# **Lecture 10:** *Lecture 10, p. I– 1* **The Antarctic Ozone Hole**

# I. INTRODUCTION

# **A. BASIC DESCRIPTION**

The Antarctic ozone hole is a region of massive ozone loss that has been annually appearing since the 1970s. The hole begins to develop each August and culminates by early October, subsequently disappearing by early December. October column ozone amounts are now at least 50% lower than values seen in the 1970s.

Experiments conducted in the Antarctic region including aircraft, ground based, and satellite data have demonstrated that the ozone hole results from the increased stratospheric chlorine and bromine concentrations, combined with the peculiar meteorology of the southern hemisphere winter (Cite 6,7).

### **B. HISTORY**

#### **1. Ozone observations**

The physics of ozone was thought to be well understood in the early 1980's, as evidenced by reasonable simulations of observed data (e.g. Garcia and Solomon, 1983). This understanding was shaken by the observations by Farman et al. [1985] of a large 50% decrease in springtime column ozone over Antarctica during the decade 1975-1984. The large losses were primarily confined to the spring season (September-October). Farman et al. [1985] used a ground based Dobson spectrophotometer data at Halley Bay (76° S, 27° W) (cite 1,2). Figure I.B.1.1 displays a plot of these same Halley Bay observations which have been extended from the original 1957-1984 to include 1985 to 1995.



Figure I.B.1.1

Farman et al. found that spring total ozone values in the late 1950s and early 1960s had decreased from values higher than 300 Dobson Units (DU) to values in the low 200 DU range in the early 1980s. The original Farman et al. data only included points from 1957 to 1984, and did not include any satellite data. In was immediately clear that a large depletion of ozone was occurring over Halley Bay, Antarctica, reaching lowest values during the early October period. Farman et al. suggested that these large depletions were a result of the uniquely cold temperatures over Antarctica combined with the increasing burden of chlorine in the stratosphere. While the suggestion that the ozone hole results from the cold temperatures and the increasing chlorine was eventually shown to be correct, the proposed mechanism of Farman et al. was not correct. However, by 1985 the Farman et al. paper had opened up serious questions about the morphology and physics of these Antarctic losses, and had radically altered our perception of the capability of models to represent ozone loss processes.

Analysis of TOMS satellite data by Stolarski et al. (1986) showed that the depletion of ozone during SH spring occurred over a large area centered over the south pole, comparable to the size of Antarctica, confirming the Farman et al. results.



Figure I.B.1.2 displays 8 false color images of the Antarctic ozone hole derived from the BUV instrument (1970, 1971, and 1972), the Nimbus–7 TOMS (1979, and 1992), the Meteor–3 TOMS (1993, and 1994), and the Earth Probe TOMS in 1996 (the minimum values of the October averages from these satellite instruments are included in Fig. I.B.1.1, showing excellent agreement with the Halley Bay ground-based measurements). The ozone hole is defined as the large region of reduced ozone over Antarctica seen in the 1992–1995 in comparison to the values observed in earlier years. The spring low of total ozone over Antarctica (seen in the top 4 images) is a natural phenomena which was first noted in the 1960s (Cite 8). This ozone minimum results from normal winter Antarctic circulation patterns (Cite 9), and is not an ozone hole. The reasons for this ozone minimum will be discussed in a later section.

The largest ozone losses are observed over the Antarctic continent, but there is still substantial loss of ozone at subpolar latitudes. Figure I.B.1.3 displays the average of the October 1970, 1971, 1972, 1979 (top left), and the average of October 1992, 1993, 1994, 1995 (top right). The percent difference of these two October averages is shown in the bottom panel of I.B.1.3.



As is clear from the figure, largest ozone losses are confined to the Antarctic region. However, ozone losses are also seen in region of the high ozone collar towards the mid-latitudes. This "subpolar" ozone loss was first noted by Schoeberl, et al., [1986] using TOMS data.



Figure I.B.1.4 displays a longitudinally averaged (commonly referred to as a zonal mean) plot of each year of data displayed in Figure I.B.1.2. The precipitous drop from total ozone values above 300 DU in the 1979's \*\*\*1980s?\*\*\* is in sharp contrast to the total ozone values below 200 DU

that are now common over Antarctica. The decrease and equatorward shift *Lecture 10, p. I– 5* of the subpolar ozone maximum is also evident in this plot. It is now recognized that almost all of the ozone loss is generally confined to the Antarctic polar vortex (to be discussed in section II).

This spring low of ozone over Antarctica is a natural phenomena (see the top panels of Figure I.B.1.2 illustrating the preozone hole years), and was first noted by Dobson [1966]. Fig. I.B.1.5. (adapted from Dobson, 1966) shows the difference between the northern polar and southern polar values. In this paper, Dobson showed that Antarctic ozone values were anomalously low in comparison to springtime polar measurements in the northern hemisphere.

> "Annual Variation of Ozone in Antarctica" by G. M. B. Dobson Quart. J. Royal Met. Soc. 92, 549 552 (1966)



Figure I.B.1.5

R. Stolarski/NASA/GSFC

The black line in Fig. I.B.1.5 displays northern hemisphere polar total *Lecture 10, p. I– 6* ozone values observed in the 1960s, while the blue line illustrates the values observed in the southern hemisphere during 1964 and 1965 (the October averages of these October values are shown in Fig. I.B.1.1). The much smaller values in the southern hemisphere are a result of the circulation differences between the northern and southern hemispheres (see section II). Superimposed are 1994 observations at Halley Bay, showing that springtime total ozone levels over Antarctica are significantly lower in 1994 than during the mid-1960s, consistent with Fig. I.B.1.1. During the 1960s, ozone values were rather constant at about 300 DU between May and October over Antarctica. Over the last decade, ozone values begin to dramatically decrease during the August period, and reach minimal amounts by early October.



Other observations have shown the ozone hole, such as those from Syowa station in Antarctica [Chubachi, 1984]. Fig. I.B.1.6 displays ozone values measured by a Dobson spectrophotometer at Syowa station from February 1982 through January 1983, as adapted from Chubachi (84). These observations show very low values during the October period, consistent with

the Halley Bay data in 1994 (see Fig. I.B.1.5). The ozone decrease oc- *Lecture 10, p. I– 7* curred during the August to October period. Ozone values dramatically recovered on October 28, 1982 as the ozone hole moved away from Syowa station.



Figure I.B.1.7

Figure I.B.1.7 shows September-October 1982 false color images of the Nimbus-7 TOMS total ozone fields for individual days during the September through October period with Syowa at the center of the image denoted by the white dot. As is clearly apparent in the images, ozone decreases in the Antarctic region during the September period, with Syowa generally well inside the hole. Fluctuations in ozone occur at Syowa as the high ozone values in the mid latitudes are swept back and forth across the Antarctic coast. During the final warming period, the extremely large midlatitude ozone values irreversibly move southward over the continent, dramatically increasing the ozone values measured over the station as seen in Figure I.B.1.6. As is clear from both Figures I.B.1.6 and I.B.1.7, ozone is decreasing over Antarctica during September. The Chubachi [1984] paper was an extremely important contribution, since it showed that the Halley Bay observation of Farman et al. were consistent with those of Syowa. In addition, the Chubachi paper showed the first ozone sonde profile data on the ozone hole, demonstrating that this ozone decrease

occurred in approximately the 15-24 km region, i.e. the lower stratosphere. *Lecture 10, p. I– 8* However, in contrast to the Farman et al. paper, Chubachi [1984] failed to point out that this Antarctic decrease was a large secular decrease of total ozone.

\*\*\* Need a digitized version of the Chubachi vertical profiles figure.

#### **2. Theories**

After the initial reports of Farman et al., three theories were developed to explain the Antarctic ozone hole (Fig. I.B.2.1): the dynamics theory, the nitrogen oxide theory, and the heterogeneous chemistry theory. As will be shown in this section, the heterogeneous chemistry theory was found to be consistent with all of the observations, while the dynamics and nitrogen oxide theories were found to be incorrect.

## What causes the ozone hole?

#### **Theories**

- Dynamical theory (Tung et al., 86) vertical lifting of low ozone from lowest stratosphere and troposphere. Invalid N<sub>2</sub>O from ER 2 during AAOE show low values associated with  $O<sub>3</sub>$  loss
- Solar theory (Callis and Natarajan, 86) production of reactive nitrogen (NO<sub>x</sub>). Invalidd ER 2 NO<sub>x</sub> measurements, ozone hole should have disappeared in late 80s.
- E Heterogeneous Chemistry (Solomon et al., 86; McElroy et al., 86a; Toon et al., 86; Crutzen and Arnold, 86; McElroy et al., 86b) Heterogeneous chemic free CI from reservoir species via reactions on surfaces of PSCs.

Figure I.B.2.1

The original Farman et al. paper attempted to explain the ozone losses by pointing out that there was: 1) no apparent shift in meteorological parameters (temperature and winds), 2) weak transport effects, 3) an increase in halocarbon levels, and 4) extremely cold temperature. Farman et al.

estimated over Antarctica might be shifting the chlorine balance over *Lecture 10, p. I– 9* Antarctica, leading to greater ozone loss. Based on the Farman et al. mechanisms, McElroy et al. [1986] and Solomon et al. [1986] both computed ozone loss rates that were much too small to explain the large ozone losses seen during September. Both models found that abundances of O atoms (necessary for the catalytic destruction of ozone) in the model were too low at the altitudes where Chubachi showed that most of the ozone loss was taking place. Hence, the Farman et al. theory was fond to be incorrect in some of its prime elements.

The dynamical theory of the ozone hole proposed that the Antarctic circulation had changed. It has long been recognized that the dominant circulation of the lower stratosphere in winter is such that high ozone air is carried poleward and downward. As explained in the previous sections on the circulation of the stratosphere, this will lead to a build up of ozone in the mid-to-high latitudes over the course of the winter. The dynamical theory proposed that this normal pattern was changing, and that ozone poor air from the troposphere was being transported into the lower stratosphere, instead of the ozone rich air from higher altitudes in the midlatitudes (Tung, 1986). If low ozone air from the troposphere air was being transported into the lower stratosphere, then other long-lived trace gases should also be measurable in the lower stratosphere. An example of such a tracer is nitrous oxide (N2O), which is produced in the troposphere by biological processes, and is destroyed in the stratosphere by either photolysis by UV radiation (wavelengths less than 240 nm) or by a reaction with O atoms (WMO, 1985). The loss of N2O takes place in the upper stratosphere, since O atoms are generally produced by the photolysis of O2 and these UV wavelengths that produce O2 and N2O cannot penetrate into the troposphere. Hence, N2O has fairly high values in the troposphere (~300-310 ppbv) and low values in the upper troposphere. This general profile of N2O has been confirmed by satellite, balloon, and aircraft observations. The dynamical theory predicts that Antarctic N2O

values should be high if the air was transported upward from the tropo- *Lecture 10, p. I– 10* sphere into the lower stratosphere where ozone was low. Figure I.B.2.2 displays a plot of N2O measured during the Airborne Antarctic Ozone Experiment on September 9, 1987. The observations show that N2O is substantially lower than values characteristic of the troposphere (300 310 ppbv) in the region where ozone losses had been observed. These N2O observations (amongst other long-lived trace gas observations) clearly demonstrate that air inside the lower stratospheric Antarctic polar vortex had descended from the middle and upper stratosphere, and that the air ought to contain the higher ozone concentrations (e.g., see Loewenstein, et al., 1989).



Figure I.B.2.2

The nitrogen oxide theory of the ozone hole was proposed by Callis and Natarajan (1986), and suggested that large amounts of NOx was being produced during the solar maximum in 1979. This NOx would be transported into the polar lower stratosphere by a slow poleward and downward advection. The loss process would occur catalytically as:

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$$
NO+O3 \rightarrow NO2+O2\nNO2+O \rightarrow NO+O2\nO3+O \rightarrow 2 O2
$$

Measurements of NO2 at high latitudes indicate very low concentrations during the spring period of the ozone hole (e.g. Farmer et al., 1986; Coffey and Mankin, 1989).



Figure I.B.2.3

Figure I.B.2.3 displays column abundances of NO and NO2 measured from the NASA DC-8 on September 21, 1987 (Toon et al., 1989). The data show that NOx decreases between the mid-latitudes and the interior of the polar vortex, in disagreement with the predicted effect of the downward transport. In addition, the satellite observations of total ozone (Figure I.B.1.1 and I.B.1.2) reveal no solar cycle variation of the depth of the ozone hole. As was pointed out by both McElroy et al. (1986) and Solomon et al. (1986),

The third theory of the ozone hole involves heterogeneous chemical reactions on the surfaces of particles that formed in the cold lower stratosphere of the Antarctic vortex. Originally proposed by McElroy et al. *Lecture 10, p. I– 12* (1986) and Solomon et al. (1986), this theory proposed that reactions which normally do not occur in gas phase, might be greatly enhanced if a chlorine containing compounds such as ClONO2 and HCl could collect on the surfaces of these particles and then react to free the chlorine into a reactive form that could cause large ozone losses. As will be described in the following sections, this heterogenous theory explains the polar ozone losses.