Introduction

In this exercise you will participate in a group activity which involves measuring and then interpreting the profile of ozone in the atmosphere from the ground to the stratosphere.

This activity has two distinct aims:

- **1.** To give you experience on how to plan a field experiment to make the best use of limited resources to investigate worthwhile scientific questions.
- **2.** To understand the properties of ozone in the troposphere and stratosphere and to understand and interpret data from an ozonesonde profile.

Format of activity

Ozonesondes are much like normal meterological sondes as they are carried on a balloon and measure some aspect of the atmosphere. They are moderately expensive (\pounds 500) pieces of atmospheric monitoring equipment used to produce profiles of atmospheric ozone in the vertical. On Arran we have available **a single** ozonesonde. It is therefore important that we choose to launch the ozonesonde in conditions where it will produce the most scientifically interesting and valuable data. The ozonesonde activity has three parts:

- On the first afternoon each group will have one hour to design a short project proposal for when to launch the ozonesonde. You will have been informed in the introductory lecture about any restrictions on when the ozonesonde can be launched. Each group will produce a proposal of **1 side of A4** which should be submitted to the shared drive with your groups name by 1600 Local Time. The proposal should contain the following information:
 - When you would like to launch the ozonesonde?
 - What scientific questions you hope to answer?
 - The reasons behind your launch choice

When designing you experiment, a critical part of your choice will be the meteorological conditions predicted for the day in question. You can make use of the forecast charts provided for the weather forecasting activity and the other data sources described later.

• Once the hour is over each group will nominate a spokesperson to present their case to the scientific steering group made up of three members of staff. You should present your groups case using **no overheads** and talk for **not longer than five minutes** outlining the case as written in your document. Following all the presentations the steering group will meet to decide which of the proposals to take forward and will announce the chosen proposal during dinner.

You will not be assessed on the project proposal that you write but on your reflective discussion of the comparison of your group's proposal with the proposal which is successful (see below for more details). The criteria for assessing the project proposals will be as follows:

- i. Maximum chance of observing interesting atmospheric phenomena.
- ii. Best scientific arguments for launching at that particular time.
- iii. Best technical arguments for launching at that particular time.

- The ozonesonde will be launched following the instructions in the chosen proposal. Once the data is collected it will be available to you on the shared drive. Your group should produce a plot of the ozone profile from the ozonesonde and then follow the instructions in the assessment section on how to complete your analysis.
 - Some scientific projects that you might like to consider for your launch proposal are as follows, see below for more details of these phenomena:
 - i. The identification of different tropospheric air masses and their origin above Arran.
 - ii. An investigation of the influence of the passage of a front on atmospheric chemical structure.
 - iii. The investigation of high ozone smog in the boundary layer.
 - iv. The analysis of the structure within a tropopause fold.
 - v. The identification of an ozone mini-hole
 - vi. The validation of an ECMWF/GEMS ozone forecast

There are however many other uses for an ozonesonde and you should attempt to be as creative as possible.

Background information on atmospheric ozone

Ozone as an atmospheric gas

Ozone (O_3) plays a central role in both the chemistry and physics of the atmosphere. It is a molecule made up of 3 oxygen atoms. It is found throughout the atmosphere but its chemistry and physics is very different in the troposphere and in the stratosphere.

Ozone plays a significant role in climate. Figure 1 is taken from the latest report by the Intergovernmental Panel of Climate Change and shows the radiative impact of different gases. You will notice that the increase in O_3 due to anthropogenic emission in the troposphere has led to a net warming of the planet, whereas the loss of O_3 in the stratosphere again by anthropogenic emissions has lead to a net cooling.



Figure 1. Taken from: Contribution of Working Group I to the Fourth Assessment Report of the IPCC, Cambridge University Press, ISBN 978 0521 88009-1

Ozone in the stratosphere

Most of the ozone in the atmosphere resides in the stratosphere between about 70 and 1hPa. An example zonal (averaged along a latitude band) climatology of ozone (derived from a combination of models, ozonesondes and satellite data, is shown in Figure 2). There is a discussion of units for measuring the concentration of O_3 later.



Figure 2. Annual mean ozone climatology taken from Fortuin and Helder climatology. Units are parts per million by volume.

Ozone in the stratosphere is formed through the interaction of ultra-violet radiation (short-wave radiation from the sun) and standard double bonded oxygen molecules (O_2) which exist throughout the atmosphere. The high ozone concentrations in the tropical middle stratosphere are related to the large amounts of ultra-violet radiation observed there. Ozone is transported through the stratosphere by the planetary scale Brewer-Dobson circulation. This circulation involves transport of air upwards in the tropical stratosphere, toward the pole and then downward into polar regions. Due to the Brewer-Dobson circulation, total column amounts of ozone (the total amount of ozone summed from the bottom of the atmosphere to the top) are generally largest in the polar regions. The amount of ozone in a column of air (add up all the ozone molecules from the ground to the top of the atmosphere at a single point) is measured using Dobson Units (DU) (Units are described in more detail later in this section).

A typical daily maps of total column ozone, derived from two satellite instruments is shown in Fig. 3.



Figure 3: Combined SBUV/2 and TOVS observations of total column ozone in Dobson Units. Taken from http://www.osdpd.noaa.gov/PSB/OZONE/TOAST/

Stratospheric ozone has received much attention over the past thirty years because of the influence of anthropogenically produced chlorofluorocarbons or CFCs on ozone concentrations. CFCs are long-lived atmospheric gases used for refrigeration and aerosol sprays. Although these gases are normally unreactive, through a sequence of complex chemical and physical transformations in the stratosphere they are able to destroy stratospheric ozone. The ozone depleting reactions require the presence of sunlight and are much faster in the presence of polar stratospheric clouds. Polar stratospheric clouds form at very low temperatures in the stratosphere (< 195K). Some of the, normally slow, gas phase reactions involved in ozone depletion can proceed much faster on the surfaces of polar stratospheric cloud droplets. Although chemical ozone depletion has been observed in both the Arctic and Antarctic, it is generally much more intense and persistent in the Antarctic. In the Antarctic, stratospheric temperatures are colder than the Arctic, and allow polar stratospheric clouds to form more frequently and over a larger area leading to the more intense ozone depletion.

The destruction of stratospheric ozone is important to understand because ozone forms the primary shield against the dangerous effects of incoming stratospheric UV-B radiation. When stratospheric ozone amounts are low, large amounts of UV-B can reach the surface. Exposure of biological life, including humans, to UV-B radiation increases the risks of cataracts, skin cancer and suppression of the immune system.

Ozone in the troposphere

Ozone in the troposphere is usually a destructive force. It is an oxidizing agent and thus causes human health impact by attacking people's lungs, it attacks plants reducing crop yields and damages plastics and other materials increasing wear etc.

Not enough high-energy radiation from the sun enters the troposphere for O_3 to be made by the photolysis of O_2 , instead tropospheric O_3 is made by a complex set of chemical catalytic reactions involving oxides of nitrogen (NO and NO₂ collectively knows as NO_x) and oxides of hydrogen (OH and HO₂ collectively known as HO_x)

 NO_x is naturally emitted into the atmosphere by microbes in the soils and from lightning. However the dominant source is the high temperature combustion associated with internal combustion engines, jets etc. Eventually the NO_x emitted into the atmosphere reacts to form nitric acid. This is stable and soluble and is eventually removed to the surface by rain.

 HO_x is mainly made in the atmosphere by the photolysis of O_3 and the subsequent reaction of the high energy oxygen atom with water. This produces an OH radical. The OH radical can be converted into an HO_2 radical through its reaction with CO. The HO_2 radical can be converted back to an OH radical through its reaction with NO.

It is the interaction between HO_x and NO_x that leads to the production of an O_3 molecule. NO can react with HO_2 to produce NO_2 and OH. The NO_2 can rapidly be photolysed by radiation from the sun (indicated by h below) which returns an NO molecule and an oxygen atom which rapidly reacts with an oxygen molecule to make an O_3 molecule. This can all be represented as

$$NO + HO_2 \rightarrow NO_2 + OH$$

$$NO_2 + hv \rightarrow NO + O$$

$$O + O_2 \rightarrow O_3$$

$$OH + CO + O_2 \rightarrow CO_2 + HO_2$$

$$Overall$$

$$2O_2 + CO \rightarrow CO_2 + O_3$$

This cycle is known as being catalytic as neither the NO_x or the HO_x are used up in making the O_3 . Each NO_x molecule can make many O_3 molecules. On the other hand the CO molecule is used up. Other species can act to convert OH into HO_2 and these are dominated by hydrocarbons. Overall the oxidation of gases such as CO and hydrocarbons in the presence of NO_x leads to the production of O_3 .

Ozone is removed from the atmosphere through the reaction of sun light and water vapour

 $O_3 + h\nu \rightarrow O_2 + O(^1D)$ $O(^1D) + H_2O \rightarrow 2 OH$ Overall $O_3 + h\nu + H_2O \rightarrow O_2 + 2 OH$

Thus air which has been recently subject to NO_x emissions and sunshine are likely to have high O_3 concentrations, whereas those which been away from recent emission of NO_x and have been in wet sunny conditions are likely to be low in O_3 .

Remember that airmasses can be lifted in the atmosphere by convection and frontal activity. These processes lead to 'layers' being formed which are different O_3 concentrations.

Tropopause dynamics and ozone mini-holes

In addition to the long-term trends in stratospheric ozone caused by chemical ozone destruction there is also a great deal of variability in the amount of ozone in the total column above a particular location (see Fig. 2). Most of this variability occurs on the time and spatial scales associated with typical synoptic processes in the middle and high latitudes. In the Northern Hemisphere (NH) ozone mini-holes are regions of around 1000km with total column ozone values around 100DU less than the seasonal mean ozone column at their centre.

Ozone mini-holes are formed when there is divergence in the atmospheric column at lower and middle-stratospheric levels, causing ozone rich air to flow out of the column. Most studies (see for example James and Peters, Annales Geophysicae, 2002) of the meteorological state associated with ozone mini-holes suggest that this divergence is caused by a combination of a tropospheric anti-cyclonic anomaly and a stratospheric cyclonic anomaly. The coincidence of these two meteorological structures causes strong lifting of the tropopause and horizontal transport of ozone-rich air out of the column. Over the UK, there are typically 2-3 events of this size each year, lasting for a few days. In some cases, particularly at high northern latitudes (e.g. Scandinavia) ozone mini-holes can occur in regions where some chemical ozone loss is also taking place, thereby causing very large ozone deficits. However, for latitudes close to the UK this is very uncommon. The characteristic signature of an ozone mini-hole is the reduction of ozone content below typical climatological values in the lower and middle stratosphere.

Measuring ozone using an ozone-sonde

Ozone-sondes measure O_3 using a chemical reaction in the liquid phase between potassium iodide (KI) and Ozone (O_3) which produced iodine molecules (I_2).

$$2 \text{ KI} + \text{O}_3 + \text{H}_2\text{O} \rightarrow \text{I}_2 + \text{O}_2 + 2 \text{ KOH}$$

We can measure the concentration of I_2 using an electro-chemical cell so that the concentration of I_2 is proportional to the the current that flows through the system. By measuring the current within the cell, the I_2 concentration can be found and so the O_3 concentration can be deduced.



Figure 4. Makeup of a ozone sonde cell. The pump draws air through the KI solution. The ozone sensor then measures the current within the electro chemical cell (ECC) and reports this to the radio system which relays the information to the ground.

Units

We can think about O_3 in many different ways. Some times we are interested in the fraction of ozone molecules in a sample of air compared to all the other molecules in the air. This is known as a volume *mixing ratio*. In the troposphere there are usually 40 O_3 molecules for every billion air molecules (mainly nitrogen and oxygen) so we refer to this as 40 part per billion air molecules (ppbv). In the stratosphere there are usually 5 O_3 molecules for every million air molecules (ppmv).

Sometime we not interested in the relative concentration of the gas to the air but its number density – how many molecules of gas are there per cubic cm of air (# cm⁻³).

People who make ozone-sonde observations often use the 'partial pressure' of ozone as their unit. This is the pressure that the ozone molecules would exert if all the other molecules in the air were removed. If you look at Figure 5 the O₃ is presented as a pressure in milli-Pascals (mPa). You can convert these numbers to a mixing ratio by dividing by the pressure of the air at that point. So for example at the surface the O₃ partial pressure is 5 mPa. The pressure at that point is ~1013 hPa so the mixing ratio of O3 is $5x10^{-3} / 1013x10^2 = 5x10^{-8}$ molecules of O₃ per molecule of air or 50 parts per billion.

Sometimes we are interested in the total amount of O_3 above our heads. In this case we use Dobson units. If you image you took all the O_3 from above your head and brought it down to the surface at 0°C and a pressure of 1013 hPa how thick would it be? For historical reasons this thickness is given in units of 0.01 mm. So if you brought all the O_3 above your head down to the ground at 0°C and it formed a column 3 mm thick the O_3 column would be 300 DU

You may like to attempt to estimate the total ozone column from your sounding of temperature and ozone. To do this, you will need to calculate the number of molecules of ozone present in different parts of the profile if the air were at standard temperature and pressure. The ozone number density (in molecules cm⁻³ can be estimated using the formula:

$$N_{O_3} = \frac{vmr_{O_3} \text{ x pressure}}{1.38x10^{-19} \text{ x temperature}}$$

You will then need to calculate the absolute number of molecules in that layer using the thickness relation and sum the total number of molecules. One Dobson Unit is equivalent to 2.69×10^{19} molecules of ozone per square centimeter.

Typical Ozone soundings

Here is a typical ozone-sounding:



Figure 5: Typical Ozone sonding. Taken from the Scientific Assessment of Ozone Depletion: 1994, Executive Summary, World Meteorological Organization Global Ozone Research and Monitoring Project - Report No. 37

You can see the tropopause at around 15 km with high concentrations of O_3 above in the stratospheric ozone layer and lower concentrations in the troposphere. The O_3 concentrations peaks at around 22km and then drops off above that. In the troposphere the O_3 concentration is fairly constant and then increases towards the surface due to recent pollution (this isn't a feature of all soundings). A small peak in O_3 at 13km is probably due to convection lifting polluted airmasses with higher O_3 into the upper troposphere (again this isn't a feature of all soundings).

Data sources

The observations of O_3 made during our sonde launch will be placed on the shared drive and you will be told where to find it. The file will contain the observations made by the sonde as a function of time from the launch. They contain the pressure (hPa) and altitude (m) of the sonde, the temperature (deg C), O_3 concentration (parts per billion by volume ppbv) and the relative humidity (%). We will also give you a tephigram of the sonde ascent.

The European Centre for Medium Range Weather Forecasting (ECMWF) makes forecasts for the O₃ concentration at various pressures over the next few days. You can find their forecasts at: <u>http://gems.ecmwf.int/d/products/grg/realtime/daily_fields!Ozone!SFC!06!Europe</u>! You may have to ask a member of staff to use a staff computer to see this page.

We may (depending upon the speed of the internet connection) provide you with forecast back trajectories for Arran, and we will provide trajectories for the ozone-sonde itself.

You can use met charts to investigate your O₃ profile.

Assessment

Your analysis of the ozonesonde sounding will be expected to contain the following (each section is worth 50% of the final grade):

- **a.** A comparison of your proposal and the proposal chosen for the launch (you will need to stick a copy of each proposal in your lab book). You should discuss the strengths and weaknesses of each proposal and comment on why you think the successful proposal was chosen. For the group that submitted the successful proposal you should compare your winning proposal with another unsuccessful proposal.
- **b.** A discussion of the resulting ozonesonde profile. You should produce a plot of the ozonesonde profile as a minimum. You also might like to compare the ozone data with data obtained from other experiments. Your final report should consider some of the following questions (depending on the properties of the profile which you should discuss with course staff):
 - i. What are the main features of the profile?
 - **ii.** Can you see the presence of different air masses based on the concentration of ozone? Are these properties confirmed by the temperature structure from a standard tephigram? Where might the air masses have come from given the synoptic picture and the available trajectories?
 - **iii.** Can you see the position of the tropopause? Is it high or low? Does this fit with the synoptic picture?
 - **iv.** How do the concentrations of ozone in the troposphere and stratosphere compare to climatological amounts? Is there evidence of active chemistry in any of the air masses in the column? Is there evidence of significant advection of ozone rich air out of the column?
 - v. Does the profile answer the scientific questions posed in the successful proposal? If it does, what are the answers and how does this improve our knowledge of the chemistry and dynamics of the atmosphere? If it doesn't, what went wrong and how could you change the experimental design to avoid these problems in the future?

This activity is very open-ended. We want you to explore the data and the background material as much as possible. Marks will be awarded for innovative use of the data and discussion of the results.