0.90
-0.5 24.9 0.87
1.8 21.1 0.91
2.3 22.4 0.88
1.6 25.3 0.91
3.9 20.9 0.95
Figure 3.3. Ozone from sonde observations (solid) versus ozone from monthly PV-O$_3$ relationships (dash-dotted) on 345 K over Hohenpeissenberg in 1999.

Figure 3.4. Same as Figure 3.3 but for Lauder.
Figure 3.5. Ozone from sonde observations (solid) versus ozone from monthly PV-\textit{O}_3 relationships (dash-dotted) on 345 K over Boulder in 1999. The diamonds are the cases when the observed ozone mixing ratios are less than exp(\beta_0).

Figure 3.6. Same as Figure 3.5 but for Kagoshima.
concern in this study, as the isentropic cross-tropopause transport mostly occurs at mid-latitudes (addressed in Section 4.4).

On 335 K and 345 K in 1990 and on 335 K in 1999, the modeled ozone mixing ratios are systematically (~10%) lower than the observations. This bias is smaller than the bias of the SAGE II ozone observations on which the ln(O3)/PV fits are based. The SAGE II ozone mixing ratios are ~30% low in much of the troposphere (Wang et al., 2002). This unexpected result occurs because of the overestimation of the low SAGE tropospheric ozone values by the linear regression based on the PV mapping procedure (see where PV<1 PVU in Figure 3.1). According to Equation 3.1, ln(O3)=β₀+β₁|PV|, the retrieved ozone value is always ≥exp(β₀) because |PV| is always ≥0. When the observed ozone mixing ratio is less than the value exp(β₀), the retrieved ozone mixing ratios from this model would be 'overestimated'. Examples are five of the 40 collected profiles at Boulder and two of the 45 collected profiles at Kagoshima on 345 K shown as the diamonds in Figures 3.4 and 3.5. In these cases, the monthly ln(O3)/PV fits cannot properly retrieve the ozone mixing ratios. Despite these cases, using the monthly PV-O3 relationships still works fairly well in deriving ozone maps in the UT. In Table 3.7, the comparisons are made for data points at Boulder and Kagoshima only when observed ozone mixing ratios are lower than 0.08 ppmv, which are usually considered as tropospheric (Bethan et al., 1996). Comparing to the values in Table 3.6, the correlation coefficients are smaller, indicating that PV and ozone are less correlated in the troposphere than in the stratosphere. The median differences in Table 3.7 increase approximately 4% on 345 K and 355 K and 9% on 335 K at Kagoshima; the difference is 4% less negative on 335 K at Boulder. The standard deviations of the differences are still
within 30%. This indicates that the \( ln(O_3)/PV \) fits tend to overestimate the tropospheric values but not to increase the uncertainties.

The difference between the PV mapped ozone and the sondes in both the LS and the UT are therefore sufficiently small (~10%) that no corrections for possible ozone measurements biases have been made to the calculated ozone fluxes.

Table 3.7. Similar to Table 3.6 but for the comparisons of tropospheric ozone values. \( N^* \) is the number of observational data that are tropospheric.

<table>
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<td>((32.0^\circ N, 131.0^\circ E))</td>
</tr>
<tr>
<td></td>
<td>( N = 40 )</td>
<td>( N = 45 )</td>
</tr>
<tr>
<td>( \theta ) (K)</td>
<td>( \mu ) (%)</td>
<td>( \sigma ) (%)</td>
</tr>
<tr>
<td>365</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>355</td>
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<tr>
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<tr>
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CHAPTER 4

ESTIMATED ISENTROPIC CROSS-TROPOPAUSE OZONE FLUXES

Using the quantification method based on contour advection as described in Chapter 2, the isentropic cross-tropopause ozone transport has been estimated. This chapter analyzes the seasonal, inter-annual, and inter-hemispheric variations of the estimated isentropic ozone fluxes and their associations with the observed column ozone changes in the lower stratosphere and upper troposphere. The geographical distributions of the isentropic ozone STE are also discussed in this chapter.

4.1. Seasonal variations of the isentropic cross-tropopause ozone fluxes

The calculated monthly average ozone fluxes within the layer between 330 K and 370 K in each hemisphere in 1990 and 1999 are plotted in Figure 4.1. According to Equations 2.2 and 2.3, the S→T fluxes are negative and the T→S fluxes are positive. The S→T fluxes are greater than the T→S fluxes in magnitude except for April in the NH in 1990. This is not only because the isentropic transport of air mass is stronger on the direction from S→T than on the direction from T→S (Dethof et al., 2000a) but also because stratospheric ozone mixing ratios are higher than tropospheric ozone mixing.
Figure 4.1. Estimated monthly average isentropic cross-tropopause ozone fluxes (in Tg day\(^{-1}\); 1 Tg = 10\(^{12}\) kg) in the layer between 330 K and 370 K in the NH (left) and SH (right) in 1990 (top) and 1999 (bottom). The dashed lines are from S\(\rightarrow\)T fluxes (negative), dash-dotted lines are from T\(\rightarrow\)S fluxes (positive), and solid lines are net ozone fluxes. Note that the x-axis is shifted in the SH.
ratios (Bethan et al., 1996). Therefore, the estimated net ozone fluxes are almost always
directed from the extratropical LS to the subtropical UT.

The isentropic ozone transport displays a similar seasonality in each hemisphere,
which is the strongest in summer and the weakest in winter. In the NH, both the S→T
and the T→S fluxes are maximum in June/July/August (northern summer) and minimum
in December/January/February (northern winter). In the SH, they are strong in
January/February/March (late austral summer) and weak in June/July/August (austral
winter), and the seasonality in the SH is weaker than in the NH. This seasonality of the
isentropic ozone STE is opposite to that of the downward diabatic ozone STE at mid-
lattitudes, which is strongest in winter and weakest in summer (Olsen et al., 2002, 2003).
This is because the two ozone STE pathways have different mixing properties. The
diabatic STE is part of the Brew-Dobson circulation, which is driven by wave-induced
forces and these forces are strongest in winter; the Brewer-Dobson circulation is therefore
greatest in winter (Holton et al., 1995). On the other hand, the isentropic mixing across
the tropopause is strongest in summer and weakest in winter because the extratropical
tropopause barriers are strongest in winter and are considerably weakened by the
monsoon circulations in summer (Haynes and Shuckburgh, 2000). Therefore, in
wintertime the ozone-rich air, which has been transported from higher altitude by the
large-scale diabatic circulation, will be stored in the extratropics because the
photochemistry is weak and the extratropical tropopause barrier is strong. This ozone-
rich air stored in winter will spread into the subtropical UT via isentropic transport in
summer because the PV gradients are the smallest in summer and thus act as weaker
barriers to the cross-tropopause transport (Chen, 1995; Haynes and Shuckburgh, 2000).
Wang et al. (1998a) showed that from spring to summer, the SAGE II measurements in the NH display a rapid decrease in the ozone columns poleward of 30° N accompanied by an increase in the ozone columns at low latitudes in the layer between 330 K and 380 K, and the extratropical ozone continues to decrease in the fall. Monthly column ozone in the layer between 340 K and 360 K is then calculated using ozonesonde observations over Hohenpeissenberg (47.8° N, 11.0° E; from 1979 to 2001), Boulder (40.0° N, 105.3° W; from 1979-2000), Lauder (45.0° S, 169.7° E; from 1986-2000), Kagoshima (31.6° N, 130.6° E; from 1991-2001), and Naha (26.2° N, 127.7° E; from 1991-2001). Their seasonal variations are shown in Figure 4.2. Generally speaking, the 340–360 K layer is located in the extratropical LS over Hohenpeissenberg, Boulder, and Lauder; and it is located in the subtropical UT over Kagoshima and Naha. There are cases during which the thermal tropopause lies above 360 K over the first three ozonesonde stations or when the thermal tropopause lies below 340 K in the latter two. It is noted that column ozone in the extratropical LS (i.e., over Hohenpeissenberg, Boulder, and Lauder) is highest in spring and lowest in fall, while the column ozone in the subtropical UT (i.e., over Kagoshima and Naha) is highest in summer and lowest in winter. It is also shown in Figure 4.2 that the seasonal trends of the column ozone changes over Kagoshima and Naha are anti-correlated with those over the extratropical stations. This is consistent with the concept that ozone first increases in the extratropics in winter/spring due to the strong diabatic downward flux and then it spreads into the subtropics via the isentropic transport in summer/fall. It is also noted that the column ozone changes in the subtropical UT are positive in early summer. This means that ozone levels in the UT increase almost immediately after the tropopause barrier breaks because
Figure 4.2. Monthly means (left column) and changes of the monthly means (right column) of the column ozone in the layer between 340 K and 360 K from ozonesonde observations. Error bars are percentiles.
Figure 4.3. Estimated monthly ozone changes between 340 K and 360 K over Kagoshima and Naha in 1999 due to the isentropic cross-tropopause transport.
the isentropic STE occurs quite fast in days to weeks along isentropic surfaces (Chen, 1995).

As the photochemistry of ozone is also more active in summer, it is hard to infer a direct connection between the ozone changes in the subtropical UT with the isentropic transport. According to Wang et al. (1998c), the zonal averaged rate for net photochemical ozone production in July should be \(-0.5\) ppbv day\(^{-1}\)\((-0.01\) DU km\(^{-1}\) day\(^{-1}\)) around 30° N above 200 hPa. The observed monthly changes in column ozone between 340 K and 360 K are up to 3 DU mon\(^{-1}\) from May to July at Kagoshima and in April and May at Naha. Considering the layer between 340 K and 360 K is approximately 2–4 km thick, photochemistry would only cause approximately 0.6–1.2 DU mon\(^{-1}\) increase of column ozone over Kagoshima and Naha. Therefore, the observed column ozone increases cannot be explained by the photochemical production alone. Figure 4.3 plots the estimated monthly ozone changes in 1999 over Kagoshima and Naha due to the isentropic STE, and they are shown to be 0.5–1.5 DU mon\(^{-1}\) over Naha and 2–3 DU mon\(^{-1}\) over Kagoshima in May and June, 1999. It suggests that the isentropic ozone STE might be an important controlling factor of the seasonal ozone variations in the subtropical UT. The ozone column changes at Kagoshima and Naha are the greatest in May but not in July or August as our estimated monthly ozone fluxes are. This is probably because the photochemical destruction is the greatest in the subtropics in summer and ozone is net destroyed by photochemistry (Wang et al., 1998c).

Among the four isentropic layers (i.e., 335, 345, 355, 365 K), the seasonality of the ozone fluxes is more obvious on isentropic surfaces above 340 K (i.e., 345, 355, and 365 K) than below (i.e., 335 K) (Figures 4.4 and 4.5). For 335 K, there is a secondary
Figure 4.4. Estimated monthly average isentropic ozone fluxes across the tropopause in the NH in 1999. Negative values are the fluxes from S→T and positive values are T→S.
Figure 4.5. Same as Figure 4.3 but for the SH.
maximum of net ozone flux around February/March. This is because the barrier posed by the horizontal PV gradients in winter is not as strong on lower surfaces as on the upper ones and therefore the cross-tropopause transport can occur all year-round on lower levels. This is consistent with the characteristics of the two mass transport regimes in the middle-world found by Chen (1995) and Dethof et al. (2000a).

Table 4.1. Estimated annual isentropic ozone fluxes (in 10^{8} kg yr^{-1}) in the layer between 330 K and 370 K across the tropopause. Negative values are from S→T and positive values are from T→S. The cutoff scale used is 250 km. The tropopause is defined by 3.5 PVU.

<table>
<thead>
<tr>
<th></th>
<th>1990</th>
<th></th>
<th>1999</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NH</td>
<td>SH</td>
<td>Globally</td>
<td>NH</td>
</tr>
<tr>
<td>S→T</td>
<td>-100.0</td>
<td>-89.0</td>
<td>-189.0</td>
<td>-127.8</td>
</tr>
<tr>
<td>T→S</td>
<td>54.2</td>
<td>43.1</td>
<td>97.3</td>
<td>58.0</td>
</tr>
<tr>
<td>Net</td>
<td>-45.8</td>
<td>-45.9</td>
<td>-91.7</td>
<td>-69.8</td>
</tr>
</tbody>
</table>

4.2. Inter-annual variation of the isentropic cross-tropopause ozone transport

4.2.1. Estimated annual isentropic cross-tropopause ozone fluxes

The estimated annual isentropic cross-tropopause ozone fluxes are listed in Table 4.1. The integrated S→T annual ozone fluxes are approximately twice the T→S fluxes in magnitude both in the NH and in the SH. Globally, the amount of ozone transferred from S→T is estimated to be ~189x10^{8} kg in 1990 and ~210x10^{8} kg in 1999 while the T→S ozone transport is ~97x10^{8} kg in 1990 and ~92x10^{8} kg in 1999. This means that the
isentropic cross-tropopause transport is a two-way process, but its net effect is to transfer ozone from the extra-tropical LS into the subtropical UT quasi-horizontally. This net transferred ozone is estimated to be approximately $92 \times 10^9$ kg in 1990 and $118 \times 10^9$ kg in 1999.

We are unaware of any other studies which have provided estimates of the isentropic cross-tropopause ozone transport. However, Olsen et al. (2002, 2003) estimated the downward ozone flux including diabatic effects across the tropopause at mid-latitudes, but they did not consider the upward flux. Their annual downward S→T ozone flux in 2000 was estimated to be $-470 \times 10^9$ kg yr$^{-1}$ (with $260 \times 10^9$ kg yr$^{-1}$ in the NH and $210 \times 10^9$ kg yr$^{-1}$ in the SH), which is twice our estimated isentropic S→T flux ($206 \times 10^9$ kg yr$^{-1}$) and four times the net isentropic ozone flux ($115 \times 10^9$ kg yr$^{-1}$) in 1999. This emphasizes that, from a global perspective, large-scale diabatic transport processes make important contributions to the ozone STE.

From an annual view point, the isentropic ozone exchange seems to be a smaller contributor to the total ozone STE than diabatic exchange. However, in summer when the isentropic exchange is strong and the diabatic exchange is weak, the isentropic ozone flux is likely comparable to the diabatic ozone. For example, as shown in Figure 4.6, the monthly mean downward diabatic ozone flux is approximately twice the monthly mean S→T isentropic ozone flux in magnitude except for summer (June/July/August) when the isentropic S→T flux becomes greater than the downward flux.

Shepherd et al. (2000) have suggested that the ability of contour advection to reproduce small-scale structures from low-resolution wind fields may be restricted to
Figure 4.6. Estimated monthly average isentropic $S\rightarrow T$ (orange diamonds) and net (green triangles) ozone fluxes in the layer between 330 K and 370 K in the NH in 1999 in this study and estimated downward diabatic (blue squares) ozone flux between 30°-60° N in 2000 from Olsen et al. (2002).
regions such as the winter stratospheric polar vortex or the upper stratosphere, where the
dynamics are known to be dominated by large-scale processes. Near the tropopause there
is more energy at small scales and the dynamics are more controlled by local processes.
It is possible therefore that the contour advection technique does not capture all the small-
scales evolving around the tropopause using the coarse resolution (~250 km) wind fields
from the GMAO assimilation models and of the observed fields on which these wind
fields are based. Higher resolution winds might yield larger estimates of the isentropic
fluxes at the tropopause. The possibility that the air near the tropopause could undergo
‘fake’ cross-tropopause transport when the transported air had a very short residence time
has not been investigated.

4.2.2. Inter-annual variation

According to Equations 2.2 and 2.3, the estimated ozone fluxes are dependent
both on the isentropic ozone density and on the horizontal area where the cross-
tropopause isentropic STE occurs. The S→T flux in the NH is ~28% higher in 1999 than
1990, but the relevant area in which the S→T ozone flux is diagnosed is only ~8% higher
in 1999 (Table 4.2). This would indicate that ozone concentrations within the layer
between 330 K and 370 K in the northern LS and UT in 1999 should also be greater than
those in 1990.

As explained in Chapter 3, the ozone mixing ratios are obtained from the monthly
PV-O$_3$ relationships ($\ln(O_3)=\beta_0+\beta_1|PV|$) based on SAGE II ozone observations.
According to Tables 3.1 and 3.3, the derived parameters $\beta_0$ and $\beta_1$ for the NH are greater
in 1999 than 1990. For the same PV values, these monthly PV-O$_3$ relationships ratio in
1999 would yield ozone mixing ratios 10–17% higher than in 1990. For example, on 345 K in the NH, the median differences of the derived ozone mixing ratios between 1999 and 1990 are ~14% for PV=4.5 PVU and ~9% for PV=2.5 PVU (Figure 4.7).

Table 4.2. The area (in $R^2$ and $R=6370$ km is the radius of the earth) where the isentropic cross-tropopause ozone fluxes are diagnosed. Negative values are from S→T and positive values are from T→S.

<table>
<thead>
<tr>
<th></th>
<th>1990</th>
<th></th>
<th></th>
<th>1999</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NH</td>
<td>SH</td>
<td>Globally</td>
<td>NH</td>
<td>SH</td>
<td>Globally</td>
</tr>
<tr>
<td>S→T</td>
<td>-41.8</td>
<td>-40.7</td>
<td>-82.5</td>
<td>-45.0</td>
<td>-34.5</td>
<td>-79.5</td>
</tr>
<tr>
<td>T→S</td>
<td>28.8</td>
<td>28.4</td>
<td>57.2</td>
<td>28.1</td>
<td>24.1</td>
<td>52.2</td>
</tr>
<tr>
<td>Net</td>
<td>-13.0</td>
<td>-12.3</td>
<td>-25.3</td>
<td>-16.9</td>
<td>-10.4</td>
<td>-27.3</td>
</tr>
</tbody>
</table>

These larger fluxes in 1999 than in 1990 are therefore mainly caused by the fact that SAGE II observed ozone mixing ratios are ~20% higher in 1999 than in 1990 (Figure 4.8). Ozonesonde observations at Hohenpeissenberg show a similar difference (~20%) between the two years (Figures 4.9 and 4.10). There are also large negative deviations (up to 25 Dobson Units) from seasonal means in the total column ozone values around 45° N in 1990 according to the ozone mapping spectrometer (TOMS) measurements in 1990 (Hood and McCormack 1997). The direct reasons for the observed differences between the two years are not clear. Hood and McCormack (1997) showed that the negative total ozone anomalies at 45° N in 1990 were associated with positive 100 hPa
Figure 4.7. Derived ozone mixing ratios at PV values 2.5 and 4.5 PVU using the monthly relationships in the NH for 1990 and 1999 in Chapter 3.
Figure 4.8. Monthly medians of SAGE II ozone mixing ratios at 40°-50° N within the layer between 340 K and 360 K from 1984 to 2000.

Figure 4.9. Monthly medians of observed ozone mixing ratios around 345 K over Hohenpeissenberg from 1979 to 1999.
height anomalies, which were due to horizontal advective transport from the subtropics and would bring in ozone-poor air to the high latitudes. Other factors that could contribute to the inter-annual ozone variability in the LS are the stratospheric quasi-biennial oscillation (QBO), temporal changes in the abundance of stratospheric aerosols, and the 11-year solar cycle (SPARC, 1998).

At for the SH, the estimated ozone fluxes (both S→T and T→S) are ~19% smaller in 1999 than in 1990 (Table 4.1). This is mainly because the area of the isentropic ozone STE is ~15% lower in 1999 than in 1990 (Table 4.2) and ozone mixing ratios do not show a big difference between 1990 and 1999 (Figure 4.11).
Figure 4.11. Monthly medians of SAGE II ozone mixing ratios at 40°S-50°S within the layer between 340 K and 360 K from 1984 to 2000.

Globally, the estimated annual entropic S→T (T→S) ozone flux is ~10% greater (5% smaller) in 1999 than in 1990. The net isentropic ozone STE is ~28% greater in 1999 than in 1990.

4.3. Inter-hemispheric variation

Although the magnitude and seasonality of the ozone STE are similar in both hemispheres, the estimated individual ozone fluxes (both S→T and T→S) are larger in the NH than in the SH (Table 4.1), and the seasonal variations of the estimated ozone fluxes in the NH are more pronounced than in the SH. This is mainly because the isentropic STE is stronger in the NH than in the SH, and thus the subtropical UT and extratropical LS are better mixed in the NH than in the SH (Dethof et al., 2000a). This is reflected by the differences in the isentropic STE area (Table 4.2 and Figure 4.12).Another reason is that SAGE ozone mixing ratios are smaller in the SH than in the NH
(Wang et al., 1998a). The inter-hemispheric difference in the estimated isentropic ozone STE is smaller in 1990 than in 1999. This is because ozone concentrations in the LS/UT are lower in 1990 than in 1999 in the NH but they are similar in the SH between the two years. This is also because the inter-hemispheric difference of the isentropic ozone STE area is only ~5% in 1990 and it is ~30% in 1999 (Table 4.2). The differences in the isentropic STE area between the two years reflect the uncertainty caused by the wind fields from different GMAO models (GEOS-1 for 1990 and GEOS-3 for 1999), and different strength of the isentropic transport.
Figure 4.12. Average horizontal area in which the isentropic cross-tropopause ozone fluxes are diagnosed among the four isentropic surfaces. The dash line represents the area of the S→T flux, the dash dot line is of the T→S flux, and the solid line is of the net flux. R is the radius of the earth.
4.4. **Geographical distributions of the estimated monthly ozone fluxes**

Figure 4.13 shows the geographical distributions of the estimated monthly isentropic ozone fluxes from S→T and from T→S on 345K and 355 K in the NH for January and July in 1990. The S→T fluxes in magnitude are more significant than the T→S fluxes. Therefore, the distributions of the net fluxes (which are not shown in this thesis) are very similar to those of the S→T fluxes. In January, the S→T ozone fluxes occur predominantly in the mid-latitude regions of eastern North Pacific, eastern North Atlantic, and northwest Africa. The distributions for the NH in January 1999 (Figure 4.14) show similar patterns to those in 1990. These results are consistent with the distribution of the wave breaking intensity in winter proposed by Scott and Cammas (2002). In July, the S→T ozone fluxes are located primarily over the North Pacific Ocean and have secondary ozone flux maximum over the southeast United States and around the Mediterranean Sea, where Rossby wave breaking preferentially occurs around 350 K in summer (Postel and Hitchman, 1999; Scott and Cammas, 2002). Although they are smaller in magnitude, the T→S fluxes are shown to occur more frequently over the Pacific Ocean in July and over Europe and Asia in January. This agrees with the findings in Scott and Cammas (2002) that wave breaking also occur in the direction from T→S especially in summer.

The isentropic ozone fluxes in the SH (Figures 4.14 and 4.15) occur mostly over the mid-latitude oceans and their geographical distributions are more zonally homogeneous than those in the NH. This is mainly because the wave breaking is less longitudinal dependent due to the smaller land-sea temperature gradient and less topography in the SH (Scott and Cammas, 2000).
Figure 4.13. Geographical distributions of the estimated monthly isentropic S→T fluxes (left column) and T→S fluxes (right column) in the NH in January and July, 1990. The lower four plots are for the isentropic surface 345 K and upper four are for 355 K.
Figure 4.14. Same as Figure 4.13 but for the NH in 1999.
Figure 4.15. Same as Figure 4.13 but for the SH in 1990.
Figure 4.16. Same as Figure 4.13 but for the SH in 1999.
4.5. Sensitivity analyses

4.5.1. Cutoff scale in contour advection

The surgery routine in contour advection removes the filaments below a prescribed cutoff scale \( \delta \). Dethof et al. (2000a, 2000b) used a cutoff scale of 0.05R (approximately 320 km; R is the radius of the earth), which was close to the grid size of the analyzed PV field they employed. The cutoff scale is set to be 0.04R (~250 km) because the GMAO analyzed data used in this study have a finer spatial resolution. To test how sensitive the estimated ozone fluxes are to the cutoff scale values, calculations are made in February and August, 1990 with three different \( \delta \) values: 0.03R (~190 km), 0.04R (~250 km), and 0.05R (~320 km). The testing results are listed in Table 4.3. They show that the differences in the monthly ozone fluxes (both S\rightarrow T and T\rightarrow S) in February and August are less than 10%.

<table>
<thead>
<tr>
<th></th>
<th>S\rightarrow T</th>
<th>T\rightarrow S</th>
<th>Net</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>190 km</td>
<td>250 km</td>
<td>320 km</td>
</tr>
<tr>
<td>Feb</td>
<td>-5.55</td>
<td>-6.20</td>
<td>-6.56</td>
</tr>
<tr>
<td>Aug</td>
<td>-14.25</td>
<td>-14.60</td>
<td>-15.38</td>
</tr>
</tbody>
</table>

Table 4.3. Estimated monthly isentropic cross-tropopause ozone fluxes (in \( 10^8 \) kg mon\(^{-1} \)) between 330 K and 370 K in the NH in February and August, 1990 for different cutoff scale values. The shaded values are for the cutoff scale chosen in this study. The tropopause is defined by 3.5 PVU.
It was indicated in Chapter 2 the small blobs in the analyzed PV maps have been neglected in the initialization of the contour advection calculations. These small blobs typically coincide with filaments of PV from earlier initiated contour advection calculations. Therefore, the contribution of the blobs to the fluxes will have been included in the calculations made a few days earlier.

Table 4.4. Similar to Table 4.3 for a cutoff scale of 250 km but for different PV values chosen to define the tropopause. The shaded values are for the PV value used in this study.

<table>
<thead>
<tr>
<th></th>
<th>S→T</th>
<th>T→S</th>
<th>Net</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>3.5</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>PVU</td>
<td>PVU</td>
<td>PVU</td>
</tr>
<tr>
<td>Feb</td>
<td>-4.13</td>
<td>-6.20</td>
<td>-8.01</td>
</tr>
</tbody>
</table>

4.5.2. PV value used to define the tropopause

The flux calculations have been compared using three different PV values to define the tropopause: 2.5 PVU, 3.5 PVU, and 4.5 PVU. It is shown in Table 4.4 that the magnitudes of the estimated ozone fluxes (both S→T and T→S) decrease with increasing PV value in August. This is mainly because the area of the filaments that are identified as S→T or T→S transport decreases as a higher PV value is chosen to represent the tropopause (Scott and Cammas, 2002). In February, however, the fluxes increase as a higher PV value is used to define the tropopause. This is in part because the ozone
mixing ratio increases more dramatically with PV in winter than in summer (Figure 3.2). It is also noted that the changes in \( S \to T \) fluxes are more pronounced than those of the \( T \to S \) fluxes. This can be explained by the function employed to derive the ozone maps: 
\[
\ln(O_3) = \beta_0 + \beta_1 \cdot |PV|
\]
which means that ozone mixing ratio increases exponentially with PV. Therefore, the ozone fluxes increase faster with PV at higher PV values (\( S \to T \)) than at lower PV values (\( T \to S \)).

The estimated ozone fluxes seem to be sensitive to the tropopause definition. It might be better that the tropopause would be considered as a region within a range of PV values than as a single surface determined by a critical PV value.

Table 4.5. Estimated monthly isentropic ozone fluxes (in \( 10^8 \) kg mon\(^{-1}\)) across the 3.5 PVU tropopause between 330 K and 370 K in the NH in February and August, 1990 for PV values <1.5 PVU (from \( T \to S \)) and >5.5 PVU (from \( S \to T \)). The percentages in the column of <1.5 PVU are calculated by comparing to the monthly \( T \to S \) fluxes for PV <3.5 PVU. The percentages in the column of >5.5 PVU are with respect to the monthly \( S \to T \) fluxes for PV >3.5 PVU.

<table>
<thead>
<tr>
<th></th>
<th>&lt; 1.5 PVU</th>
<th>&gt; 5.5 PVU</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feb</td>
<td>0.09 (- 3%)</td>
<td>-0.81 (- 13%)</td>
</tr>
<tr>
<td>Aug</td>
<td>0.46 (- 5%)</td>
<td>1.66 (- 11%)</td>
</tr>
</tbody>
</table>

4.5.3. Cross-tropopause ozone transport outside the 1.5-5.5 PVU range

Table 4.5 shows how much of the ozone exchange across the 3.5 PVU tropopause occurs outside the range of 1.5-5.5 PVU (i.e., 0<PV<1.5 PVU, or PV>5.5 PVU) in
February and August 1990. The ozone flux within the range of 0<PV<1.5 PVU (or PV>5.5 PVU) is estimated by calculating the amount of ozone enclosed by the 1.5 PVU (or 5.5 PVU) tropopause contour and the 3.5 PVU tropopause contour. The amount of ozone transferred into the stratosphere from PV values less than 1.5 PVU is less than 5% of the estimated total T→S ozone fluxes. For PV values greater than 5.5 PVU, it is ~10% of the total S→T ozone fluxes. This demonstrates that the isentropic ozone STE mostly occurs between 1.5 PVU and 5.5 PVU in the middle-world. This is consistent with the results of Dethof et al. (2000a), which showed that 80% of the S→T (or T→S) isentropic air mass transport occurs with 15° (or 10°) equivalent latitude from the 3.5 PVU tropopause contour, as the distance between 1.5 PVU and 5.5 PVU is approximately 20° in equivalent latitude.

4.5.4. Estimated ozone fluxes using ECMWF data

The isentropic cross-tropopause ozone fluxes have been estimated using the GMAO winds. In order to test how sensitivity of the estimates on different datasets, the European Centre for Medium-Range Weather Forecast (ECMWF) data are used to estimate the ozone fluxes in the NH in February and August 1990. The ECMWF temperature and horizontal winds are available 6 hourly (0000, 0600, 1200, and 1800 UTC) on 17 pressure levels (1000, 925, 850, 775, 700, 600, 500, 400, 300, 250, 200, 150, 100, 70, 50, 30, 10 hPa) with a horizontal resolution of 2.5° latitude by 2.5° longitude. The tropopause is defined at the 3.5 PVU contour and the cutoff scale is 250 km in the surgery routine of contour advection.
Figure 4.17. PV fields on 7 February, 1990 after five-day contour advection calculations using GMAO (left) and ECMWF (right) initial PV fields and advecting winds. 'EQ' represents the Equator and 'NP' is the North Pole.
It is shown in Figure 4.17 that the contour advection calculations generate similar fine-scale structures using the ECMWF winds as using the GMAO winds. For the four isentropic layers combined, in February, the estimated ozone fluxes using ECMWF data are <15% smaller in magnitude than those using GMAO winds and the difference of the net fluxes is <30%; in August, the T→S flux is ~37% lower using the ECMWF than using the GMAO although the difference between the S→T fluxes is only ~1%; the estimated net flux is ~60% bigger in magnitude using ECMWF than using GMAO data (Table 4.6).

### Table 4.6. Estimated monthly cross-tropopause isentropic ozone fluxes (in 10⁶ kg mon⁻¹) between 330 K and 370 K in the NH in February and August, 1990 using GMAO and ECMWF assimilated products. The tropopause is defined by 3.5 PVU and the cutoff scale is 250 km.

<table>
<thead>
<tr>
<th></th>
<th>S→T</th>
<th>T→S</th>
<th>Net</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GMAO</td>
<td>ECMWF</td>
<td>GMAO</td>
</tr>
<tr>
<td>Feb</td>
<td>-6.20</td>
<td>-5.24</td>
<td>3.36</td>
</tr>
<tr>
<td>Aug</td>
<td>-14.60</td>
<td>-14.72</td>
<td>8.90</td>
</tr>
</tbody>
</table>

Comparing their geographical distributions (Figures 4.18 and 4.19), the estimated monthly S→T fluxes using ECMWF data occur mostly over the eastern Atlantic and northwest Africa in February and over the Atlantic and Pacific Oceans in August, very similar to those that using the GMAO data; the distributions of the estimated monthly
Figure 4.18. Geographical distributions of the estimated monthly isentropic ozone fluxes both from S→T and from T→S in the NH in February and August, 1990 using ECMWF data. The upper four plots are for the isentropic surface of 355 K and the lower four are for 345 K.
Figure 4.19. Same as Figure 4.18 but using GMAO data.
T→S fluxes in February are similar by using the two different datasets, but in August, the ECMWF T→S flux is 37% smaller in magnitude than using GMAO. Overall, the ECMWF and the GMAO data generate similar patterns in the geographical distributions of ozone STE and the differences in the estimated ozone fluxes between using the two datasets are within 30% except for the T→S flux in August.
CHAPTER 5

ON THE RELATIONSHIP BETWEEN ROSSBY WAVE BREAKING AND ISENTROPIC OZONE STE

Rossby wave breaking (RWB) is an important dynamical process associated with stratosphere-troposphere exchange (Holton et al., 1995). During a RWB event, potential vorticity (PV) contours become severely distorted, and tongues with relatively high PV values stretch away from the dynamical barriers (i.e., the edge of the polar vortex and the tropopause) and extend into the tropical latitudes (e.g., McIntyre and Palmer, 1983; Norton, 1994; Appenzeller et al., 1996). Physically, Rossby wave breaking is characterized by the rapid and irreversible deformation of material contours and is often identified by the reversed latitudinal gradient of potential vorticity (Postel and Hitchman, 1999). Scott and Cannas (2002) used the stretching rate of PV contours calculated by contour advection to indicate the intensity of RWB, and they noticed that the strongest RWB in the NH occurs over the eastern Atlantic and northwest Africa in winter and over the western Pacific in summer. These places are also where our estimated isentropic S→T ozone exchange in the NH is mostly found (Section 4.4). This chapter thus investigates the association between RWB and isentropic ozone STE.
5.1. Identification of RWB

The identification of RWB in this study follows the method in Postel and Hitchman (1999), which is based on the reversed latitudinal gradient of PV. On a given isentropic surface, PV contours are quasi-parallel to the latitude circles and the absolute value of PV increases from the equator to the pole for a standing Rossby wave (Figure 5.1.a). When RWB occurs, PV contours will overturn and the local latitudinal PV gradient will change sign accordingly (Figure 5.1.b).

![Figure 5.1. Schematic of RWB (provided by J. Wright).](image)

Postel and Hitchman (1999) calculated PV gradients globally in order to locate the regions where RWB occurs preferentially. In this study, several ozonesonde stations
are selected and the frequencies of RWB occurring on isentropic surfaces are calculated over these places using analyzed GMAO potential vorticities.

The extratropical tropopause is defined as $\text{PV}^* = 3.5\ PVU$ in the NH and $\text{PV}^* = -3.5\ PVU$ in the SH. Stratospheric air is assumed to be where $|\text{PV}| > 3.5\ PVU$ and tropospheric air where $|\text{PV}| < 3.5\ PVU$. The PV value at an ozonesonde station $(x_0, y_0)$ is $\text{PV}(x_0, y_0)$, in which $x_0$ is longitude and $y_0$ is latitude. The dependence of our identified RWB events on the PV value used to define the tropopause will be addressed in Section 5.5.

On a certain isentropic surface $\theta$, an S→T RWB is identified over $(x_0, y_0)$ if both the following conditions are satisfied on anyone of the nine horizontal grid points $(x_i, y_i)$, $i=1,...,9$, that are closest to $(x_0, y_0)$:

1. $|\text{PV}(x_0, y_0)| \geq |\text{PV}^*| + 0.5\ PVU$; and
2. $|\text{PV}(x_i, y_i)|$ within $10^\circ$ latitude poleward of $(x_0, y_0)$ becomes $\leq |\text{PV}^*| - 0.5\ PVU$.

On the other hand, a T→S RWB is identified if both the following conditions are met:

1. $|\text{PV}(x_0, y_0)| \geq |\text{PV}^*| - 0.5\ PVU$; and
2. $|\text{PV}(x_i, y_i)|$ within $10^\circ$ latitude equatorward of $(x_0, y_0)$ becomes $\geq |\text{PV}^*| + 0.5\ PVU$.

A RWB index, $\text{IB}(x_0, y_0)$ is defined as: $\text{IB}(x_0, y_0)=+1$ if there is an identified S→T RWB event over $(x_0, y_0)$; $\text{IB}(x_0, y_0)=-1$ if there is a T→S RWB event; and $\text{IB}(x_0, y_0)=0$, if there is no identified RWB. The latitudinal PV gradients are checked on $\theta$ over $(x_0, y_0)$ daily. If $\text{IB}(x_0, y_0)=+1$ (or -1) for several continuous days, it is assumed that they belong to the same S→T (or T→S) RWB event.
This identification method can detect the RWB events in which PV contours tilt longitudinally (as in Figure 5.1b) but cannot detect those in which PV contours extend latitudinally. Fortunately, the latter case rarely occurs in this study.

5.2. Identification of isentropic ozone STE

Daily net isentropic ozone fluxes have been estimated on standard grids (2.5° longitude by 2.0° latitude) on several isentropic surfaces using the quantification method based on contour advection as described in Chapter 2. For the location \((x_0, y_0)\), the net ozone flux \(F(x_0, y_0)\) on surface \(\theta\) is calculated as the average net flux among the nine horizontal grid points that are closest to \((x_0, y_0)\). These nine grids are selected because they enclose an area that is approximately \((x_0 \pm \delta, y_0 \pm \delta)\), in which \(\delta \approx 250 \text{ km}\) is the final cutoff scale used in the surgery routine of contour advection.

On isentropic surface \(\theta\), an S→T isentropic ozone STE is identified over \((x_0, y_0)\) if \(F(x_0, y_0)<0\); a T→S isentropic ozone STE is identified if \(F(x_0, y_0)>0\). If \(F(x_0, y_0)\) persists negative (or positive) for several continuous days, it is assumed that the fluxes belong to the same isentropic S→T (or T→S) ozone STE event.

5.3. Comparative analysis of RWB and isentropic ozone STE

According to Scott and Cammas (2002), RWB makes a major contribution to isentropic mixing around 350 K. Therefore, two isentropic surfaces, 345 K and 355 K, are chosen to investigate the relationship between RWB and isentropic ozone STE.

Seven ozonesonde stations are selected for the comparison between RWB and isentropic ozone STE: Hohenpeissenberg(47.8° N, 11.0° E), Payerne(46.5° N, 6.6° E),...
Sapporo(43.1° N, 141.3° E), Boulder(40.0° N, 105.3° W), Tsukuba(36.1° N, 140.1° E), Kagoshima(31.6° N, 130.6° S), and Lauder(45.0° S, 169.7° E). We count the number of identified S→T (T→S) RWB events on 345 K and 355 K over these locations in 1990 and 1999. For an identified S→T (T→S) RWB event on Day k, if there is a net S→T (T→S) ozone flux within ±1 day of Day k, it is assumed that this S→T (T→S) ozone transport is a coincident event for the identified S→T (T→S) RWB. The number of RWB events and the number of their coincident isentropic ozone STE on 345 K in 1990 and 1999 are listed in Tables 5.1 and 5.2 respectively.

Over Payere on 345 K in 1999 (Figures 5.2 and 5.3), for example, there are 23 total identified S→T RWB events and of these 16 occur in summer/fall; 14 of the 23 S→T RWB events are associated with coincident S→T isentropic ozone fluxes; 12 out of these 14 coincident cases are identified in summer/fall. On the direction from T→S, there are 28 identified RWB events and 17 of them occur in summer/fall; 10 of the 14 T→S RWB events with coincident isentropic T→S ozone fluxes are detected in summer/fall. Ozone anomalies in Figures 5.2 and 5.3 will be discussed in Section 5.5.

It is noted that Hohenpeissenberg and Payere have more identified RWB events (either S→T or T→S) than the stations at lower latitudes (Tables 5.1 and 5.2). RWB is rarely identified over Kagoshima. This is mainly because Hohenpeissenberg and Payere are located near the area with strongest RWB (Scott and Cammas, 2002) and Kagoshima is not.
Table 5.1. Ratios of the identified RWB events that are associated with isentropic ozone STE on 345 K in 1990. Denominators are the total number of the identified S→T (T→S) RWB events. Numerators are the number of S→T (T→S) RWB events that are associated with incident S→T (T→S) net isentropic ozone fluxes. The ‘All Year’ columns are for the comparisons all year around and the ‘S/F’ columns are for summer/fall comparisons only.

<table>
<thead>
<tr>
<th>Year 1990</th>
<th>S→T</th>
<th>T→S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>All Year</td>
<td>S/F</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hohenpeissenberg</td>
<td>47.8°N</td>
<td>10/33</td>
</tr>
<tr>
<td>Payeme</td>
<td>46.5°N</td>
<td>13/37</td>
</tr>
<tr>
<td>Sapporo</td>
<td>43.1°N</td>
<td>4/15</td>
</tr>
<tr>
<td>Boulder</td>
<td>40.0°N</td>
<td>5/18</td>
</tr>
<tr>
<td>Tsukuba</td>
<td>36.1°N</td>
<td>4/8</td>
</tr>
<tr>
<td>Kagoshima</td>
<td>31.6°N</td>
<td>4/6</td>
</tr>
<tr>
<td>Lauder</td>
<td>45.0°S</td>
<td>12/23</td>
</tr>
<tr>
<td>Over all</td>
<td>52/140</td>
<td>38/70</td>
</tr>
</tbody>
</table>
Table 5.2. Same as Table 5.1 but for 345 K in 1999.

<table>
<thead>
<tr>
<th>Year 1999</th>
<th>S→T</th>
<th></th>
<th>T→S</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Lat.</td>
<td>All Year</td>
<td>S/F</td>
<td>All Year</td>
<td>S/F</td>
</tr>
<tr>
<td>Hohenpeissenberg</td>
<td>47.8°N</td>
<td>10/19 9/15</td>
<td>9/27 7/16</td>
<td></td>
</tr>
<tr>
<td>Payerne</td>
<td>46.5°N</td>
<td>14/23 12/16</td>
<td>14/28 10/17</td>
<td></td>
</tr>
<tr>
<td>Sapporo</td>
<td>43.1°N</td>
<td>5/12 5/11</td>
<td>3/10 3/8</td>
<td></td>
</tr>
<tr>
<td>Boulder</td>
<td>40.0°N</td>
<td>9/10 5/6</td>
<td>9/12 4/5</td>
<td></td>
</tr>
<tr>
<td>Tsukuba</td>
<td>36.1°N</td>
<td>4/5 2/3</td>
<td>0/1 0/1</td>
<td></td>
</tr>
<tr>
<td>Kagoshima</td>
<td>31.6°N</td>
<td>0/0 0/0</td>
<td>0/0 0/0</td>
<td></td>
</tr>
<tr>
<td>Lauder</td>
<td>45.0°S</td>
<td>18/33 17/24</td>
<td>7/15 4/12</td>
<td></td>
</tr>
<tr>
<td>Overall</td>
<td>60/102 50/75</td>
<td>42/93 28/59</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 5.2. Ozone anomalies (blue histograms), RWB indices (vertical grey lines), and net isentropic cross-tropopause ozone fluxes (magenta shaded areas) at Payette on 345 K in 1999. Positive RWB indices and positive ozone fluxes are from S→T and negative RWB indices and negative ozone fluxes are from T→S. ‘A’ and ‘B’ represent 7 June and 29 October, 1999.

Figure 5.3. Same as Figure 5.2 but for summer/fall on 345 K in 1999 only.
Overall, 37% of the identified S→T RWB events are associated with S→T isentropic ozone fluxes on 345 K in 1990 and 59% in 1999. During summer/fall, the percentages are higher: 54% in 1990 and 67% in 1999. On the T→S direction, 45% of the identified T→S RWB events are associated with T→S ozone fluxes in 1990 and 1999. Of all the identified RWB with coincident isentropic ozone STE, approximately 70% are detected during summer/fall. Therefore, it seems that RWB and isentropic ozone STE are more clearly correlated during summer/fall than during winter/spring on 345 K. This is because both RWB and isentropic STE are most active in summer/fall and RWB is possibly a major driving force for the occurrences of isentropic ozone STE during this time period.

On the isentropic surface 355 K in 1999, over 80% of the identified RWB events are detected in summer/fall and 30% (50%) of the S→T (T→S) RWB events are associated with S→T (T→S) isentropic ozone STE both all around the year and in summer/fall (Table 5.3). It is noted that there are 50% fewer S→T RWB events at 355 K compared with 345 K over Hohenpeissenberg, Payerne, Sapporo and Lauder. The differences between the two isentropic levels are small over the other locations and for the direction from T→S. For example, on 355 K over Payerne in 1999 (Figures 5.4 and 5.5), there are only 10 S→T identified RWB and 6 of them are in summer/fall, but 16 out of a total of 23 are detected in summer/fall on 345 K. For those big RWB and isentropic transport events, they are usually detected both on 345 K and on 355 K, for example, Case B on 29 October, 1999 over Payerne. It is shown that an S→T RWB event is associated with S→T ozone flux both on 345 K and on 355 K in Figures 5.2 to 5.5. It is
Table 5.3: Same as Table 5.1 but for 355 K in 1999.

<table>
<thead>
<tr>
<th>Year 1999</th>
<th>S→T</th>
<th>T→S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lat.</td>
<td>All Year</td>
</tr>
<tr>
<td>Hohenpeissenberg</td>
<td>47.8°N</td>
<td>2/8</td>
</tr>
<tr>
<td>Payerne</td>
<td>46.5°N</td>
<td>3/10</td>
</tr>
<tr>
<td>Sapporo</td>
<td>43.1°N</td>
<td>0/5</td>
</tr>
<tr>
<td>Boulder</td>
<td>40.0°N</td>
<td>8/15</td>
</tr>
<tr>
<td>Tsukuba</td>
<td>36.1°N</td>
<td>4/5</td>
</tr>
<tr>
<td>Kagoshima</td>
<td>31.6°N</td>
<td>1/4</td>
</tr>
<tr>
<td>Lauder</td>
<td>45.0°S</td>
<td>4/5</td>
</tr>
<tr>
<td>Over all</td>
<td>22/52</td>
<td>20/41</td>
</tr>
</tbody>
</table>
Figure 5.4. Same as Figure 5.2 but for 355 K in 1999.

Figure 5.5. Same as Figure 5.4 but for summer/fall in 1999.
Figure 5.6. Ozone mixing ratio with respect to potential temperature over Payenne. The solid line is the monthly mean profile in October, 1999. The dash-dotted line is the ozone profile on 29 October, 1999.
also shown that the observed ozone mixing ratio remains greater than the monthly mean till 415 K (Figure 5.6).

5.4. Chi-square test of the independence of RWB and isentropic ozone STE

Chi-square test is applied to measure the independence between isentropic ozone STE (A) and RWB (B). The null hypothesis $H_0$ is: the two variables (A and B) are statistically independent; the alternate hypothesis $H_a$ is: isentropic ozone STE (A) and RWB (B) are related. The Chi-square test is made for each ozonesonde station in 1999. The test for Hohenpeissenberg is included here as an example.

Table 5.4. Contingency table for RWB and isentropic ozone STE over Hohenpeissenberg on 345 K in 1999.

<table>
<thead>
<tr>
<th></th>
<th>S→T RWB</th>
<th>T→S RWB</th>
<th>Neither</th>
<th>Totals</th>
</tr>
</thead>
<tbody>
<tr>
<td>S→T STE</td>
<td>17</td>
<td>17</td>
<td>16</td>
<td>50</td>
</tr>
<tr>
<td>T→S STE</td>
<td>4</td>
<td>20</td>
<td>57</td>
<td>81</td>
</tr>
<tr>
<td>Neither</td>
<td>15</td>
<td>11</td>
<td>208</td>
<td>234</td>
</tr>
<tr>
<td>Totals</td>
<td>36</td>
<td>48</td>
<td>281</td>
<td>365</td>
</tr>
</tbody>
</table>

First, a contingency table (Table 5.4) is made, which lists the observed number of days under RWB and under isentropic ozone STE events over Hohenpeissenberg on 345 K in 1999. The expected value (which would be expected if A and B were unrelated) in a
A cell (in row \(i\), column \(j\)) is calculated as: 
\[
E_{ij} = \frac{(f_i)(f_j)}{N},
\]

in which \(f_i\) and \(f_j\) are the row and column marginals of Table 5.4 and \(N\) is the total sample size (=365). For example,
\[
E_{ii} = \frac{(50)(36)}{365} = 4.9.
\]
The expected values are listed in Table 5.5.

<table>
<thead>
<tr>
<th></th>
<th>S→T RWB</th>
<th>T→S RWB</th>
<th>Neither</th>
<th>Totals</th>
</tr>
</thead>
<tbody>
<tr>
<td>S→T STE</td>
<td>4.9</td>
<td>6.6</td>
<td>38.5</td>
<td>50</td>
</tr>
<tr>
<td>T→S STE</td>
<td>8.0</td>
<td>10.6</td>
<td>62.4</td>
<td>81</td>
</tr>
<tr>
<td>Neither</td>
<td>23.1</td>
<td>30.8</td>
<td>180.1</td>
<td>234</td>
</tr>
<tr>
<td>Totals</td>
<td>36</td>
<td>48</td>
<td>281</td>
<td>365</td>
</tr>
</tbody>
</table>

The test statistic Chi-square is 
\[
\chi^2 = \sum_{i=1}^{R} \sum_{j=1}^{C} \frac{(O_{ij} - E_{ij})^2}{E_{ij}},
\]
in which \(R\) is the number of rows (=3) and \(C\) is the number of columns (=3) in Table 5.5; \(O_{ij}\) and \(E_{ij}\) are the observed and expected values in row \(i\), column \(j\). The critical value of Chi-square for significance level \(\alpha=0.05\) with the degrees of freedom \((R-1)(C-1) = (3-1)(3-1) = 4\) is 9.5.

The statistic Chi-square for Hohenpeissenberg is 96.0 (>> the critical value 9.5) and we therefore reject \(H_0\). Because 96.0 is >> the 0.999 quantile of a Chi-squared random variable with 4 degrees of freedom (=18.5), the \(p\)-value of the test is <<(1-0.999). Such a small \(p\)-value indicates that the data strongly disagree with the null hypothesis \(H_0\) and we
therefore conclude that isentropic ozone STE and RWB over Hohenpeissenberg are statistically related at significance level 0.05. Then, the Cramér’s contingency coefficient ($R_c$) is calculated, which is currently the most widely used measure of dependence for $R \times C$ contingency tables. $R_c$ is defined as $R_c^2 = \frac{\sum_{i=1}^{R} \sum_{j=1}^{C} (O_{ij} - E_{ij})^2}{N(q-1)}$, in which $q$ is the smaller value of $R$ and $C$ and $q=3$. $R_c$ is close to 1.0 if A and B have a strong dependence. For Table 5.6, $R_c = \sqrt{\frac{96}{365(3-1)}} = 0.36$. Table 5.6 lists the results of the Chi-square tests on the relationship between RWB and isentropic ozone STE for Hohenpeissenberg and other ozonesonde stations on 345 K in 1999 and the relevant Cramér’s contingency coefficients. Among the seven locations, all except Kagoshima conclude that RWB and isentropic ozone STE are statistically related; according to the $R_c$ values, RWB and isentropic ozone STE seem to be more strongly related over Hohenpeissenberg, Payerne, and Lauder than over Sapporo and Tsukuba.
Table 5.6. Results of the Chi-square tests and the Cramér’s contingency coefficients over selected ozonesonde stations on 345 K in 1999.

<table>
<thead>
<tr>
<th></th>
<th>$X^2$</th>
<th>p-value</th>
<th>Decision</th>
<th>$R_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hohenpeissenberg</td>
<td>96.0</td>
<td>&lt;0.001</td>
<td>$H_a$</td>
<td>0.36</td>
</tr>
<tr>
<td>Payerne</td>
<td>93.7</td>
<td>&lt;0.001</td>
<td>$H_a$</td>
<td>0.36</td>
</tr>
<tr>
<td>Sapporo</td>
<td>15.3</td>
<td>0.005</td>
<td>$H_a$</td>
<td>0.14</td>
</tr>
<tr>
<td>Boulder</td>
<td>45.8</td>
<td>&lt;0.001</td>
<td>$H_a$</td>
<td>0.25</td>
</tr>
<tr>
<td>Tsukuba</td>
<td>17.2</td>
<td>0.005</td>
<td>$H_a$</td>
<td>0.15</td>
</tr>
<tr>
<td>Kagoshima</td>
<td>0</td>
<td>-</td>
<td>$H_0$</td>
<td>0</td>
</tr>
<tr>
<td>Lauder</td>
<td>132.9</td>
<td>&lt;0.001</td>
<td>$H_a$</td>
<td>0.43</td>
</tr>
</tbody>
</table>

5.5. Influence of the identified RWB and isentropic ozone STE on ozone levels

When there is a RWB and/or isentropic ozone STE, how will the local ozone levels change? For example, an S→T RWB event or isentropic S→T ozone transport would transfer ozone-rich air to a certain location from higher latitudes and we would expect to see observed ozone mixing ratios greater than the monthly means (i.e., positive ozone mixing ratio anomalies). On the other hand, if there is a T→S RWB and/or T→S ozone flux, smaller ozone mixing ratios (i.e., negative ozone anomalies) should be observed. Using ozonesonde data from the 7 selected stations, we then check whether the observations reflect these ozone changes under the influences of RWB and isentropic ozone STE.

Ozone anomalies are calculated with respect to the monthly means of ozone mixing ratios on 345 K and 355 K from observations in 1990 and 1999 at
Hohenpeissenberg and Payerne. Observations are routinely made at these locations once every other day. Because there are only ~3 observations made every month at the other five stations, their ozone anomalies are calculated with respect to their monthly mean climatology. There are no observations in 1990 at Sapporo, Boulder, Tsukuba, and Kagoshima and thus the comparisons are made only in 1999 at these locations. We then count the ratios of cases with positive (negative) ozone mixing ratio anomalies that are associated with identified S→T (T→S) RWB or isentropic ozone STE. The results are listed in Table 5.7.

Over the stations at latitudes less than 40° (i.e., Boulder, Tsukuba, and Kagoshima), the percentages of the positive ozone anomaly cases that are associated with S→T isentropic ozone STE are 56% all year around and 76% for the summer/fall cases in 1999. They are greater than the percentages over the stations at latitudes higher than 40° (i.e., Hohenpeissenberg, Payerne, Sapporo, and Lauder), which are 21% all year around and 48% in summer/fall. This is because our estimated S→T isentropic ozone STE mostly occurs in the regions equatorward of ~40° latitude (Section 4.4). This does not mean that ozone variations at higher latitudes are less controlled by isentropic processes. Some isentropic processes may not cause cross-tropopause transport, but they still can bring high ozone concentration air from higher latitudes and cause positive ozone anomalies. This will be discussed in the uncertainties of the comparisons in Section 5.6. For negative ozone anomalies, approximately 38% of them are associated with T→S isentropic ozone transport.
Table 5.7. Ratios of observed ozone anomalies that are associated with RWB and/or net isentropic ozone STE on 345 K over selected stations in 1999. ‘F’ columns list the ratios of ozone anomalies associated with net isentropic ozone fluxes; ‘R’ columns list the ratios that are associated with RWB events; and ‘B’ columns list those that are associated with both ozone fluxes and RWB.

<table>
<thead>
<tr>
<th></th>
<th>345 K</th>
<th>+ O₃</th>
<th>- O₃</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1999</td>
<td>F</td>
<td>R</td>
<td>B</td>
</tr>
<tr>
<td></td>
<td>All Year</td>
<td>S/F</td>
<td>All Year</td>
<td>S/F</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>R</td>
<td>B</td>
<td>F</td>
</tr>
<tr>
<td>Hohen-</td>
<td>11</td>
<td>9</td>
<td>8</td>
<td>11</td>
</tr>
<tr>
<td>pressen-</td>
<td>53</td>
<td>53</td>
<td>53</td>
<td>23</td>
</tr>
<tr>
<td>berg 47.8°N</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Payene</td>
<td>16</td>
<td>10</td>
<td>8</td>
<td>15</td>
</tr>
<tr>
<td>46.5°N</td>
<td>69</td>
<td>69</td>
<td>69</td>
<td>30</td>
</tr>
<tr>
<td>Sapporo</td>
<td>1</td>
<td>2</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>43.1°N</td>
<td>21</td>
<td>21</td>
<td>21</td>
<td>7</td>
</tr>
<tr>
<td>Boulder</td>
<td>10</td>
<td>2</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>40.0°N</td>
<td>19</td>
<td>19</td>
<td>19</td>
<td>8</td>
</tr>
<tr>
<td>Tsukuba</td>
<td>10</td>
<td>1</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>36.1°N</td>
<td>17</td>
<td>17</td>
<td>17</td>
<td>6</td>
</tr>
<tr>
<td>Kago-</td>
<td>8</td>
<td>0</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>shima</td>
<td>14</td>
<td>14</td>
<td>14</td>
<td>7</td>
</tr>
<tr>
<td>31.6°N</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lauder</td>
<td>6</td>
<td>4</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>45.0°S</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>9</td>
</tr>
<tr>
<td>Over all</td>
<td>62</td>
<td>28</td>
<td>21</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td>213</td>
<td>213</td>
<td>213</td>
<td>90</td>
</tr>
</tbody>
</table>
It is noted that observed ozone anomalies are rarely associated with RWB at Sapporo, Boulder, Tsukuba, and Kagoshima (Table 5.7). This is mainly because fewer RWB events are identified over these locations than over Hohenpeissenberg, Payerne, and Lauder (Table 5.1 and 5.2). For the stations of Hohenpeissenberg, Payerne, and Lauder, approximately 32% (35%) of the positive (negative) ozone anomalies are associated with S→T (T→S) RWB in summer/fall 1999. There are 21(27) cases when positive (negative) ozone anomalies are associated with both S→T (T→S) RWB and S→T (T→S) isentropic ozone STE among all the seven stations and 19 (17) of them are detected in summer/fall.

The results for the comparisons on 355 K are listed in Table 5.8. There are fewer positive ozone anomalies that are associated with S→T RWB and/or S→T isentropic ozone STE than those on 345 K over Hohenpeissenberg, Payerne, and Lauder. This is consistent with the previous findings in Section 5.3 that there are fewer S→T RWB events and less S→T isentropic ozone STE on 355 K than on 345 K. The differences between the two levels are small on the T→S direction for all the ozonesonde stations.

Two dates, 6 June and 29 October, 1999, are selected over Payerne as examples for the comparisons. On 6 June, 1999, the PV fields at 345 K both from contour advection calculations and from GMAO analyzed data are plotted in Figure 5.7. On the analyzed PV field, there is an air mass with PV value less than 3.5 PVU around Hohenpeissenberg and Payerne and it is surrounded by stratospheric air. It is therefore identified as being caused by T→S RWB. The PV field from Contour Advection calculations shows that this air mass is located poleward of the tropopause and it is diagnosed as T→S isentropic transport. The observed ozone over Payerne on 345 K on
Table 5.8. Same as Table 5.7 but for 355 K.

<table>
<thead>
<tr>
<th></th>
<th>355 K</th>
<th></th>
<th></th>
<th>0.5°C</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>+ O₃</td>
<td></td>
<td></td>
<td>- O₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1999</td>
<td></td>
<td>S/P</td>
<td>1999</td>
<td></td>
<td>S/P</td>
<td></td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>R</td>
<td>B</td>
<td>F</td>
<td>R</td>
<td>B</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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Figure 5.7. PV fields from contour advection calculation (top) and from GMAO analyzed data (bottom) on 345 K at 00 UTC on 6 June, 1999. The thick black line in the top figure represents the final 3.5 PVU tropopause from the surgery routine of contour advection. 'P' and 'H' represent Payerne and Hohenpeissensberg.
Figure 5.8. Ozone mixing ratio with respect to potential temperature over Payirne. The solid line is the monthly mean profile in June, 1999. The dash-dotted line is the ozone profile on 7 June, 1999.
Figure 5.9. Same as Figure 5.7 but for 29 October, 1999.
7 June, 1999 is ~0.22 ppmv and it is ~0.13 ppmv smaller than the monthly mean (~0.35 ppmv) (Figure 5.8). On 29 October, 1999 (Figure 5.9), there is a stream of stratospheric air with PV>5.5 PVU around Hohenpeissenberg and Payerne. It is identified as S→T RWB and is diagnosed as S→T isentropic transport. The observed ozone mixing ratio over Payerne on 345 K on 29 October, 1999 is ~0.26 ppmv and it is ~0.08 ppmv bigger than the monthly mean.

Figure 5.10. Ozone anomalies (blue histograms), RWB indices (vertical grey lines), and net isentropic cross-tropopause ozone fluxes (magenta shaded areas) at Payerne on 345 K in 1999. The tropopause in identifying RWB events is defined as 2.5 PVU.

5.6. Uncertainties in the comparisons

5.6.1. Tropopause definition in the identification of RWB

In order to test if the comparisons are sensitive to the tropopause definition, 2.5 PVU is used to represent the tropopause to test whether our identified RWB events are
sensitive to the tropopause definition; 50% less RWB (both S→T and T→S) events are detected than those using 3.5 PVU to define the tropopause. However, for those RWB events that are associated with isentropic ozone STE and/or ozone anomalies using the 3.5 PVU tropopause, 90% are detected using the 2.5 PVU tropopause. For example, the RWB events detected by using 2.5 PVU tropopause at Payerne on 345 K in 1999 are plotted in Figure 5.10. Comparing Figure 5.10 with Figure 5.2 (using 3.5 PVU tropopause), it is noted that most of the RWB events that last more than two continuous days are associated with isentropic ozone fluxes and/or ozone anomalies and these events are detected in both tropopause definitions. This is consistent with the findings in Scott and Cammas (2002) that estimates of the mixing during weak wave breaking are more sensitive to the tropopause definition than during strong wave breaking.

5.6.2. Isentropic transport may not cause cross-tropopause transport

Over 50% of the observed ozone anomalies are neither associated with RWB nor with isentropic ozone STE and they are mostly found during winter/spring. They could be the result of the diabatic cross-tropopause transport, because the diabatic STE is the strongest and the isentropic STE is the weakest in winter/spring. However, those unrelated cases in summer/fall could be mostly due to the fact that not all the isentropic transport would result in cross-tropopause transport. For example, the GMAO analyzed PV map for 5 July, 1999 (Figure 5.11) shows that there is a part of stratospheric air near Sapporo on 345 K. Figure 5.12 shows that the region on 345 K over Sapporo is in the troposphere and the observed ozone is ~0.07 ppmv greater than the monthly mean (~0.13 ppmv) and the ozone anomaly remains positive in the layers above 345 K (Figure 5.12).
Figure 5.11. PV fields from contour advection calculation (top) and from GMAO analyzed data (bottom) on 345 K over Japan at 00 UTC on 5 July, 1999. The thick black line in the top figure represents the final 3.5 PVU tropopause from the surgery routine of contour advection. ‘S’ represents Sapporo, ‘T’ for Tsukuba, ‘K’ for Kagoshima, and ‘N’ for Naha.
Figure 5.12. Ozone mixing ratio with respect to potential temperature over Sapporo. The solid line is the monthly mean profile in July, 1999. The dash-dotted line is the ozone profile on 5 July, 1999.
However, this air mass is not diagnosed as due to S→T transport because it is located poleward of the tropopause on the contour advection PV chart (Figure 5.11). It is not identified as a RWB event over Sapporo either because the air within 10° latitude north of Sapporo does not have PV values less than 3.0 PVU, although in fact Sapporo is located on the edge of this blob of air mass.

5.6.3. Different spatial sales of isentropic STE and RWB

There are more cases with net isentropic ozone STE than RWB events that are identified (Tables 5.1 to 5.3). This difference might be due to the different spatial resolution of the two processes. For those rather thin filaments in the isentropic transport, the analyzed PV may not be able to distinguish them. For example, on 26 July, 1999 (Figure 5.13), there is an isolated blob of air with high PV values to the south of Hohenpeissenberg on the analyzed PV map; on the contour advection PV chart, there is a thin stream of air that runs through Hohenpeissenberg and connects this isolated blob of air with the stratosphere to the northeast of Hohenpeissenberg. Therefore, the discrepancies between the identified RWB and isentropic ozone transport may be largely due to the different spatial resolutions of the analyzed PV field and the contour advection generated PV fields.
Figure 5.13. PV fields from contour advection calculation (top) and from GMAO analyzed data (bottom) on 345 K at 00 UTC on 26 July, 1999. The thick black line in the top figure represents the final 3.5 PVU tropopause from the surgery routine of contour advection. 'P' and 'H' represent Payerne and Hohenpeissenberg.
CHAPTER 6

SUMMARY AND DISCUSSION

The objective of this investigation is to estimate how much ozone is transported across the tropopause through isentropic processes. These processes are acknowledged to be an effective mechanism of stratosphere-troposphere exchange (STE) (Holton et al., 1995; Chen, 1995; Dethof et al., 2000a, 2000b), however there have been few attempts made to date to quantify the magnitude of isentropic ozone transport or to investigate the conditions (times and places) under which it can make a significant contribution to tropospheric ozone concentrations. This research develops a novel approach for calculating isentropic ozone transport.

This new method applies the technique of contour advection with surgery, which has previously only been used to estimate the isentropic fluxes of air mass and water vapor (Dethof et al., 2000a; Dethof et al., 2000b). It is difficult to estimate isentropic ozone fluxes due to the limitations in the spatial and temporal resolutions of global ozone distributions from observations. We make a new use of the old finding that PV and ozone fields are tightly correlated (e.g., Danielson, 1968; Gidel and Shapiro, 1980; Danielson et al., 1987; Morgenstern and Marenco, 2009; Olsen et al., 2002, 2003). Using SAGE II ozone measurements and potential vorticities from the GMAO model, monthly
PV-O$_3$ relationships are developed on several isentropic surfaces; daily ozone maps are derived based on these monthly PV-O$_3$ relationships and daily analyzed PV maps. The procedure for deriving ozone maps from monthly PV-O$_3$ relationships is shown to be an effective way to obtain global ozone distributions in the mid-latitude lower stratosphere (LS) and upper troposphere (UT). Comparing the PV-mapped ozone with ozonesonde observations, the agreement in the mean is within $\pm 10\%$ (\textit{i.e.} \{PV-mapped\}-sonde)/sonde) and the correlation coefficient is $\sim 0.90$.

The net isentropic ozone fluxes across the tropopause have been estimated for 1990 and 1999 using contour advection. Although the monthly isentropic ozone fluxes from stratosphere-to-troposphere (S$\rightarrow$T) and from troposphere-to-stratosphere (T$\rightarrow$S) are of the same order of magnitude, the net effect is that ozone is transported from the extratropical LS into the subtropical UT. As the calculated monthly ozone fluxes are the strongest in summer, the isentropic STE tends to produce a decrease of ozone in the LS and an increase of ozone in the UT in summertime. These ozone changes in the LS and UT have been observed by SAGE II measurements (Wang et al., 1998a). We have calculated the column ozone in the layer between 340 K and 360 K using ozonesonde observations in the extratropics (i.e., Hohenpeissenberg, Boulder, and Lauder) and in the subtropics (i.e., Kagoshima and Naha). It is noted that these contributions to the total column ozone decrease from May till September over Hohenpeissenberg and Boulder in the Northern Hemisphere and from October till March over Lauder in the Southern Hemisphere; the contribution to column ozone increases in early summer over Kagoshima and Naha. According to Wang et al. (1998c), the zonally averaged rate for net photochemical ozone production should be less than 0.01 DU km$^{-1}$ day$^{-1}$ around 30$^\circ$
N above 200 hPa. Considering that the layer between 340 K and 360 K is approximately 2–4 km thick, the average amount of ozone generated by net photochemical production would be 0.6–1.2 DU mon$^{-1}$. The observed monthly column ozone increases between 340 K and 360 K are ~3 DU mon$^{-1}$ in early summer over Kagoshima and Naha, which cannot be explained by the net photochemical production alone. The estimated net S→T ozone fluxes over the two locations are 0.5–2 DU mon$^{-1}$ in early summer. This indicates that isentropic transport may play an important role in controlling seasonal ozone variations in the subtropical UT.

Our estimated annual isentropic S→T ozone flux between 330 K and 370 K is 189 ±55 Tg yr$^{-1}$ in 1990 and 210±61 Tg yr$^{-1}$ in 1999. The annual T→S ozone flux is estimated to be 97±25 Tg yr$^{-1}$ in 1990 and 92±24 Tg yr$^{-1}$ in 1999. The net amount of ozone that is transported into the subtropical upper troposphere annually is therefore 92±60 Tg yr$^{-1}$ in 1990 and 118±68 Tg yr$^{-1}$ in 1999. The possible sources of uncertainties in our estimates of S→T and T→S isentropic ozone STE have been indicated: the bias (±10%) of the PV mapped ozone in the LS and UT; the uncertainty (±5%) induced by a change of ±60 km in the cutoff scale used in the surgery routine of contour advection; the uncertainty (±26% in S→T; ±13% in T→S) caused by ±1 PVU in the tropopause definition; and the uncertainty (±8% in S→T; ±20% in T→S) by using different meteorological data sets, GMAO and ECMWF.

These estimates are considerably smaller than the downward S→T ozone flux due to diabatic effects, which has been estimated to be 470 Tg yr$^{-1}$ (Olsen et al. 2003), but they are nevertheless significant. According to IPCC (2001), present model estimates of total stratosphere-to-troposphere ozone transport are 400–1,400 Tg yr$^{-1}$ and there is other
evidence that diabatic processes may dominate the exchange (Schoeberl, personal communication, 2003). In certain circumstances though, such as at mid-latitudes during summer, isentropic transport may be comparable with diabatic transport. It should also be noted that the calculations in our study could have underestimated the isentropic ozone fluxes due to the restricted ability of contour advection to reproduce the small-scales at the tropopause from coarse resolution wind fields (Shepherd et al., 2000).

The differences between the estimated annual ozone fluxes in 1990 and 1999 are caused by two factors: the quasi-horizontal area where the isentropic ozone STE is diagnosed and the ozone concentrations of the transported air. The uncertainties caused by the wind fields from different GMAO models (GEOS-1 for 1990 and GEOS-3 for 1999) are included in the differences between the STE areas in 1990 and in 1990. In the NH, the area of the isentropic ozone STE is ~8% higher in 1999 than in 1990; ozone mixing ratios from ozonesondes and SAGE II measurements are ~20% higher in 1999 than 1990. Altogether, the estimated annual ozone flux in the NH is ~28% higher in 1999 than in 1990. In the SH, the estimated ozone fluxes are ~10% lower in 1999 than 1990, and this difference is mainly caused by the smaller isentropic ozone STE area in 1999. The inter-hemispheric difference of the estimated annual ozone fluxes is that ozone fluxes in the NH are ~35% higher than in the SH in 1999. This is because both the isentropic ozone STE area and the ozone mixing ratios are smaller in the SH than in the NH. The estimated annual ozone fluxes are only ~10% higher in the NH than in the SH in 1990 because of the low ozone mixing ratios in the NH in 1990.

From a global viewpoint, the isentropic cross-tropopause exchange of ozone seems to be a smaller contributor to the total ozone budget in the troposphere than
diabatic exchange. However, the two STE processes play different roles in affecting the ozone budget in the UT. The diabatic processes transfer stratospheric ozone downward into the UT mainly in the extratropics (Holton et al., 1995) and tend to increase the latitudinal gradient of ozone concentrations between the extratropical LS and tropical UT. On the other hand, isentropic transport tends to decrease this gradient by spreading the ozone-rich air that is stored in the extratropics into the tropics quasi-horizontally across the subtropical tropopause. Therefore, isentropic transport could be an important controlling factor for ozone variations in the tropical/subtropical UT under certain circumstances. For example, laminae with high ozone mixing ratios (up to 120 ppbv) were often observed in the upper troposphere over the tropical Indian Ocean during February-March 1998 (Zachariasse et al., 2000). Back-trajectory analysis indicated that these ozone-rich laminae had stratospheric origins and were transported quasi-horizontally toward the equator by the filamentations around the subtropical jet stream. In another study, Morgenstern and Carver (2001) showed that anomalies of ozone mixing ratios derived from the MOZAIC (Measurement of Ozone and Water Vapor by Airbus In-Service Aircraft) observations for five winters in 1995 to 1999 occurred most frequently in a belt spanning the subtropical North Atlantic and the Mediterranean, which coincided with filaments of isentropic transport, according to their model studies. However, neither of these papers quantitatively analyzed how much ozone had been transported through those filaments of isentropic transport.

Studies have acknowledged that isentropic transport is associated with wave breaking events (i.e., Norton, 1994; Holton et al., 1995; Postel and Hitchman, 1999). In this paper the isentropic cross-tropopause ozone transport is found predominantly over
the eastern Atlantic Ocean and Mediterranean in winter and over the Atlantic and Pacific Oceans in summer, where Rossby wave breaking (RWB) preferentially occurs (Postel and Hinchman, 1999; Scott and Cammas, 2002). According to Scott and Cammas (2002), RWB is a major contribution to isentropic mixing around 350 K. The relationship between isentropic ozone transport and RWB has been analyzed over seven ozonesonde stations on 345 K and 355 K. It is found that ~ 50% of the identified S→T (T→S) RWB cases are associated with net S→T (T→S) isentropic ozone transport; they are shown to be better associated during summer/fall than in winter/spring.

Qualitatively, it is safe to say that isentropic ozone transfer across the tropopause is important for sporadic short-term ozone variations in the subtropical upper troposphere especially in summer. However, it is difficult at present to corroborate the quantitative contribution of isentropic processes to the ozone budget in the subtropical/tropical UT, due to the lack of ozone observations with global coverage and fine resolution in the upper troposphere. Recent modeling studies (Lamarque et al., 1999; Emmons et al., 2003) have addressed the influence of STE on tropospheric chemistry. However, their modeling regime is located below the 300 hPa isobaric surface (~310 K), where the tropopause seldom intersects with isentropic surfaces and cross-tropopause transport mostly occurs diabatically (Hoskins, 1991; Holton et al., 1995). Using the available measurements from seven selected ozonesonde stations, it is noted that over 50% of the observed positive (negative) ozone anomalies are associated with net S→T (T→S) isentropic ozone fluxes in summer/fall.

The isentropic cross-tropopause ozone transport has been shown to be a potentially important controlling factor for the ozone budget in the subtropical upper
troposphere especially during summertime. However, some important research issues remain to be addressed.

(1) *Evaluations of the estimated isentropic cross-tropopause ozone fluxes*

Because isentropic STE occurs sporadically in small-scale structures, it is difficult for the present routine satellite and ozonesonde measurements to capture them, and the challenge remains to seek observational evaluations of the estimates of isentropic ozone STE. It is practically impossible at present to increase the temporal and spatial resolutions of ozone measurements globally to make them comparable to those of the isentropic ozone STE, but aircraft missions with high resolution could focus on the areas where isentropic STE mostly occurs, i.e., mid-latitude Atlantic and Pacific Oceans in summer.

(2) *Influence of the isentropic ozone STE on photochemistry*

Ozone is a primary source for the formation of hydroxyl free radical OH, which is the major oxidant in the troposphere. It is not clear to what extent ozone-rich filaments transported isentropically would contribute to the tropospheric ozone budget the photochemistry and thus change the lifetimes of species in the upper troposphere. A transport model based on contour advection could be incorporated into a chemistry model to study this issue.

(3) *Irreversibility of the isentropic ozone STE*

We have assumed that smaller spatial scale air masses would not return to the stratosphere (or troposphere) after having been transported across the tropopause, but some of these might return to the LS (or UT). Our estimated isentropic cross-tropopause ozone fluxes are sensitive to the PV value used to define the dynamical tropopause

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(which is defined as 3.5 PVU in this study). It is also noted that ~90% of the estimated ozone fluxes occur in the region enclosed by PV contours that are 3.5 PVU± 2 PVU around the tropopause (3.5 PVU). This is consistent with the singular nature of the isentropic mass transport in Dethof (2000a) and in Hall and Holzer (2003). It is possible that air masses around the tropopause could return if their residence time is short. This adds uncertainty to the ozone flux estimates and needs further investigation.

In conclusion, this research has developed a new way to quantify the isentropic cross-tropopause ozone transport. Modeling should be combined with observational data in order to better evaluate the role of the isentropic transport contribution in the build-up of tropospheric ozone at mid-latitudes in summer.
1. Contour dynamics

Contour surgery is an extension of the basic contour dynamics. The origin of contour dynamics algorithm is from the inversion of Laplace's equation \( \Delta \psi = \omega \):

\[
\psi = \int \int G(x, y; x', y') \omega(x', y') \, dx' \, dy'
\]  

(a1)

in which \( \psi \) is a stream function and \( \omega \) is the vorticity distribution, \( G = (2\pi)^{-1} \log|\mathbf{x} - \mathbf{x}'| \) is the Green's function. At each point \( \mathbf{x} \) in the fluid, the velocity is obtained by

\[
\frac{dx}{dt} = \mathbf{u}(x) = (-\frac{\partial \psi}{\partial y}, \frac{\partial \psi}{\partial x}).
\]

Exchanging the operator \( (-\frac{\partial}{\partial y}, \frac{\partial}{\partial x}) \) for \( (-\frac{\partial}{\partial x}, \frac{\partial}{\partial y}) \) and using Green's theorem to convert the area integral into line integral in (a1), the velocity can be calculated by:

\[
\frac{dx}{dt} = \mathbf{u}(x) = -\sum_i \tilde{\omega}_i \int_{\partial C_i} G(x; x_s) \, dx_s
\]  

(a2)

where \( C_i \) is the \( i \)th contour, \( \partial C_i \) is the jumps in vorticity crossing each contour \( C_i \) inwards, \( x_s \) is a point on \( C_i \), and \( x \) is any point in the fluid.

2. Contour representation

The local density of nodes \( \rho \) on a contour is approximated by:

\[
\rho = (\mu L)^j \langle xL \rangle^f
\]  

(a3)
where \( \mu \) is a dimensionless number, \( L \) is a length typical of the large-scale vorticity distribution, \( a \) is a number between 0 and 1 that determines how steeply \( \rho \) rises with curvature \( k \). Generally, the number of nodes changes in response to the complexity of the contour. The local density of nodes \( \rho \) increases where the curvature along the contour \( k \) is increasing, while \( \rho \) decreases as \( k \) is decreasing. According to Dritschel (1989), \( a = 2/3 \) is the optimum power to which the local node density increases. At each node \( i \), \( k \) is calculated by passing a circular arc with radius \( R \) through the nodes \( i-1 \), \( i \), and \( i+1 \). However, sometimes, the local density of nodes is sensitive to the nearby small-scale features as well. Therefore, Dritschel (1989) incorporated nonlocal effects by replacing the local curvature \( k_i \) in (a.1) by a weighted sum of the curvature values at all nodes,

\[
\tilde{k}_i = \sum_j \frac{e_j |\omega_j|}{d_{ij}^3} \sum_j \frac{e_j |\omega_j|}{d_{ij}^3}^{-1}
\]

where \( e_j \) is the distance between nodes \( j \) and \( j+1 \), \( \omega_j \) is the jump in vorticity across the contour segment joining \( j \) and \( j+1 \), \( \tilde{k}_j = (k_j + k_{j+1})/2, d_{ij} = \left|x_i - \frac{1}{2}(x_j + x_{j+1})\right| \), and the summation is over all nodes on all contours.

The contour between two adjacent nodes is determined by cubic spline interpolation.

The placement of nodes is consistent with the computed density of nodes and depends on the interpolation between nodes. After one time step of advecting all the nodes on contours, the desired fractional number of nodes \( a_i \) to be placed between \( i \) and \( i+1 \) is calculated by \( a_i = \sigma \rho i \), where \( e_i \) is the distance between \( i \) and \( i+1 \) and \( \rho_i \) is the desired average density of nodes between \( i \) and \( i+1 \). Fix the nodes at corners on the contour. Starting at one of the fixed nodes, let \( n \) be the next fixed nodes, therefore, the old contour
has \( n \)-2 nodes between the two adjacent fixed nodes. Compute \( q = \sum_{i=1}^{n} \sigma_i \) and define \( \tilde{n} = [q] + 2 \) (the nearest integer to \( q \) plus two). The \( \tilde{n} - 1 \) entirely new nodes will be distributed along the curved contour segments connecting the old nodes in such a way that the spacing of new adjacent nodes is approximately consistent with the desired average density.

3. Surgery

The surgery is performed when the distance between two contours that enclose the same value of vorticity or two different parts of a contour becomes less than the cutoff scale \( \delta \).

Flow chart of Dritschel (1989)'s contour surgery algorithm

1. Initiation
   a. Read in data specifying the initial conditions and algorithm parameters
   b. Calculate the cubic interpolation coefficients
   c. Redistribute nodes
   d. Save data for post-processing

2. Advection
   a. Re-calculate the cubic interpolation coefficients
   b. Calculate the velocity field
   c. Repeat steps (a) and (b) three more times to complete the Runge-Kutta integration

3. Surgery
   a. Search contours for new corners
   b. Search for contour merger situations. If a single contour satisfies the contour merger condition, break it into two contours, and introduce two new corners, one for each new contour, at the break. If two contours enclosing the same interior vorticity satisfy the contour merger condition, join them together and introduce two new corners. And, if the surgery is done near the end of a filament, remove the end of the filament if it consists of 4 or fewer nodes after surgery.
   c. Repeat step (b) until all merger possibilities have been exhausted
4. Post-surgery
   a. Re-calculate the cubic interpolation coefficients
   b. Redistribute nodes
   c. Periodically save data for post-processing
   d. Return to item (2) unless the desired number of time steps have been taken
REFERENCES


Ping Jing was born on 11 December, 1974 in Cili, Hunan, China. She attended the Nanjing Institute of Meteorology in 1992 where she graduated with a B.S. in Atmospheric Physics in 1996. She then entered the Chinese Academy of Meteorological Sciences in Beijing and earned her M.S. degree in Atmospheric Environment in June 1999. In August 1999, she came to the United States to pursue a Ph.D. degree in Atmospheric Dynamics at the Georgia Institute of Technology under the supervision of Dr. Derek M. Cunnold. This thesis marks the completion of that goal.