

## The ozone depletion story

Ozone depletion is a subject that's now been in the news for some 30 years. The topic seems neither to come to a head nor go away. My question today is: "Is it a real threat, or simply a topic of marginal interest that is pushed into the news when there's a lull in the political weather?"

Ozone is discussed in chapter 18 of the later editions of Ahrens' textbook, the chapter devoted to air pollution. If ozone is a pollutant, why is everyone concerned about ozone depletion? The situation is not straightforward. In brief, tropospheric ozone is a pollutant, stratospheric ozone is not. It's the same stuff in both places, but location is everything. This section is mainly about stratospheric ozone, what it does, how it's formed, how it's depleted and why we need it.

Ozone is a completely naturally occurring form of oxygen. Oxygen, we all know, is the gas of life, but is ozone as good for us as our regular brand of oxygen? Our regular oxygen is made of molecules composed of 2 oxygen atoms - molecular oxygen, for short. Ozone molecules have 3 oxygen atoms. That's all. Ozone is indeed pure oxygen. However, as far as breathing is concerned, more isn't better, which you might be forgiven for thinking since ozone depletion is the storyline. If we breathed ozone instead of regular oxygen, we'd seriously damage our lungs, because ozone is chemically highly reactive. It's probably as good as 'Domestos' at killing living cells stone dead. Ozone has caught our attention, and the attention of governments around the world, because of its rôle as an UV (ultra-violet) absorber. I'll expand on this, soon. You can see the presence of ozone in the twilight sky by its characteristic blue colour. You can also see it in side-on pictures of our atmosphere from space.

### *Where do we find ozone?*

Ozone occurs naturally at all heights, but at differing concentrations. Its maximum concentration is about 12 ppm, occurring at a pressure of 25 mb in the stratosphere at a height of about 23 km. Given what I've said about ozone being bad to breathe, the height is just as well. The US Environmental Protection Agency have a simple saying: "Good up high, bad nearby". We'll see shortly why it's 'good up high'.

Ozone constitutes a tiny fraction of our atmosphere. If you bought all the ozone in a column of air down to the ground, it would occupy a slab only about 3 mm thick, the thickness of a pound coin. This is the basis of the unit used to measure ozone, called a 'Dobson unit'. 3 mm is 300 Dobson units, about the average ozone level around the world. Not much! 10 Dobson units represents a layer of ozone at ground level pressure only as thick as a normal sheet of A4 paper. Think of ozone like spice in a soup – its tiny presence changes the experience of the whole thing.

### *Gordon Dobson & Aberdeen*

Dobson units are named after the British meteorologist Gordon Miller Bourne Dobson (1889 – 1976), who made the measurement of ozone almost a lifetime's obsession, long before it was fashionable. It's not at all well known, even locally, that Gordon Dobson set up one of his pioneering ozone spectrometers at Aberdeen in 1939 and this was run for about 5 years, the results being converted to ozone concentrations decades before it became internationally

desirable to record ozone. At Aberdeen, results were recorded at midday every day from a hut that was close to where we are now (on the slide you can see St Machar's cathedral in the background). What was measured was the amount of UV reaching the ground in the wavelength range where ozone absorbs. This number was converted into the total ozone in a vertical column of air above us and telegraphed to the Met Office.

The reason Dobson set up a spectrometer in Aberdeen, and at around the same time ones in Lerwick, Valencia, Eskdalemuir and Oxford, was to follow an idea he had that variations in ozone concentration gave an indication of the synoptic state of the lower atmosphere, suggesting for example whether depressions were likely to develop or a high pressure area would expand over the country. The project years, 1939 to 1944, are the clue to this interest. During the Second World War, meteorological observations were not as available as they were in peace-time and could have enormous strategic implications. Any further clues were worth looking for. The effort was discontinued eventually because Dobson became convinced that the correlation he looked for wasn't there. This is therefore a digression from our story of the importance of stratospheric ozone, except to introduce Dobson himself. The spectrometer illustrated is actually the copy that went to Lerwick and, much later, was the one with which ozone depletion was first discovered over Antarctica – a bit of meteorological history.

### *Is ozone beneficial?*

I'll return to the story. Stratospheric ozone is good for us on two counts. First, it absorbs harmful UV B radiation that reaches Earth from the Sun. Ozone is the Ambre Solaire of the world, our UV B shield. You can see in the rainbow on the slide where the UV B is in the electromagnetic spectrum. Secondly, ozone absorbs sufficient of the sun's rays to heat the stratosphere, which has the effect of putting a lid on the weather in the lower atmosphere. For example, convective clouds rise up to the bottom of the stratosphere, at a height of ~10 km in these latitudes, and no further. Their precious water so essential to life on Earth is kept by this means comparatively close to the Earth's surface, as mentioned earlier.

It is the UV screening effect that is most easily upset by ozone depletion.

### *The effects of ozone reduction*

What would happen if the ozone above us were to be destroyed, in whole or in part? UV arrives in basic energy packets, called photons, whose size depends on the wavelength of the UV. A typical photon in the UVB has a wavelength of 300 nm, where the photons have an energy of 4 eV (electron volts – a unit of energy frequently used by atomic and molecular scientists). This is quite sufficient to break apart many chemical bonds, notably those in DNA and many proteins within us that are the stuff of life. Energy sufficient to break some chemical bonds is also sufficient to promote chemical reactions that join together molecules that would not otherwise have united. Here are some of the overall effects of UV:

- increased photo-chemical activity in the troposphere
  - more smogs; more pollution generating chemistry taking place on atmospheric particles. i.e. air quality in the lower atmospheric would decrease.
- increased degradation of natural and artificial polymers in buildings and other construction.

- increased UV irradiation of animals, plants and phytoplankton. The textbook lists some UV induced effects that might occur with decreased concentration of our O<sub>3</sub> screen. They include:
  - o increases in skin cancer, which can spread to other organs leading to death. (Which animals are the most vulnerable? Possibly the 'naked ape' - us. It would be a different story if it were elephants or rhinos or mosquitoes that produced ozone destroying chemicals!)
  - o increase in cataracts
  - o adverse effects on crops and animals in general
  - o decrease in oceanic phytoplankton that are at the base of the oceanic food chain.
  
- cooling of the stratosphere

### *Solar UV index*

In one sense it's not the ozone that is everyone's final concern, but the ultra-violet that reaches ground level. This is measured by the solar UV index. During the summer months this index is frequently quoted on TV weather forecasts and elsewhere in the media. It's a bit like the Beaufort numerical wind scale (discussed later in our course): 0 – 2 (min); 3 – 4 (low); 5 – 6 (medium); 7 – 9 (high), 10+ (very high). Each unit represents an exposure of 40 J hr<sup>-1</sup> m<sup>-2</sup> of UV. The index is intended to be a measure of the UV reaching the ground. As far as I know it does not distinguish between UVA and UVB (the amount of UVC reaching the ground is negligible).

The Met Office produce a daily predictive map, all year round. Monitoring stations report UV daily. The nearest station to here is Kinloss on the Moray coast, that gets a bit more sun than we do. How the UV affects people depends on their skin. The accompanying table gives a standard summary. You need to know what kind of skin you have.

All this isn't unnecessary scare mongering. Ozone depletion is a reality.

Can we not just make more ozone industrially to ensure there's enough 'up there'? No! 1 ppm of atmosphere = 5000 million tonnes! To make matters even worse, the lower stratosphere has to be continually fed with ozone, otherwise the amount there naturally decays.

The 'ozone dilemma' mentioned in the textbook is that our influence on the ozone layer is indirect, long-term, global and tends to destroy O<sub>3</sub>. If we wait until we know enough about our influence on ozone concentrations, we may have waited too long to be able to recover from a disastrous reduction. On the other hand, if we act now, we may be acting unnecessarily and ineffectually.

### *The ozone hole*

Ozone has a natural variability of many percent, as Dobson found out all those years ago, and it wasn't until the early 1980s that quite dramatic evidence for ozone depletion was suddenly found – the so-called 'ozone hole' over the Antarctica. In this picture of a recent ozone hole, on the slide, half of the ozone is missing. The ozone hole kick-started much more scientific work on the measurement of ozone levels, on the understanding of ozone related chemistry

and on the need for international agreements to 'do something about it'. This was because it became ever more clear that the ozone hole was not part of the natural variability of our ozone shield but a man-made effect.

### *Ozone now*

Ozone is monitored globally, by satellite. Here is a recent picture of ozone over the northern hemisphere. The ozone level looks healthy but you can't tell from a daily map on its own what is happening to ozone levels in the long term. However, on top of the natural variability, there has been a steady decline since the 1980s, by about 0.5% per year. The World Ozone and Ultraviolet Data Centre (WOUDC) enables you to compare the current situation with 10-year averages, such as is shown on the next slide. Looking over the whole globe, this highlights a decline.

This *next slide* shows 4 pictures:

- The distribution of ozone around the world (top left)
- The corresponding UV irradiation at sea level (below left). This is in the UV units mentioned above.
- The ozone distribution in early Antarctic spring (top right)
- The UV distribution around our mid summer (bottom right).

Satellites are not the only means of measuring ozone, though. Ground-based stations provide important additional measurements and also a means of monitoring and re-calibrating if necessary the satellite-based measurements.

The *next slide* shows the location of ground-based monitoring stations around the world.

### *Ozone formation*

Ozone differs from ordinary oxygen not only chemically but in another very important way. Ozone is continually being created and destroyed. If you were an ozone molecule, you could expect a short life. Let me tell you about creation first. This is the technical bit.

To form ozone, which is  $O_3$ , a single O, called **atomic oxygen**, must meet an  $O_2$ , called **molecular oxygen**, in the presence of a 3<sup>rd</sup> molecule. Any molecule will do. Where does the single O come from? Atomic oxygen is formed very high in the atmosphere, in the region above 100 km called the thermosphere. There, very energetic UV strikes molecular oxygen, breaking  $O_2$  into 2 separate O. Molecular oxygen does a good job of screening us from the most harmful of all UV, namely UV C.

Now in the very high atmosphere, the air is so thin that the chance of the 3 molecules needed to form  $O_3$  all coming together at once is very slim. The O ends up drifting downwards into the stratosphere, where the atmosphere is more dense. It is in the stratosphere that most of the ozone forms.  $O_3$  forms throughout the stratosphere, particularly in the top half and it itself diffuses downwards (like pouring cream onto the top of your coffee) to reach maximum concentration around 23 km. In brief:  $O_3$  formation is driven by UV induced formation of O and natural collision. We have no control.

*Destruction of Ozone by UV*

In the stratosphere the ozone does what we want it to do – absorbs UVB. In doing so, the ozone molecule is itself destroyed, creating  $O_2$  and  $O$ . However, the  $O$  is in the right place to form more ozone quite quickly, which it does. The right-hand side of the destruction relationship is almost the left-hand side of the formation relationship, missing only the presence of the extra molecule. So, not long after the UV disintegrates an ozone molecule, another one forms from its residual atomic  $O$ . One UV photon destroys an  $O_3$  molecule but in the scheme of things, another quickly forms.

*Ozone destruction by Cl and other species*

All would be well for our UV shield except that there are other chemical elements in the stratosphere that also break up ozone, but in the process they capture the single oxygen atom and hence stop the recombination of  $O$  and  $O_2$ .

The first process is that ozone is destroyed by collision with  $O$  or another  $O_3$  molecule. The reactions are given in text book. The net effect is that  $O_3 \rightarrow O_2$ .

Secondly, catalytic reactions with  $NO$ ,  $NO_2$ , and  $Cl$  all remove  $O_3$  from the atmosphere without destroying the participating substance [the textbook gives an example reaction]. All these species are naturally present in the atmosphere. The slide shows a  $Cl$  atom destroying ozone.  $Cl$ , for example, naturally comes from evaporated sea salt, which is pure  $NaCl$ . The Chemistry was particularly worked out by Molina and Rowland, who shared the 1995 Nobel Prize for Chemistry with Paul Crutzen for their combined work on atmospheric chemistry.

These processes happen naturally and the balance between formation and natural destruction determines how much ozone there is around the Earth. This balance has been kept for the past billion years or so. Suddenly, on this time-scale, mankind came along. About 50 years ago chemists produced in industrial quantities a family of wonder chemicals that had all sorts of applications. This family were the CFCs.

*What happens to a CFC molecule*

CFCs, chlorofluorocarbons, are extremely stable - so much so that they are excellent in fire extinguishers. The lighter ones, with low boiling points, are excellent as propellants for aerosol cans and for making expanded foam. They are without smell and were recognised to have all the right properties to completely displace ammonia as the working liquid inside refrigerators and air conditioners. Unfortunately, for almost all these applications the CFCs ended up in the atmosphere, where their stability ensured they would gradually accumulate. If they remained unreactive at all times, we wouldn't worry because compared with the bulk of the atmosphere the amount of them is negligible. Although CFCs are stable enough to put out fires, once in the stratosphere they can be broken apart by UV. The really bad news is that the chlorine in CFCs once it has been liberated from a CFC molecule has the distinction of being able to cause the break-up of ozone, without being destroyed itself. A single released  $Cl$  atom can be re-used to break ozone molecules again and again and again, perhaps 100,000 times, before finally being taken out of the system by a different reaction.

Our polluting gases are produced in the troposphere and take some time to diffuse up into the stratosphere. They take even longer to come out of the stratosphere. CFCs in particular can have lifetimes of more than 100 years. They pose a very real threat.

*“Why us?” penguins might ask*

Why does the ozone hole occur in spring-time over Antarctica? This is a question that had atmospheric scientists puzzled for years and the lack of an obvious answer was one reason why the ozone hole was unexpected. The story is given briefly on the slide. Can we say it's in someone else's backyard and in fact sunburn isn't really one of a penguin's real problems?

Unfortunately, it's not a problem that's just on the other side of the world. The polar circulation around the arctic isn't that much different from that around the Antarctic. Polar stratospheric clouds form in Arctic air and ozone depletion does occur on a smaller scale over the arctic. A big 'hole' like that over Antarctica is unlikely to develop. What saves us is not so much that it can't occur here but it's less severe because Arctic air doesn't get as cold as Antarctic air. One contribution to the additional cold in Antarctica is the high Antarctic plateau and mountains. In contrast, there is a vast sea over the North Pole. It's the intense cold that encourages the formation of the damaging PSCs (see the slide).

*[Serious threat?]*

*Ozone Creation and Destruction Analogy* (omit from lecture): Let me paint you a slightly odd picture. Imagine a very large village ball with many couples on the floor. At the entrance door a slow trickle of individuals arrive. Each one finds their way to the floor and is introduced by a bystander and invited to join with an adjacent couple to make a threesome. The threesome dance happily until spotted by the local head-man, whose pleasure it is to pick on threesomes with a flash of his large spotlight. When a threesome is illuminated by a blaze of this light, they must break apart into a couple and a single. The single goes off but most singles are soon introduced again by bystanders to other couples and different threesomes form. Sometimes, a single rests besides one of the decorations, to be joined soon after by another single. The two form a new couple. You can see that the floor at anyone time may contain lots of couples, some threesomes and some singles waiting to be introduced. This is just like the case of O<sub>2</sub>, O<sub>3</sub>, and O. The music plays on without interruption.

Suddenly, a party of moral spoilers arrives from the neighbouring village. They have a large banner “3-some, sin some”. They infiltrate the floor and each one starts breaking up threesomes into couples and singles, holding on to the singles until they can find another one to make the two singles into a couple. Quite quickly, the number of threesomes falls because the reforming process has been interfered with, and the head-man can find very few threesomes to pick out with his spotlight. He then turns his full beam continuously onto the massed crowds behind. They don't like it. They are us.]

*The long-term trend*

The downward trend in stratospheric ozone has been going on for three decades or more now. Is the ozone destruction a real threat? In short, yes. We need the UV protection. It's true that there are other atmospheric constituents that absorb UV, notably aerosols and sulphur compounds, but in clean air they are not present in big enough quantities. The round figure is that a 1% decrease in stratospheric ozone increases UV levels by 2%.

*What's being done?*

The Montreal Protocol aimed to reduce and eventually eliminate man-made ozone depleting substances in the stratosphere. This means finding substitutes for their use and not making CFCs. Atmospheric CFCs are distributed around the world by air circulation and easily detected, so you can't say that no-one will notice or that a country's production affects only itself.

The original protocol was signed in 1987 and has been modified at least 5 times since. Is it having any effect? There's not much to show for it yet. The Antarctic ozone hole shows annual variations but the annual emission of ozone depleting substances (abbreviated ODS by the UN) reduced by 30% in the 1990s. It will take a long time to make a big effect. One of the reasons why there's not much to show is that the lifetime of important CFCs in the atmosphere is not much short of a century. Even if the Montreal Protocol and its amendments work as well as is hoped, ozone levels won't recover properly until around 2040 and the earliest – past my time, in the absence of medical miracles.

*An overview of Ozone Depleting Substances*

The IPCC have published a policy-makers' summary of the ozone depleting issue, in a chemical manufacture to destruction overview. The slide shows the elements of their analysis. A link to their site is on our 'links' web page. The Intergovernmental Panel on Climate Change are concerned with ozone on two counts. First, ozone is a greenhouse gas in its own right and secondly many ozone depleting substances are also greenhouse gases. I'll say more on these topics in the section on global warming, which we're coming to soon.

*What can we do?*

Personally, not a lot. Make informed judgements of what you read. Vote for politicians who take the issue seriously, and don't throw your old fridge on the tip. It's now illegal in this country to do so. Globally, mankind can reduce, and is reducing, the production of O<sub>3</sub> destroying chemicals.

## In summary:

- Is ozone depletion a reality? “yes”
- Is there a man-induced component of the change? “yes”
- Will a reduction in O<sub>3</sub> affect life on Earth as we know it? “*Slightly at current levels of depletion, increasingly so for higher depletions*”

## [Ozone own notes:

- the lifetime of O above about 100 km is at least a day, and hence not much difference in day time and night time concentrations
- at ~ 105 km, concentration of O<sub>2</sub> and O are similar
- at night in the stratosphere, production of O from O<sub>3</sub> stops, i.e. UV driven dissociation stops, but so does collision production of O<sub>3</sub> with O since the source of most of O has gone. The two main reactions conserve 'odd oxygen'.]

### *Weather & Climate*

Having made a diversion to chapter 18 in the textbook, the story returns to the end of chapter 1 with a brief discussion of the difference between weather and climate, leading on to chapter 2.

**Weather** is the daily variation (or values) of *temperature, pressure, humidity, clouds, precipitation, visibility, wind*.

**Climate** is the behaviour over decades of these quantities, including their average values and their typical variation. Climate change is the long term variation in climate, over centuries, thousands or even millions of years. Scotland was buried under a km or more of ice only 20,000 years ago. Scotland was on the equator a few hundred million years ago. *Climate* change over millions of years has been immense. We'll come back to climate change in the next chapter.

### *Weather and climate affect our lives*

See the slide and the section in Ahrens' textbook on meteorology in our lives.

### *Conclusion*

The point of this following link is to indicate that science is a demanding discipline and to introduce you to one of meteorology's unsolved problems relevant to climate change. Explanation should not just be in the form of hand-waving suggestions but quantifiable, verifiable, logical links.

This chapter has emphasised that the weather as we know it is at the bottom of the atmosphere. By way of introduction to the next chapter, which is about the influence of the Sun, consider the following. The Sun's output of radiation that heats and lights the Earth is constant over time by better than 1 part in a thousand. Not only does the Sun rise and set with stunning constancy, it also shines with stunning constancy. Yet there are established cyclical changes in weather, one apparently to match the 11 year sunspot population cycle. Indeed, when the sunspots disappeared for decades a few centuries ago, Europe seemed to be in the grip of the 'little ice age'. If the Sun shines constantly, how can sunspots affect the weather?

The correlation is real, though it's one that by and large baffles atmospheric scientists who haven't been able to work out a causal connection yet. It's possible that there may not be one. Science works like this. If you say that two phenomena are necessarily related, there must be a mechanism linking them. If your science is good, the linkage should let you calculate the exact extent of the dependence and what controls it. The problem here is to find the linkage. Associated with sunspots is an outward flux of particles from the Sun called the solar wind. The solar wind is highly variable. These highly energetic particles are trapped by, and heat, the very top layers of our atmosphere. The 'thermosphere' can change in temperature by a factor of two in response to the solar wind, significantly altering the outer boundary of our atmosphere. If the weather depends to some extent on sunspot activity, then perhaps there is a coupling between the outer regions and the low level atmosphere. One idea is that the thermosphere, which is one boundary of the atmosphere, influences pressure waves throughout the whole atmosphere, down to the lower regions. However, from here on the story becomes vague because there is no simple linkage between global scale atmospheric

pressure waves and climate. There is another potentially completely different coupling between the solar wind and the weather system via the influence of the solar wind on the ionisation produced in the atmosphere and hence on the nucleation of clouds. So here you have one unsolved problem and two ideas that hint at a possible solution but nothing quantitative. Actually it's the second idea that has more going for it. What appears in textbooks is what we definitely know about, but there are plenty of problems still to solve. Research is about looking for solutions that really work, down to the fine detail.

Now, onward to the next section that will look at temperature, radiant energy and warming the Earth's atmosphere.

JSR