Lecture 3: Morphology of Ozone

INTRODUCTION

Ozone is a molecule consisting of three oxygen atoms that is found mainly in the stratosphere where it is created. Figure 3.1 provides a sketch of how ozone is formed.



Figure 3.1

First, extreme ultraviolet radiation (EUV) breaks apart oxygen molecules (O_2) to free oxygen atoms (O). These free O atoms then react with other O_2 molecules to form ozone (O_3) . Because O_3 production depends upon sun-

light, it is not surprising that the distribution of ozone varies considerably with altitude, latitude, season, year, and time of day. Before we look at the variation of ozone, however, we should first examine the units in which ozone is measured.

Ozone measurements are typically reported in one of four units:

- mixing ratio in parts per million by volume (ppmv)
- number density (molecules/cm3)
- partial pressure in nanobars (nb)
- total column amount in Dobson units (du).

Each of these ways of quantifying ozone provides its own perspective on ozone distribution.

OZONE PROFILES

If we want to understand how ozone is distributed vertically, we examine profile measurements of ozone concentration. Profile measurements can be made by balloon borne instruments known as ozonesondes, laser instruments called lidar, and profiling satellite instruments (see Lecture 7 for more instrument details). These measurements are usually reported in mixing ratio, number density, or partial pressure. Mixing ratio in ppmv relates the fractional concentration of ozone as the number of ozone molecules per million air molecules. Number density refers to the absolute concentration as the number of ozone molecules per cubic centimeter. Partial pressure refers to the fraction of the atmospheric pressure at a given altitude for which ozone is responsible.

Ozone profiles (ozone versus altitude) as measured in each of these units appear somewhat different, as evidenced by Figure 3.2. This figure shows three ways of looking at the same ozone data. The satellite instrument known as the Stratospheric Aerosol and Gas Experiment II (SAGE II) reported this measurement at 40° S on September 11, 1994, late winter in the Southern Hemisphere. We first notice that the partial pressure and number density profiles are very similar.

SAGE O₃ Profile 940911 (40°S, 105°E)



This similarity is due to the fact that the partial pressure of ozone can be expressed as a function of the number density where

 $P_{ozone} = (number density)kT$

k is Boltzman's constant (1.38 x 10²³ J/K) and T is temperature measured in degrees. While all three profiles peak between 20 and 40 km and fall off rapidly above and below the peak, the mixing ratio profile peak is significantly higher in altitude than that for the profiles measured in number density or partial pressure. Also, features appearing prominently in the number density and partial pressure profiles (such as those marked with arrows) appear insignificant in the mixing ratio profile. The basis for these differences can be derived from Lecture 2.

Recall from Lecture 2 that Earth's atmosphere is not homogeneous: the higher you go in altitude, the fewer molecules there are. A cube 1 m on each side at the ground will contain about 45 moles of air (1 mole = 6.022×10^{23} molecules). That same cube at 10 km altitude will contain just over 13 moles of air. Clearly, number density declines with altitude.

Mixing ratio, however, behaves differently. This measure of concentration takes into account the fact that there are fewer molecules higher up, and

reports the fractional composition of the air molecules everywhere. Here's another way to think about mixing ratio: the cube we used to compute number density was rigid—it always contained 1 cubic meter of air. To compute mixing ratio, we will use an elastic balloon that always holds 1 20th of a mole of air. At the ground, this balloon will fill a volume of about one liter (10⁻³ m³). At 10 km, however, the balloon will have to be quite a bit larger (about 4 times as large, in fact) to contain the same number of molecules. In each case, the ozone mixing ratio will be the fractional number of molecules in our balloon that are ozone molecules. If we were to fill our balloon at the ground with a mixture of one part ozone to nine parts air (an ozone mixing ratio of 0.10), seal it, then slowly carry it upward to 10 km, the balloon would expand to a volume about four times as large as it occupied at the ground. Nevertheless, the balloon would still contain exactly the same ozone mixing ratio since we've neither let gas into the balloon nor let gas out. Ozone mixing ratio is therefore said to be conserved following air parcel motion. This characteristic makes mixing ratio an excellent tool for diagnosing atmospheric motion. The type of question you are trying to answer helps to determine whether mixing ratio or number density is more appropriate. Can you now explain why the small bumps in the mixing ratio profile result in such large bumps in the number density profile near 10 km?

We still need to explain why ozone profiles peak at all, especially given that in Lecture 2 we learned that the number density of molecules in the atmosphere drops off rather rapidly with height. Why should ozone behave differently? The answer to this question relates to photochemistry and will be explored more thoroughly in Lecture 5. Here's a brief explanation for now.

Recall that ozone is created mainly in the stratosphere. It is not surprising, therefore, that most ozone molecules will be found in the stratosphere. Below the peak and closer to Earth's surface, less ultraviolet (UV) light penetrates to break apart the oxygen molecules (see Lecture 5). The shielding of the lower atmosphere from UV light is actually provided by the ozone molecules above (see Lecture 4). In a sense, ozone in the stratosphere inhibits the formation of ozone lower in the atmosphere, keeping ozone concentrations small at low altitudes. Above the peak, a decrease in the density of air molecules (including oxygen) leads to increased intense UV radiation (which causes quick formation and destruction of ozone). The net result is smaller ozone concentrations above the peak. Therefore, we expect ozone to peak in the stratosphere (which it does) and to decrease both above and below.

OZONE COLUMN AMOUNTS

A third measure of ozone is the one you're most likely to have encountered in the media: the Dobson unit. A Dobson unit is a measure of the total amount of ozone in a column extending vertically from Earth's surface to the top of the atmosphere. This measure of ozone is directly related to the amount of UV exposure received at the surface: the less total ozone, the more UV light penetrates, the faster you get sunburned. While the consequences of less ozone are rather straightforward, understanding the unit in which column ozone is measured will require a bit of explanation.

Let's start at the top of the atmosphere. And let's say we've created a special net that collects ozone molecules but lets every other molecule in the air pass right through. We pull our net straight down from the top of the atmosphere to the ground and stack up our ozone molecules nice and neat at the surface at a temperature of 0°C. The Dobson unit is a measure of the height of our stack of ozone molecules: 1 du = 10^{-5} m. A typical mid latitude air column contains about 300 du of ozone, which is equivalent to a stack of ozone molecules about 3 mm high, about the thickness of two stacked pennies, see Figure 3.3.

For comparison, a column taken in the ozone hole (see Lecture 10) contains only about 100 du of ozone, a stack of molecules about the height of a dime.

<section-header> Jobson Units Image: Stress of the stress of the

Figure 3.3

OZONE DISTRIBUTION

Now that we have a better understanding of the language of ozone measurements, let's take a closer look at the distribution of ozone.

We have seen that a typical ozone profile has low values at the surface, increasing values with altitude into the stratosphere, and decreasing values in the upper stratosphere and mesosphere. The exact altitude of the peak varies with latitude and season. Figure 3.4 shows an average of ozone profiles taken at tropical, mid, and high winter latitudes.



SAGE II O₃ Profiles September 1994

SAGE II measurements from September 1994 again provide all the ozone profiles seen in this figure. The altitude of the peak of the ozone distribution is clearly higher in the tropics than the mid and high latitude profiles. The somewhat narrower peak of the tropical profile and midlatitude profile leads to smaller total column ozone amounts in the tropics than in the mid to high latitudes. There are exceptions to this behavior: frequently ozone profiles show laminae-sharp positive and negative variations in ozone from the normal ozone profile shape (***need reference). Most of these laminae are associated with dynamical events such as those described in Lecture 6. High latitude profiles (outside the ozone hole) have peaks that are typically lower in altitude than both the midlatitude and tropical peaks. These peaks (in number density) are also typically larger in magnitude than their tropical and midlatitude counterparts, as demonstrated in Figure 3.4.

The most noteworthy, abnormal ozone profiles to date are those associated with the Antarctic ozone hole. Figure 3.5 shows an average high latitude ozone profile taken outside the ozone hole and an average profile taken inside by the SAGE II instrument in September 1994.



SAGE II O₃ Profiles September 1994

Note the large notch in the ozone hole profile, exactly at the point where ozone values are reaching their maximum in the more typical high latitude profile. What is clear from comparing these two ozone profiles is that something unusual is happening inside the ozone hole, destroying ozone in exactly the place where it is normally plentiful. The cause of this notch is related to the meteorology of the southern hemisphere winter and to chemical reactions of ozone with chlorine. The details of this type of ozone loss are explored more thoroughly in Lecture 10.

Let's investigate one more characteristic of the vertical behavior of ozone. Figure 3.6 shows a map of ozone as measured by the Solar Backscatter Ultraviolet (SBUV) instrument for the 50 mb (about 21 km) level. This altitude is below the peak in ozone (see Figure 3.4). Few UV photons therefore penetrate to this level to create or destroy ozone. As a result, the "lifetime" of an ozone molecule (or the time between its creation and destruction) at this altitude is, on average, rather long (weeks to months). Gases with long lifetimes are called trace gases because they can be used effectively to trace the motion of air parcels. As an analogy, drop a rubber ducky in your bathtub. Then stir the water in the tub. The rubber ducky floats around the tub, following the currents in the water. By tracking the position of the rubber ducky as a function of time, you can determine the motion of the water in the tub. In the same way, ozone at this level acts as a tracer of air motion.

As can be seen in Figure 3.6, the ozone mixing ratio is low in the tropics and low at higher latitudes. A ring of high ozone, often called the "collar" region, surrounds a region of low ozone centered on the south pole.





Figure 3.6



Figure 3.6a

Looking a bit higher up, Figure 3.6a shows the SBUV ozone measured at 15 mb (about 29 km, near the peak of the ozone profile expressed as a mixing ratio). Here we see high ozone in the tropics and low ozone in the polar regions. A filament of low ozone can also be seen extending away from the polar region in the southern hemisphere $(30^\circ-60^\circ \text{ S}, 210^\circ-290^\circ \text{ E})$. The air within this filament can be traced back to the polar vortex region (the isolated polar air mass of low ozone—see Lecture 2).

If we now look at a map of ozone at a higher altitude on exactly the same day, we see a very different picture. Figure 3.7 shows a map of ozone, again from SBUV, this time at 0.5 mb (about 53 km).



Figure 3.7

At this altitude few of the UV photons have been blocked out. Ozone molecules are, as a result, created and destroyed very rapidly. The lifetime of ozone is very short, so ozone is described as being photochemically controlled. We'll look into the photochemical properties of ozone in the next chapter. For now, we just need to know that at altitudes where ozone is photochemically controlled the ozone distribution will show no dynamical features. Compare Figure 3.6 with Figure 3.7. Notice that neither the filament of low ozone emerging from the southern polar vortex at 50 mb (29 km) nor the collar region of high ozone around the polar region at 15 mb (21 km) appear at the 0.5 mb (53 km) level. We will see shortly if an how these differences impact the amount of ozone in the total column.

TOTAL OZONE MEASUREMENTS

Column ozone measurements are the ones more frequently reported in the media. Interest in these measurements is generated by their relevance to biological life forms at Earth's surface. As we mentioned before, ozone absorbs UV radiation. UV radiation significantly impacts life at the surface: the less ozone overhead, the more harmful UV radiation gets through. The impact of UV radiation on life is discussed further in Lectures 4 and 8.



Figure 3.7a

Figure 3.7a shows a global map of total column ozone for the same day as the SBUV maps in Figures 3.6 and 3.7. We see low values of total ozone in the tropics, a small region of low total ozone in the North Polar region, and a large region of low ozone over Antarctica. This latter low ozone region is known as the Antarctic ozone hole (see Lecture 10). While in some ways this map appears similar to Figures 3.6 and 3.6a, in many ways it is quite different. The filament of low ozone visible in Figure 3.6a is not apparent in Figure 3.7a. Furthermore, the tropics are high in ozone in Figure 3.6a but low in ozone in Figure 3.6 and low in total column ozone (Figure 3.7a). Meanwhile, Figure 3.7 contains almost no features in the ozone distribution whatsoever. Looking at the ozone distribution at a single altitude clearly cannot tell us what the total ozone distribution will look like.



Figure 3.8

Average Total Ozone Field

Figure 3.8 shows a global map of total column ozone as compiled from an average of all the data from the Total Ozone Mapping Spectrometer (TOMS) instrument (see Lecture 7 for a detailed description) gathered between 1978 and 1993. We see that the tropics (roughly the region between 30° N and 30° S) is relatively low in ozone, with total column amounts of between 250 and 270 du. We could have guessed that the tropical column ozone amounts would be relatively low simply from the shape of the profile in number density (see Figure 3.4). As we move northward away from the equator, typical mid latitude values fall between 300 and 350 du. At the highest northern latitudes we see the highest values—almost 400 du.

The southern hemisphere, however, appears quite different. While the southern mid latitudes again show 300-350 du ozone columns, the southern polar region reveals values of ozone again below 300 du. The difference between the two hemispheres in this figure is largely related to the presence of an ozone hole over Antarctica in the Austral spring and corresponding lack of an ozone hole over the North Pole during the northern spring. Even before the ozone hole, however, there were differences between the wintertime amounts of total ozone (as we show with Dobson's data below). The general pattern of low column ozone in the tropics and higher ozone at mid and high latitudes can be attributed to the atmospheric circulation and will be discussed in more detail in Lecture 4. In brief, rising motion in the tropics elevates the height of the ozone peak while poleward transport carries the newly created molecules away from the tropics. These processes combine to reduce the magnitude of tropical ozone profiles. At high latitudes, sinking motion lowers the height of the ozone peak, while transport brings in air rich in ozone leading to an increase in the magnitude of ozone.

Monthly Means

We've seen that ozone varies as a function of altitude and latitude. We should not be surprised to find that ozone varies as a function of season as well. Again, the creation and destruction of ozone depends on the amount of sunlight available. Sunlight varies throughout the year, most noticeably at the poles that exist for about 6 months in darkness and 6 months in light. Figure 3.9 shows the monthly mean distribution of ozone for each month of the year as derived from the TOMS record (1978–1993). The gray regions represent areas in which TOMS is unable to make observations due to the lack of sunlight (I.e., regions in polar night). While the gross features are quite similar to those seen in Figure 3.8, we notice quite a bit of variability from that data. If we were to average all 12 plots in Figure 3.9, however, the result would appear very much like Figure 3.8.



Figure 3.9

In northern winter, we see very large ozone column amounts (>400 du) at high northern latitudes. The tropics are at their lowest at the same time with less than 250 du. The mid latitudes in both hemispheres fall in the 300–350 du range. Notice that in the northern hemisphere no region of low ozone appears at any time.

As we move into northern summer the ozone values at high northern latitudes fall off such that by August they are in the 300–350 du range. Meanwhile, tropical ozone values have increased to 250–270 du.

We turn our attention southward in September. Regions of high ozone (~400 du) appear at mid southern latitudes and surround a region of low ozone (<200 du) over Antarctica. By far, the ozone values observed in the Antarctic ozone hole are the lowest values observed on the planet in any given year.

By December, the ozone hole has disappeared, ozone values at high southern latitudes have recovered to 300–350 du, and ozone appears to be falling in the tropics while increasing at high northern latitudes. An easier way to see these seasonal changes in ozone is by looking at a zonally averaged plot of ozone versus time. Figure 3.11 shows such a plot.



Mean Annual Cycle

Figure 3.11 shows the average amount of column ozone in a given latitude band (the y axis) as a function of time (the x axis). We derive this type of plot by averaging together in latitude bands plots similar to each of the 12 plots in Figure 3.9 in latitude bands. That is, we draw lines on the globe parallel to lines of latitude, then average together all the TOMS measurements falling between each pair of lines. In this way we can produce a single, "zonal mean" (average in a latitude band) value of ozone corresponding to each latitude.

These data are taken from the Total Ozone Mapping Spectrometer (TOMS) and represent an average of all the monthly mean TOMS data taken between 1978 and 1993. The gray patches in the corners again represent regions in which no data were available due to polar night (see Lecture 7). Notice that the tropics show the least variation, with values consistently between 220– 300 du. At high latitudes, however, variations of up to 50 percent can be seen in the course of a year. In the northern hemisphere peak values are found during late winter and early spring with minimum values in the fall. In the southern hemisphere the picture is somewhat more complicated. We can see in September and October the presence of the ozone hole at the southernmost boundary of the data, with values near 200 du. By December the ozone hole has disappeared, and values have returned to over 300 du. Slightly further north a region of high ozone appears in late winter and early spring with typical ozone values around 400 du. This high ozone region surrounding the low ozone found in the polar vortex has been called the "collar" region and can be seen even more prominently in the September, October, and November monthly mean plots of Figure 3.9.

By summer ozone has returned to around 325 du. The TOMS data clearly indicate an annual cycle to ozone. That is to say, ozone variations of up to 40 percent occur naturally over the course of a year due solely to differing amounts of sunlight. The annual cycle, however, cannot explain the extremely low values of ozone found over Antarctica in recent years. To generate such low values of ozone, chemical destruction of ozone is required. Other cycles can be seen in the TOMS data as well. In addition to the annual cycle, ozone displays a semiannual oscillation and a quasi-biennial oscillation, named for the periods associated with the variability. A more detailed discussion of these variations can be found in lectures 2, 6, and 8.

Total Ozone Trends

Hidden in the averaging to produce Figures 3.9 and 3.11 are the changes in ozone that have been occurring with time, particularly in the southern hemisphere winter. We noted that the lowest values in the graph of the mean annual cycle from the TOMS data were just under 200 du in September and October at high southern latitudes. Yet we also know that recent observations of the ozone hole have indicated values around 100 du. Why the discrepancy? Well, let's look more carefully at the various Octobers that we included in our averaging to produce Figure 3.9. Figure 3.13a shows monthly mean TOMS data for all the Octobers between 1979 and 1994.



Figure 3.13a

October 1979 reveals no ozone hole. Values in the polar regions in 1979 remained around 300 du during the Austral spring season. However, as we move through the '80s, ozone in the south polar region steadily decreases. By 1993 values as low as 110 du can be seen. Figure 3.13a indicates that the amount of ozone in the southern polar region has been changing quite dramatically since TOMS starting making observations. When we average all of these plots together, the result is the October map in Figure 3.9.

Historical Measurements—So how did ozone look before TOMS? To understand the answer to that question we'll need to examine ozone data from one of the pioneers in ozone studies. G.M.B. Dobson (for whom the unit of column ozone was named) had been observing ozone since the 1920s with instruments of his own design. He compiled a long record of data from the northern hemisphere and knew well how ozone behaved over Europe. Figure 3.14 shows data from one of his instruments deployed in Arosa, Switzerland. This data set represents the longest existing continuous record of ozone measurements. Each data point in the plot is an average of all the measurements made at Arosa that year. The record shows significant variation from year to year, but clearly indicates a downward trend over the last 20 years or so. The downward trend here has nothing to do with the ozone hole and will be touched upon in later lectures.

McPeters June 14, 1995



Figure 3.14

In the 1950s one of Dobson's instruments was deployed in Antarctica as part of the International Geophysical Year (IGY). IGY was a coordinated effort among a variety of Earth scientists to make measurements relevant to the Earth system in as many places as possible at the same time. By the IGY Dobson's instruments had been set up at a variety of locations around the world. In 1965 Dobson published a report on the data he had gathered. To his surprise, he observed that ozone behaved quite differently over Antarctica than over high northern latitudes. Figure 3.15 shows Dobson's data from ground stations in the northern and southern hemisphere, with one shifted relative to the other by 6 months to account for the hemispheric seasonal phase differences.

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



This figure demonstrates that during the southern winter high latitude ozone values are much lower than the corresponding period in the northern hemisphere. A clear difference in the behavior of ozone between the two hemispheres is also evident from his data. The figure indicates, however, that the low levels of ozone Dobson measured over the Antarctic were still significantly higher than those found today over the same regions. The amount of ozone over the Antarctic in late southern hemisphere winter and early southern hemisphere spring has decreased dramatically over the latter half of the twentieth century. We explore the causes of these changes in Lecture 10.

Global Mean Changes—Long-term changes in ozone can be understood by examining the global mean ozone as a function of time. Figure 3.16 shows an average of all the TOMS data taken between 60° N and 60° S as a function of time. Clearly visible in the record is an annual cycle, with the highest values in northern spring and the lowest in northern winter. The data record, however, is far from periodic. We can see that there are year to year variations in the magnitude of ozone, and some higher order variability in the data as well. Analyzing such a signal and determining trends can be complicated (see Lecture 8).



If we now look at similar average records, but over more limited latitude ranges, the picture becomes somewhat different. Figure 3.17 shows the global mean in black, an average between 30° and 50° N in blue, and an average between 20° S and 20° N in red. Note that the amplitudes of both these curves are greater than that of the global signal. Also notice that the variability of the red (tropical) data is much less than that of the blue (northern mid latitude) data. Can you explain why this might be the case? We'll tackle this issue in Lecture 8.



Figure 3.17

Day to Day Variability

We now have a good sense of how ozone varies vertically, seasonally, and with latitude. We might also be interested in how ozone varies from day to day over someplace we live.



Figure 3.18 shows such a record of ozone measurements over Fresno, California. In green are data from the TOMS instrument. In red are data from a ground based instrument known as a Brewer Photospectrometer (see Lecture 7 for more details). The scales for the two measurements have been offset from one another to facilitate comparison. First of all, we note that the two measurements agree quite well with each other: TOMS and the ground base observations seem to observe high ozone events simultaneously and low ozone events simultaneously. The two instruments also report similar magnitudes for column ozone of about 300 du. Finally, they both report day to day variations of a similar magnitude. The largest excursions seem to be about 25 percent from one day to the next, but more typically both instruments report a day to day variation of under 5 percent.



Figure 3.19

Figure 3.19 shows the frequency distribution of ozone variability from day to day. Notice that the distribution is sharply peaked around 0 percent change, with tails extending to about + or -25 percent. While ozone varies by as much as 25 percent from one day to the next at northern mid latitudes, the occurrence of such dramatic changes is rare. Figure 3.18 also suggests that variability is greater during the winter months than during the summer months. The difference in day to day changes in ozone can be attributed to more active weather patterns in winter than in summer and will be discussed further in Lecture 6.

SUMMARY: What Have We Learned About the Behavior of Ozone?

Most ozone is found in the stratosphere, with peak values of number density of 5 x 10¹² molecules/m³ around 22 km and a peak value in mixing ratio of 8–10 ppmv around 35 km. In addition to the difference in appearance of the

ozone profile due to the units in which it's measured, the shape and the peak altitude of the profile varies with latitude and season. The shape of the profile can also vary due to dynamical or chemical processes, the most notable example being profiles taken in the Antarctic ozone hole, where large chunks of ozone profile have been lost.

Below the ozone peak, ozone molecules have long lifetimes and therefore behave essentially as a tracer of atmospheric motion. Above the ozone peak, ozone is photochemically controlled—rapid creation and destruction of ozone molecules lead to a short lifetime. Dynamical features evident in ozone fields at low altitudes where ozone lifetimes are long do not appear at high altitudes where ozone is photochemically controlled.

TOMS measurements show that a typical column of ozone contains about 300 du. Measurements vary significantly with latitude and season. The largest values of ozone are typically found at high northern latitudes during winter, and mid to high southern latitudes during Austral winter. Low values are always seen in the tropics, and seen in the Antarctic regions during the Austral spring when the ozone hole is present.

Time series of the TOMS data have shown that ozone in Antarctica during the Austral spring has steadily decreased since 1978. In fact, there did not appear to be an ozone hole in the TOMS data in the late 1970s. Recent ozone measurements in the Antarctic ozone hole have fallen below 120 du.

We also know from Dobson's data that no ozone hole existed back in the 1950s. While Dobson showed that the annual cycle of ozone over Antarctica was quite different from what had been seen in the northern hemisphere, Dobson's measurements were some 180 du higher than what TOMS reports today. By examining the zonal mean TOMS data, we have been able to observe and characterize the annual variability of ozone. Long time series records of averaged TOMS data showed a clear annual cycle, but also year to year variability and some higher order variability as well. Data from the northern mid latitudes showed larger annual variability, but less high order variability. The Fresno data set indicated that ozone can vary by as much as 25 percent from one day to the next. Typical variability, however, is on the order of 5 percent or less.