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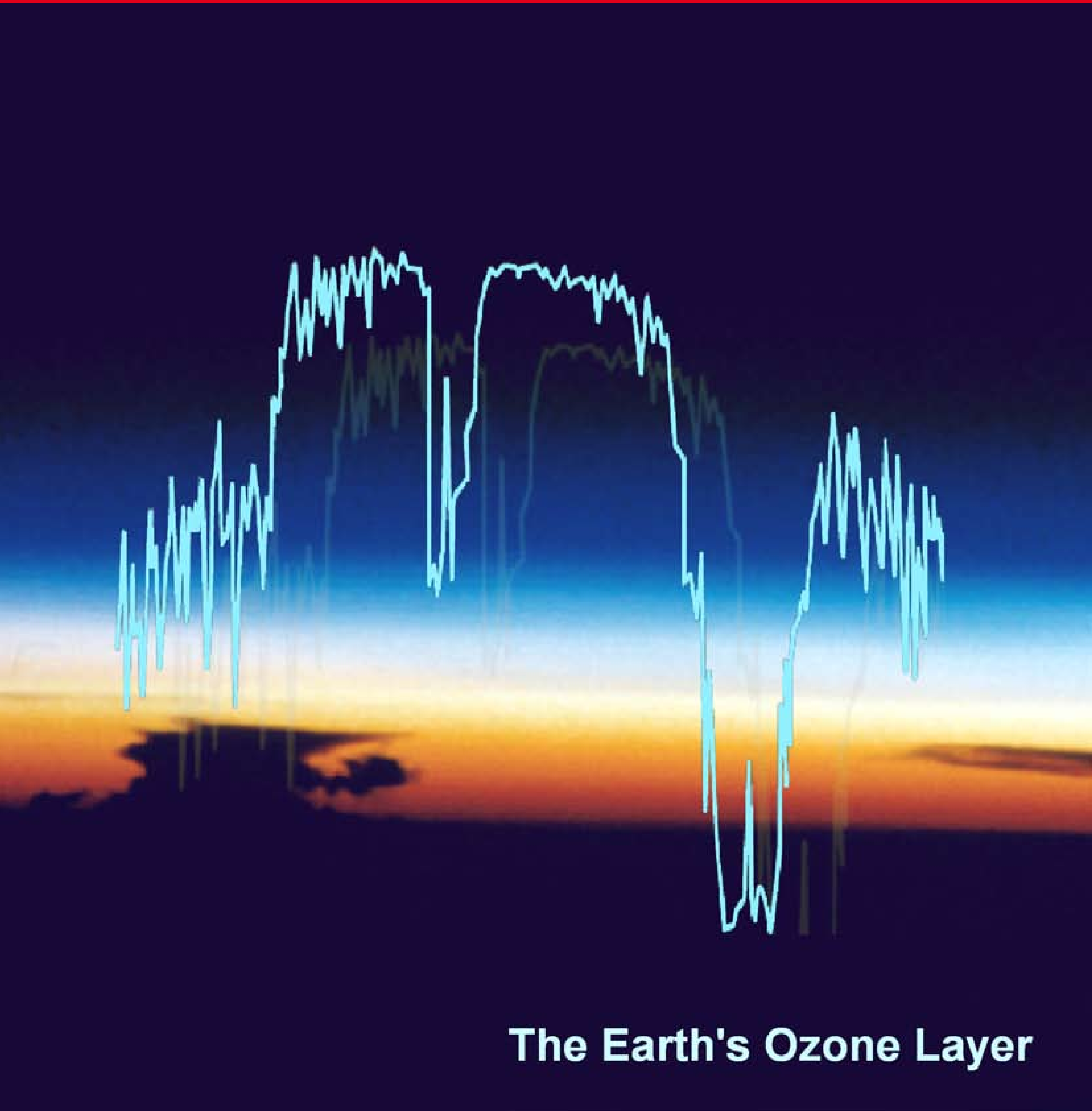

The Earth's Ozone Layer

Editorial

Eritis sicut deus scientes bonum et malum (1.Mos. 3, 5).

God created heaven, Earth, plants and animals, and he wished to populate the land with man and wife. He created Adam and Eve, and he provided them with all goods necessary for life. They were, however, submitted to the temptation of grasping the fruit of the forbidden tree. Praising the tree of wisdom, the snake prophesied: you will be God alike, conscious of good and evil. Adam and Eve ate from the tree, lost their innocence and God expelled them from paradise.

Johann Wolfgang von Goethe lets Mephisto, disguised as a professor, write these very words into the scholar's register as a warning of the dangers of unmindful use of abilities. The scholar assumed to have met great Faust, but in fact, he encountered the Devil personally.

These magnificent ciphers are true not only for the pupil in his avid search for wisdom, but for our ambivalent use of technologies as well: wisdom can increase the quality of our life, while trespassing nature's boundaries leads us to the loss of paradise.

The story of the Earth's ozone layer is the modern version of the unfortunate experience Adam and Eve were to make. This is the message that Dr. Yasmine Calisesi, an expert in atmospheric chemistry and a former scientist at ISSI, conveys in this Spatium. Based on her lecture for the Pro ISSI audience on 31 October 2007 she tells us the ozone story. This story may have found a happy end, but at the same time it is a forerunner of other stories, such as for example that of global warming, a topic requiring similar decisive actions by the industrialized societies like those taken to safeguard the Earth's ozone layer.

May the present issue of Spatium contribute to our common wisdom on the dos and don'ts in full responsibility of *scientes bonum et malum*.

Hansjörg Schlaepfer
Brissago, February 2008

Impressum

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The Earth's Ozone Layer[1]

Preface

The discovery of the ozone hole over the Antarctic in 1985 set a milestone in the history of environmental research. In addition to the profound meaning of such a finding, it also stirred the public awareness of ecological matters to an unprecedented extent. Suddenly, everyone became aware of the fact that unmindful use of "unclean" technologies can put humankind's sheer survival into question. From 1930 onwards, thousands of tons of chlorofluorocarbons (CFC's) came into use each year in a variety of applications and were finally released into the atmosphere. It took nearly half a century for science to persuade the governing instances of the threatening effects these chemicals have on the ozone layer, that shields us so efficiently from dangerous solar radiation. Fortunately, though, scientific knowledge at the time of the discovery of the antarctic ozone hole was such that, under the leadership of the United Nations, the international community was able to define and urgently implement the required concerted actions to prevent the complete destruction of the ozone layer. Today, we have observational data that indicate a decline of the CFC concentration in the stratosphere. Models predict a recovery of the ozone layer to its pre-1970's values in the next fifty to hundred years, based on the unrealistic condition, however, that the stratosphere remains untouched by the effects of climate change.

The ozone hole story provides an unprecedented example of humankind's ability to solve global environmental issues, the next challenge to be tackled being undoubtedly that of global warming.

The present issue of Spatium is devoted to the story of the ozone hole. It aims at familiarizing the reader with the crucial importance of the ozone layer for all living organisms on Earth, and to enhance his/her motivation to contribute to what we owe to future generations: a planet Earth that is capable of supporting the peaceful evolution of mankind.

Fig. 1: Observations from Halley Bay in Antarctica provided the first conclusive data on the ozone hole in 1985. This image shows the British Simpson platform in Halley Bay at sunset. What it does not show, however, is the air temperature that might have been as low as -50 °C. (Credit: http://www.flickr.com)

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[1] The text for the present isssue of Spatium was drafted by Dr. Hansjörg Schlaepfer and revised by Dr. Yasmine Calisiesi, who gave the Pro ISSI audience an introduction to the subject on 31 October 2007.

Setting the Stage

In this section, we will address the most important mechanisms governing the production and loss of ozone in the stratosphere. We will also highlight the reasons why the stratospheric ozone layer is so important for life on Earth.

The Light of the Sun

The Earth's ozone layer is the result of the combined influence of the Sun and Earth, more specifically the solar radiation and the Earth's atmosphere. Our planet circles the Sun at a distance of some 150 million km. This happens to be right within the narrow zone around the Sun, within which liquid water can exist on a planet's surface, allowing life to develop on Earth.

The amount of power that the Earth receives from the Sun can be compared to the output of some 100 million nuclear power stations. This enormous power meets the Earth in the form of electromagnetic radiation. More specifically, it consists mainly of visible light, associated to infrared and ultraviolet radiation.

As outlined in **Fig. 2**, the intensity of the radiation emitted by the Sun is not uniform at all wavelengths. Rather, its maximum is in the visible part of the spectrum. As a fascinating result, evolution led the sensitivity of the (human) eye to match exactly this maximum in the solar spectrum. The Sun's light is often termed "white", but actually, it is composed of a continuum of colours as represented in **Fig. 2.**

The sunlight enters the top of the atmosphere and passes through various layers down to the surface. In the atmosphere, though, not all the wavelengths are transmitted equally. Its constituents absorb preferentially specific portions of the spectrum; as we will see later, the part of the ultraviolet radiation denoted by UV-C in **Fig. 2** is totally absorbed by ozone in the atmosphere. The less energetic radiation, that is, parts of the UV-B and UV-A solar spectrum above 280 nm, are not completely absorbed by ozone and can penetrate through the atmosphere down to the Earth. Levels of UV-B and UV-A at the Earth's surface are thus dependent on the amount of ozone in the atmosphere. Note that, being the most energetic one, UV-C radiation is the most dangerous to human cells. As it is completely ab-

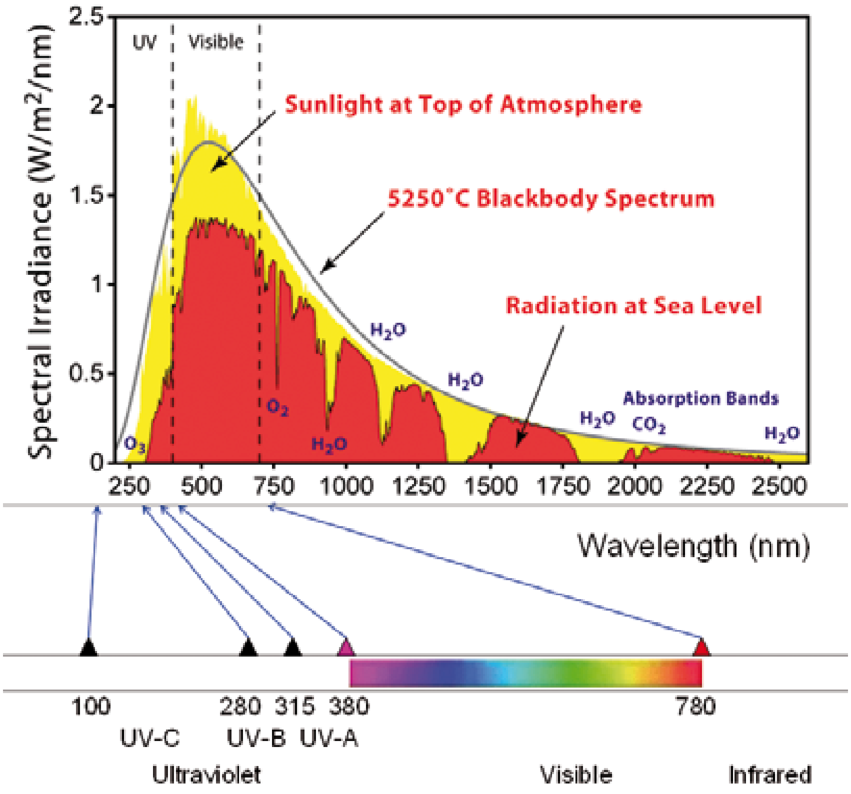

Fig. 2: The solar radiation spectrum. The upper part shows the solar radiation spectrum at the top of the atmosphere (yellow shaded area). Various components of the atmosphere absorb specific parts of the spectrum, resulting in reduced radiation strengths at sea level (red area). The lower part shows a magnified portion of the spectrum, centred on the visible wavelength range with ultraviolet to the left and infrared to the right. The ultraviolet is commonly divided into three parts, spanning from the UV-C range at the short wavelengths towards the longer wavelengths of UV-B and UV-A.

sorbed by the ozone layer, only the UV-B and UV-A parts of the solar spectrum are the target of sun-protecting lotions.

Biological Properties of Light

Light is one of the key requirements of life. Solar radiation provides cells with the energy required to support their functions. The absorption of light by a cell depends on both the wavelength of the radiation and on its intensity. In the case of the human skin, extended exposure to visible light may cause accelerated ageing and sunburn. Intensive exposure to infrared radiation may give rise to retinal damage of the eye and to skin burn. The least energetic UV-A radiation penetrates deep into the skin, and causes early aging. UV-B radiation, however, is the dangerous component of the sunlight on Earth's surface as its photons contain enough energy to destroy the desoxyribonucleic acid (DNA) in the skin cells, which is the carrier of the genetic code. Upon a certain dose of UV-B radiation, such cells can develop a malignant tumour, which is eventually fatal for the entire organism.

To summarize, light in adequate intensities and quality is a necessity for life. On the other hand, however, light at too high energies may also destroy it.

The Earth's Atmosphere

In this section, we shall take a closer look at the composition of the atmosphere in order to understand how the ozone layer is established.

Fig. 3: The Earth seen by the Apollo 17 crew. In this representation and assuming a "thickness" of 100 km, the Earth's atmosphere would measure mere half a millimetre. (Credit: NASA)

The Earth's atmosphere acts like a blanket on the planet: it is the place of the global climate and responds to varying solar radiation regimes. Still, it is a very thin blanket, and its density decreases rapidly from the surface up to interplanetary space **(Fig. 3).**

The atmosphere is a mixture of a multitude of chemical constituents. The most abundant of them are nitrogen N_2 (78%) and oxygen O_2 (21%). These gases, as well as the noble gases (argon, neon, helium, krypton, xenon), possess very long lifetimes and hence are well mixed up to about 100 km altitude. Minor constituents, such as water vapour, carbon dioxide, ozone, and many others, show lower, more strongly varying concentrations with space and time. As mentioned above, these gases pile up in an atmosphere that exhibits a decreasing pressure over height. According to the laws of elementary thermodynamics, we would thus in a first guess expect the temperature to fall from the ambient value we experience at the Earth's surface to a very low value close to space. As we will see, this simplistic approach is far from reality!

Vertical Structure of the Atmosphere

Fig. 4 shows the complex temperature profile of the atmosphere. Some regions show a decreasing temperature with increasing height, which agrees with our everyday experience: climbing a mountain brings us in colder air. Some other regions, in turn, display an increasing air temperature with increasing height. It is precisely following these differing behaviours that the atmosphere is commonly divided into different layers, each being defined by the sign of its temperature gradient.

Let us take a closer look at the different layers of the atmosphere:

- The **troposphere** extends from Earth's surface to 6–8 km over the poles and 18 km over the equator. Solar heating of the surface causes the adjacent air masses to warm up. As warm air is lighter than cold air, it rises to higher elevations where pressure is lower, leading thus to an adiabatic cooling of the rising air. Hence, air temperature in the troposphere decreases with increasing height. The troposphere is the layer within which most of the atmospheric water vapour is contained. This vapour condenses when the air temperature falls under the water dew point, giving rise to clouds. The troposphere is hence the realm of weather. The upper boundary of the troposphere, where the temperature gradient changes from negative to positive is called the tropopause.

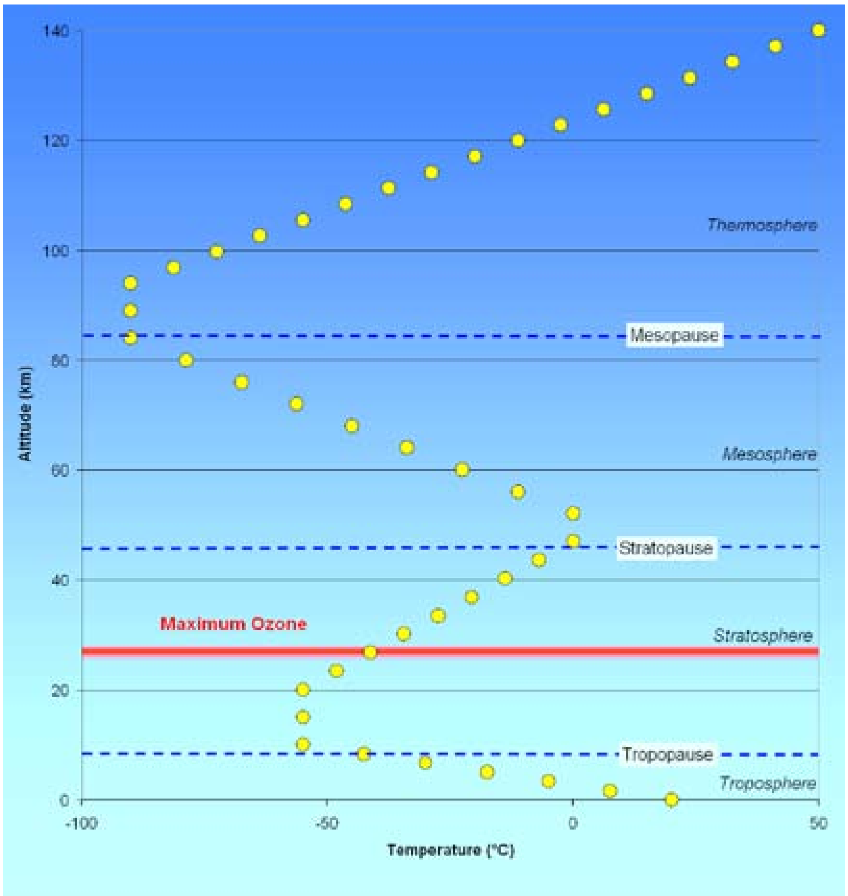

Fig. 4: The vertical structure of the atmosphere. The yellow dots mark the temperature profile compared to height. The layer boundaries are located at altitudes at which the temperature gradient changes sign.

- The **stratosphere** extends from the tropopause to an altitude of about 50 km. It is in the stratosphere that the ozone layer is found. More precisely, it is the place of the maximum ozone concentrations. As we have seen above, ozone molecules have the important property of absorbing ultraviolet radiation from the Sun and transforming it into heat. As solar radiation is stronger, and air density is lower at higher altitudes, air temperature increases here with increasing height. One of the consequences of the positive temperature gradient characterizing the stratosphere is the vertical stability of this atmospheric layer. That is, only very limited vertical mixing takes place within this layer, impeding among others the removal of long-lived pollutants and trace gases by precipitation, but also allowing the existence of local maxima in concentrations such as the one building the ozone layer.
The upper boundary of the stratosphere is called the strato-

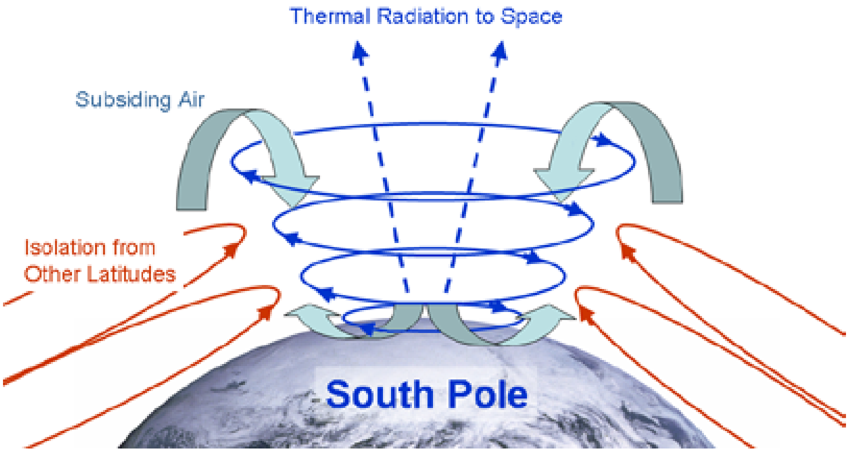

Fig. 5: The polar vortex. During the polar winter, the polar vortex leads to an isolation of the air masses. This prevents fresh air with high ozone content entering the polar region, while the ozone content within the vortex remains low due to the lack of solar radiation. The polar vortex is a natural feature taking place each year over the winter pole, independently of the existence of an ozone hole. It is, however, a key element of the development of an ozone hole in the presence of ozone depleting substances.

pause. Above this boundary, the air temperature tends to fall again with increasing height.

- The **mesosphere** extends from the stratopause to some 85 km. At these altitudes, atmospheric pressure and thus molecule density is already very low. The mesosphere is the region within which most meteorites are consumed when entering Earth's atmosphere at very high velocity. The mesosphere is delimited at its upper boundary by the mesopause. At higher altitudes, air temperature again begins to rise with increasing height.

- The **thermosphere** ranges from the mesopause to some 500 to 1,000 km. At these high altitudes, the residual atmospheric gases sort into strata according to molecular mass. Here, temperature increases with altitude due to absorption of highly energetic solar radiation by the small amount of residual oxygen still present. Temperatures are highly dependent on solar activity, and can rise up to 2,000 °C. Radiation causes the air particles in this layer to become electrically charged, enabling radio waves to bounce off and be received at distant places on Earth. In addition, the thermosphere is also the place of the auroras, which occur when fast solar wind particles hit the air molecules causing them to emit light. The density of gas molecules in the thermosphere is already so low that the International Space Station can orbit the Earth in the upper part of the thermosphere, between 320 and 380 km. The thermosphere ends at the thermopause.

- The **exosphere** begins at the thermopause. There is no defined upper limit to this layer, as the concentration of gases diminishes continuously into space. It is from the exosphere that atmospheric gases, atoms, and molecules can escape into space.

Dynamics of the Atmosphere

The Sun not only causes a complex atmospheric temperature profile in the vertical plane, but it does so in the horizontal plane too. As water surfaces heat up much slower than land surfaces when the Sun is overhead, air masses over the oceans tend to be cooler than those over large land areas. This in turn sets up air pressure differences between land and sea that give rise to winds. As the Earth spins around its axis, it transmits acceleration to all objects placed within its gravity field. The resulting force causes the direction of any moving object to be bent. It is called the Coriolis force.

The horizontal pressure gradient and acceleration provided by the Coriolis force largely dominate the movement of air masses in the troposphere. They give rise to a great variety of global wind systems like for example the trade winds that were used to carry trade ships across the world. These winds cause a continuous exchange of air masses within the troposphere and therefore a stabilization of the air temperature over the Earth. This leads to a horizontal temperature profile that decreases from the equator to the poles, as the solar input is the highest when the Sun is right overhead. While this decrease is small in the tropical and subtropical zones, more pole-ward at some 40° north and south the temperature gradient becomes steeper finally reaching temperatures in the polar regions as low as -80°C.

The Polar Vortex

One of these wind systems is specifically important when it comes to understanding the development of the polar ozone holes. During the polar winter, surface heat is lost to space by radiation. This means that the surface cools down to very chilly temperatures. The adjacent air masses cool down similarly, and as cool air is denser than warm air, the typical polar high-pressure zone builds up. This causes polar surface air masses to flow towards the Equator. As the Coriolis force is very strong near the poles, the Equator-ward movement implies that air mass trajectories are bent towards the east. There, they come in contact with surfaces of higher temperature, causing them to warm up and subsequently to rise. From here, the air flows back to the pole at high altitudes, as indicated in **Fig. 5.** This pattern of circumpolar winds is called the polar vortex. Its main feature is the isolation of the polar air masses from the adjacent, lower latitudes air. As we will see later, this structure is an essential ingredient for an ozone hole to develop over the poles.

Ozone

We have seen earlier that the Earth's atmosphere consists mainly of nitrogen and oxygen. Oxygen is present in the air predominantly in the form of oxygen-oxygen molecules O_2. In contrast, an ozone molecule consists of three oxygen atoms O_3. Ozone is a bluish gas with a sharp, irritating odour.

In the following sections, we will explore the ozone's ambivalent role depending on its location: close to the Earth's surface in the ambient air, ozone is toxic when breathed in large quantities. In the stratosphere on the other hand, ozone is an indispensable shield that protects life against the high-energy part of the sunlight.

Discovery of Ozone

The earliest mention of ozone possibly dates back as far as to the eighth century B.C. The great ancient Greek poet Homer narrates the adventures of Odysseus and his friends on their long journey home to Ithaca, following the fall of Troy. In a terrible thunderstorm, the hero's crew finds the air filled with fire and brimstone as the lightning strikes their vessel. What the plagued seamen smelled as brimstone was nothing else than ozone produced by the lightning discharge.

As for much other wisdom, no other reference to ozone was made during the mediaeval times. It was only in the late 18th century that experiments to uncover the secrets of electricity provided new insights into this miraculous gas. Ozone was first observed in a laboratory when scientists experimented with high voltage discharges. Much like in the lightning of a thunderstorm, the energy released by an electrical discharge is able to produce ozone from the oxygen in the air. Martinus van Marum[2], a Dutch scientist, constructed a giant double plate-glass frictional electrostatic generator between 1780 and 1790. The high voltage field generated by the machine caused "persons within 10 feet of the plates to experience a sort of creeping sensation over them, as if surrounded by a spider's web". The stench of ozone gas, "the odour of electrical matter", was most apparent during operation of the huge machine. Still, the cause of the strange smell was not identified yet. Rather, it was up to Christian Friedrich Schönbein[3], a professor of chemistry at the University of Basel, to detect the gas in 1840 and to give it the appropriate name: ozone, from the Greek "οζειν", the smelling.

The second half of the 19th century marks the development of qualitative methods for measuring ozone. The so-called Schönbein paper was used, that showed a colour change under the influence of ozone (and unfortunately of other gases too).

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[2] Martin von Marum, 1750, Delft (NL) - 1837, Harlem (NL), Dutch scientist.

[3] Christian Friedrich Schönbein, 1799–1868, German - Swiss chemist.

One of the first laboratories to set about routine surface ozone measurements was the Paris Municipal Observatory, located in Montsouris Park in Paris. These measurements began in 1876, and continued for 34 years. The quality of the collected ozone data is doubtful due to the imprecision of the method in use. Nevertheless, this series provides a unique source of information for pre-industrial levels of surface ozone, making it a precious data set for comparisons with present-day measurements.

In 1879, it was noted that only small parts of the Sun's UV-B and no UV-C radiation are able to penetrate Earth's atmosphere down to the surface. Shortly after this discovery, Cornu[4] and Hartley[5] deduced that this absorption was due to stratospheric ozone, as the measured surface ozone concentrations were far too low to explain the observed absorption spectra. It was thus concluded correctly that there must be much more ozone somewhere in the higher atmosphere. This reasoning was later verified by observations of the stratospheric ozone layer.

Physical Properties of Ozone

As mentioned above, an ozone molecule consists of three oxygen atoms. While the binding between the two oxygen atoms in an oxygen molecule (O_2) is very strong, the binding energy of the third oxygen atom in ozone (O_3) is rather weak. This implies that the third oxygen atom is easily lost, qualifying ozone as a potent oxidizer that is today used in many technical applications such as for example the purification of drinking water. In the present context, the most relevant are the spectroscopic properties of ozone: as outlined in **Fig. 6**, atmospheric ozone and molecular oxygen together block all incoming radiation at wavelengths shorter than 280 nm. As noted above, this is the portion of the solar spectrum that is most dangerous for living tissues in general and for the human skin specifically.

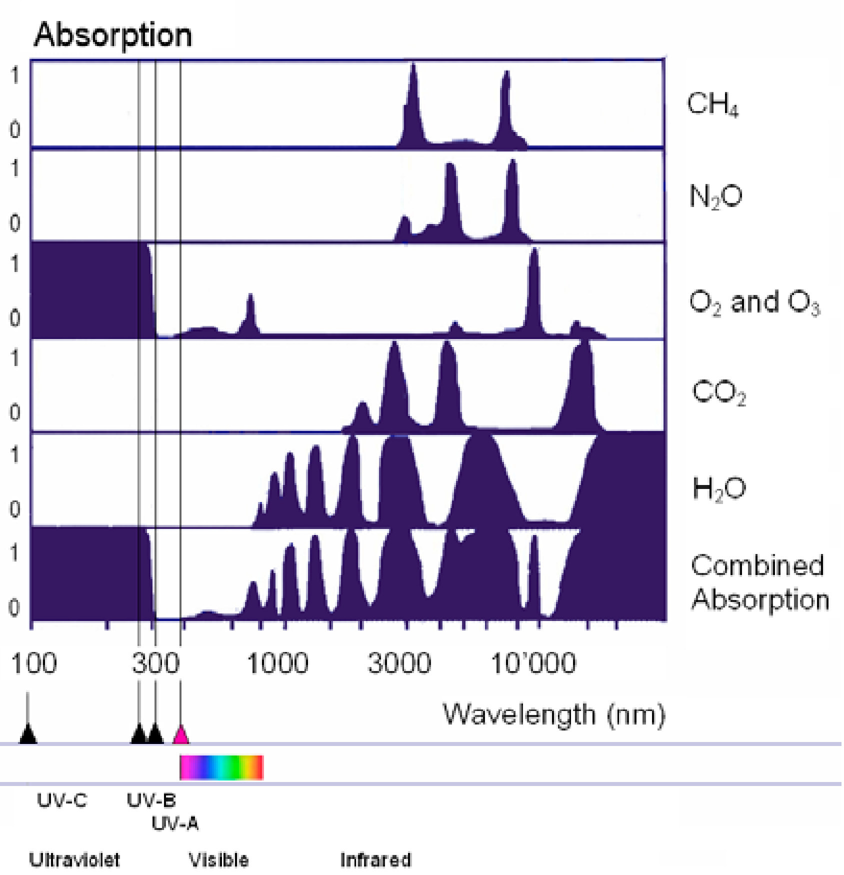

Fig. 6: Schematical representation of the absorption spectra of some constituents of the atmosphere. Note that ozone (O_3) and oxygen (O_2) are responsible for the blocking of all sunlight at wavelengths shorter than 280 nm.

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[4] Marie Alfred Cornu, 1841, Orléans, France - 1902, Romorontin, France, French physicist.

[5] Sir Walter Noel Hartley, 1845, London - 1913, Braemar, Scotland, British physicist.

The Earth's Ozone Layer

There is no major natural source of ozone in the troposphere. In contrast, stratospheric ozone is generated by the light of the Sun. More specifically, the ultraviolet light emitted by the Sun is able to split O_2 molecules in the stratosphere into their components, which then react with other O_2 molecules to form ozone. More than 90% of the atmospheric ozone is contained in the stratosphere. The existence of an ozone layer was however not a permanent feature on Earth, as atmospheric oxygen built up only late in Earth's history as a result of early forms of life. It is fascinating to note here that primordial organisms produced a waste product that became a key prerequisite for later, more complex forms of life.

Evolution of the Ozone Layer

The Earth condensed from the gas and dust of the solar nebula about 4.6 billion years ago. The proto-Earth swept up the material of the gaseous solar nebula in a process of accretion over millions of years[6]. Many of the gases now present on Earth were collected via collisions with other celestial bodies. Eventually, the bombardment subsided as the growing Earth had swept up most of the smaller bodies and the remaining gases in its orbit around the Sun. Heavier gases were trapped in the congealing molten rocks, while lighter gases captured by Earth, such as methane, ammonia, and hydrogen, formed Earth's first atmosphere. This early atmosphere was completely free of oxygen.

Later, gases originally trapped below the surface began to enter the atmosphere through volcanic eruptions and other openings in the crust. The atmosphere began to fill with carbon dioxide, nitrogen, and water vapour. Oceans developed when the surface temperature of the early Earth had fallen enough to allow water to exist in liquid form. Large amounts of carbon dioxide were removed from the atmosphere and trapped in carbonate rocks and in seawater. Photolysis of carbon dioxide and water vapour yielded some atmospheric oxygen, but at that time, every oxygen atom reacted quickly with rocks on the surface and gases already present in the atmosphere. The atmosphere therefore continued to remain free of oxygen.

Finally, life developed, and began to influence its environment[7]. As there was still no oxygen in the atmosphere, no ozone layer existed either, which could have shielded land-based organisms from the Sun's ultraviolet radiation. We assume therefore life to have originated in niches in the oceans, where the shielding role was taken over by water. Initial forms of life were various types of bacteria fit for an anoxic environment. The photosynthetic metabolism of the first plants (types of algae) and cyanobacteria (blue-green algae) initiated to produce oxygen some 2.5 billion years ago. That caused the oxygen content of the atmosphere to rise steadily, allowing the ultraviolet part of the sunlight to produce ozone in the high atmosphere. It is thought that the atmosphere reached 50% of its present ozone content as early as about one billion years ago, while oxygen levels themselves were still only a small fraction of their present value. About 400 million years ago, however, oxygen and ozone had presumably both reached their today's values. At that very time, the first land animals also appeared. It is therefore probable that the development of higher evolved forms of life outside the oceans was closely linked to the development of the protective ozone layer.

Discovery of the Ozone Layer

In contrast to tropospheric ozone, which can be readily identified by means of simple chemical methods, the measurement of stratospheric ozone requires more complex remote sensing techniques. Hartley's discovery of the existence of stratospheric ozone in 1881 opened the floor for a scientist whose name is closely linked with the ozone layer: Gordon Miller

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[6] See Spatium-6: From Dust to Planets

[7] See Spatium-16: Astrobiology

Fig 7: Gordon Miller Bourne Dobson around 1970. (Credit: photo presumably by Dr. A. Dziewulska-Losiowa 1970)

Bourne Dobson[8] **(Fig. 7)**. As a lecturer in meteorology in Oxford, he studied the trails of meteorites together with F. A. Lindemann, then Head of the Clarendon Laboratory at Oxford University. Their research led them to observe that the trails of meteorites did not disappear quickly at high altitudes. From this behaviour, they concluded that the temperature profile above the tropopause was probably not constant as was expected, but that rather it appeared to increase substantially with altitude. Dobson inferred correctly that the cause of the warm stratosphere was heating by the absorption of ultraviolet solar radiation by ozone, and he set out to make measurements of the amounts of ozone in the stratosphere and of their variability.

Dobson was not only an excellent theoretician; he was a gifted experimenter as well. In 1925, he developed the first ozone remote sensing instrument **(Fig. 8)**. The "Dobson spectrometer" working principle is based on the comparison of the sunlight intensity measured at two different wavelengths of the solar spectrum: one at which solar light is unaffected by ozone, and one at which the sunlight is strongly absorbed by ozone. By comparing the measured light intensity at the two wavelengths, Dobson was able to determine what is called the total ozone content of the atmosphere above the point of observation. This term relates to the amount of ozone integrated along a line from the observation level up to the top of the atmosphere. The first Dobson spectrometer was built in Dobson's laboratory in summer 1924. Extensive measurements performed during the following year yielded the main features of the seasonal variation of ozone, among others the springtime maximum and the autumn minimum at mid-latitudes. These results were so encouraging that Dobson decided to construct a further series of five instruments during the winter of 1925–26.

Dobson installed these instruments at various European locations, allowing him the discovery of the relationship between total ozone and synoptic-scale weather systems. It was the prospect of potential use of ozone information to improve weather forecast that spurred the initial interest in long-term ozone observations, and paved the way for the establishment of global ozone monitoring networks. Among the five instruments disposed by G.M.B. Dobson across Europe, one was placed at Arosa, in the Swiss Alps, at the Lichtklimatisches Observatorium then headed by F. W. Paul Götz. Here, routine measurements continued well after the first experi-

Fig. 8: One of the first Dobson spectrometers. Although emerging technologies have since allowed the development of a multitude of alternative ozone remote sensing methods, modern-day versions of the Dobson spectrometers still constitute the pillars of worldwide ground-based ozone monitoring networks. (Credit: University of Oxford, Atmospheric, Oceanic and Planetary Physics Dept.)

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[8] Gordon Miller Bourne Dobson, 1889, Oxford – 1976, Oxford, British physicist and meteorologist.

ments of G.M.B. Dobson, qualifying today the Arosa time series as the longest data sequence of the total ozone content worldwide **(Fig.9).** It is one of the results of F.W. Goetz's research to show that the maximum in ozone concentrations, when described in absolute values (absolute molecule densities), was likely to be at an altitude of approx. 25 km.

Honouring G. M. B. Dobson, the total ozone value is now commonly measured in Dobson Units (DU). If the total ozone column over a certain point on Earth were to be compressed to a pressure of one atm. at a temperature of 0°C, the resulting slab would have a typical thickness of 3 mm. This by definition corresponds to a value of 300 DU **(Fig. 10).**

Quite naturally, the discovery of the stratospheric ozone layer spurred physicists and meteorologists to explain the relevant production and loss mechanisms. It was only in 1929 and 1930 that Sidney Chapman[9] published the theory of ozone formation and destruction. The Chapman Reactions today provide the basis of all ozone chemistry schemes.

Diary of A Stratospheric Ozone Molecule

The Chapman Reactions describe the production and loss mechanisms for ozone under the influence of sunlight. Let us have a closer look at the life cycle of a single ozone molecule. The first step happens when ultraviolet radiation breaks apart an oxygen molecule (O_2) into two free oxygen atoms O:

$$O_2 + hc/\lambda \rightarrow O + O \quad (\lambda < 242\,\text{nm}) \qquad (1)$$

where hc/λ represents the energy supplied by an ultraviolet photon, with h the Planck constant, c the speed of light, and λ the photon's wavelength. The dissociation of the oxygen molecule can take place if the wavelength lies below 242 nm. The rate, at which ozone is formed, is slow, since (1) the sunlight intensity is low at these very short wavelengths and (2) the density of molecules in the stratosphere is low.

Free oxygen atoms are highly reactive. Typically, they react with other oxygen molecules to form an ozone molecule:

$$O + O_2 + M \rightarrow O_3 + M \qquad (2)$$

where M is an inert species, usually O_2 or N_2, which carries away the excess reaction energy. This

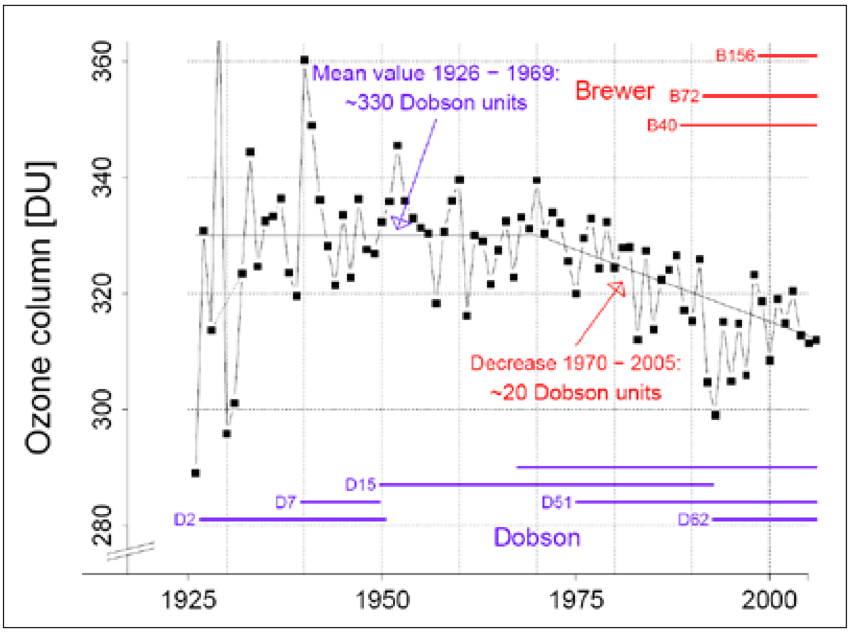

Fig. 9: The "Arosa total ozone time series" (1-year averages). One of Dobson's first instruments (the D2) was installed in Arosa in 1926. Since then, regular measurements have been made with further Dobson-(and Brewer-)instruments leading to the longest total ozone record worldwide. As shown above, total ozone amounts above Arosa were approximately constant (330 DU) until the mid 1970's. From then onwards, a significant decrease was observed. (Credit: Bundesamt für Meteorologie und Klimatologie MeteoSchweiz, 2007)

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[9] Sydney Chapman, 1888, Manchester – 1970, British physicist and geophysicist.

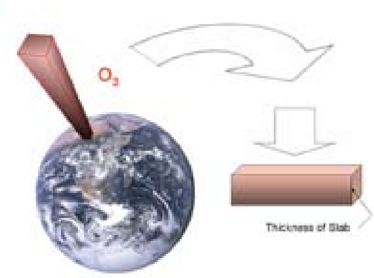

Fig. 10: Definition of the Dobson Unit. If all the ozone over a certain point on the Earth's surface were compressed to one atmosphere at a temperature of 0° C, the resulting slab would measure typically 3 mm. In this case, the total ozone amounts to 300 Dobson Units (DU).

production of heat is the reason for the higher temperatures prevailing in the stratosphere with respect to the lower troposphere.

In this process, a new ozone molecule is created. Ozone in turn also absorbs ultraviolet radiation:

$$O_3 + hc/\lambda \rightarrow O + O_2 \ (\lambda < 310\,\mathrm{nm}) \qquad (3)$$

Here the ozone molecule is split into one oxygen atom and an oxygen-oxygen molecule that can react again as in (2) to produce ozone. In another step, ozone can also be destroyed by reaction with a single oxygen atom:

$$O + O_3 \rightarrow O_2 + O_2 \qquad (4)$$

Here, two O_2 molecules are produced that are ready to participate in further sequences of the Chapman reactions. In the unpolluted stratosphere, this process may continue for a long time, and the ozone molecule may serve its important function many times.

The model described by Sidney Chapman led to predictions of ozone concentrations that are much higher than those actually found in the stratosphere. It was assumed, therefore, that additional mechanisms must exist for its destruction. In 1970, Paul Crutzen[10] suggested additional reactions involving nitrogen monoxide (NO) gas as a catalyst:

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (5)$$

$$NO_2 + O \rightarrow NO + O_2 \qquad (6)$$

Net:

$$O + O_3 \rightarrow 2\,O_2$$

In these reactions, the NO molecule combines with an ozone molecule to form nitrogen dioxide NO_2 and oxygen O_2. Then, NO_2 reacts with atomic oxygen to produce another NO molecule, and an oxygen molecule O_2. The crucial point of this reaction sequence is that the NO molecule enables the destruction of ozone but remains conserved allowing for further destructive reactions. NO is therefore called a catalyst, i.e. a chemical substance enabling a chemical reaction without being consumed itself. In other words, a single NO molecule can destroy ozone molecules as long as it is not washed out from the stratosphere by other mechanisms.

The next step towards understanding the evolution of the ozone layer was taken in 1974 when Mario Molina[11] and F. Sherwood Rowland[12] showed that chlorofluorocarbons (CFC's, **see box**) can reach the stratosphere, stay there for a long time and, under the effect of sunlight, release chlorine atoms that can destroy ozone in a catalytic reaction much like that involving NO. At that time, CFC's were widely used in many technical as well as consumer applications and thoughtlessly released into the atmosphere.

Reverting now to our ozone molecule, we conclude that its lifetime is dramatically shortened in the presence of a variety of chemicals such as chlorine, nitrogen or bromine, the products of CFC's in the stratosphere. These alarming discoveries were not a long time coming…

Chlorofluorocarbons (CFC's) are compounds containing chlorine, fluorine and carbon. Halons are compounds that contain, in addition, bromine. Compounds containing H, F and C are called hydro fluorocarbons (HFC's). During the 20th century, CFC's were marketed under the trade name Freon and other names, and became widely used as refrigerants, propellants in aerosol cans, inflating agents in foam materials, solvents and cleansing agents.

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[10] Paul Josef Crutzen, 1933, Amsterdam, Dutch meteorologist, Nobel Prize laureate 1995 in chemistry.
[11] Mario José Molina, 1943, Mexico City, Mexican chemist, Nobel Prize laureate 1995 in chemistry.
[12] Frank Sherwood Rowland, 1927, Delaware, Ohio, US-American chemist, Nobel Prize laureate 1995 in chemistry.

Discovery of the Ozone Hole

The International Geophysical Year 1958 (IGY) allowed scientists to take part in a worldwide series of coordinated observations of various geophysical phenomena. At that time, no less than 44 Dobson spectrometers were already distributed around the world. These participated in, and later continued the monitoring programme by acquiring data on the total ozone content at various places on Earth. The most frightening news came in 1985 from Halley Bay, Antarctica. There, three British scientists, Joe Farman, Brian Gardiner, and Jonathan Shanklin, of the British Antarctic survey, had observed a 30% decrease in the October total ozone values between 1970 and 1984. These results were corroborated by another report by the Japanese scientist Shigeru Chubachi, based at the Syowa Antarctic station. Although this anomaly was at first not detected by satellite-based measurements, it was soon confirmed by these, as well as by in-situ ozone probes and airborne measurements. The ozone hole had been discovered.

This finding prompted the countries to act. In September 1987, representatives from around the world met in Montreal to sign a treaty setting up sharp limits on the use of

Fig. 11: Polar stratospheric clouds. A complex chemistry takes place on the surface of the ice particles that form polar stratospheric clouds involving chlorine and bromine released from CFC's. As soon as the solar radiation reaches sufficient intensity in early spring, the Cl- and Br-radicals are released, leading to the rapid catalytic loss of O_3 in the antarctic stratosphere (Credit: H. Berg, Forschungszentrum Karlsruhe)

CFC's and halons. The Montreal Protocol established a new way of viewing environmental problems. In the past, no such issue had ever been addressed with so much determination. The Montreal Protocol tackled the ozone issue early, at a moment when damage had already been proven, but hope still existed to avoid an even larger danger.

The Montreal Protocol called also for an increase in atmospheric research, which motivated many research laboratories to launch field expeditions to inhospitable Antarctica. These aimed at solving the mystery of ozone depletion there. In contrast to all expectations, it was found that the destruction of the ozone layer took place at a much lower altitude and to a much larger extent than predicted by the theory of Crutzen, Molina, and Rowland. Farman, Gardiner, and Shanklin already had noted in their 1985 Nature paper that the observed October ozone decrease went along with an increase in concentration of CFC's in the Southern hemisphere over the same time period.

Then, further alarming news came along quickly: besides the building-up of anthropogenic chlorine in the stratosphere, scientists reported that the ozone loss is accelerated by polar stratospheric clouds, see **Fig. 11.** Within the polar vortex, icy cloud particles in the stratosphere offer surfaces to chemical reactions that transform chlorines and bromines into efficient destructive chemicals to break ozone molecules. These reactions take place so quickly that practically all of the ozone over Antarctica is destroyed within a few weeks during the September and October (antarctic spring) period. In addition, the polar vortex effectively prevents air from mixing; therefore, no fresh air containing ozone can enter the antarctic stratosphere during this period.

As a result of intensive research activities at that time, it became clear that the Montreal Protocol would not go far enough to protect the fragile ozone layer. Even with the 50 percent cuts mandated by the treaty, levels of chlorine and bromine would still rise in the stratosphere, meaning that the ozone loss would only worsen with time. In June 1990, delegations met again in London and voted to strengthen the Montreal Protocol significantly.

Given the longevity of CFC molecules, recovery times are measured in decades: according to recent estimates, a CFC molecule takes an average of 15 years to reach the stratosphere from the ground. There, it can stay for up to a century, destroying many thousands of ozone molecules during its lifetime. We have, therefore, to face the fact that even if the release of CFC's into the atmosphere were to be stopped instantly, CFC densities in the stratosphere would continue to increase and the ozone destruction would continue. There is some hope, however: as a result of the ban on CFC's imposed by the Montreal Protocol and its amendments, the latest observational data indicate a global stabilization of the CFC concentration in the stratosphere.

The Earth's Ozone Layer Today

Today, the ozone layer is one of the Earth's most closely watched environmental parameters. It is fortunate that space technology has provided unprecedented observational means covering the remote polar zones, which are so important for understanding the ozone issue but so difficult to access from ground-based stations.

Several institutions regularly publish global ozone surveys, such as for instance the World Meteorological Organization (WMO), which issues regular bulletins with up-to-date information on the state of the ozone layer. The European Space Agency (ESA) has commissioned the Koninklijk Nederlands Meteorologisch Instituut (KNMI) to implement an Internet site under the Agency's Data User Programme (DUP). The TEMIS (Tropospheric Emission Monitoring Internet Service) aims at computing and delivering global concentrations not only of ozone but also of other tropospheric trace gases and aerosols derived from data gathered by space-borne instruments such as the Global Ozone Monitoring Experiment (GOME), the Scanning Imaging Absorption Spectrometer for Atmospheric CHartographY (SCIAMACHY) and the Along Track Scanning Radiometer (ATSR) onboard ESA's Envisat spacecraft.

In the following chapters, we will look first at some global results published on the TEMIS server. We will concentrate on two specific days in the year 2007: 23 March, at the end of the antarctic summer, and 3 October, at the end of the antarctic winter.

Global Total Ozone Maps

In **Fig. 12**, the global total ozone values are shown for the two days selected. Based on our former reasoning, we would expect the highest values to be reached in the tropical zones, where the Sun is overhead and hence delivers the strongest irradiation to produce ozone.

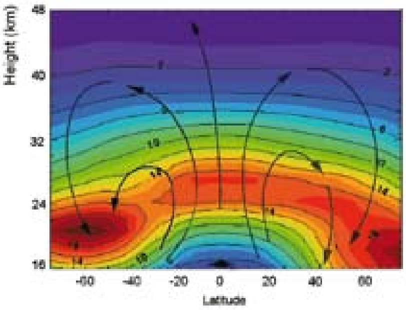

Fig. 13: The Brewer-Dobson circulation illustrated by a schematic, seasonally averaged cross-section through the global atmosphere from pole to pole. At the Equator, tropospheric air masses are lifted up to the stratosphere. At an altitude of some 40 km, they separate in two streams towards the poles. At about 60° latitude, these air masses flow down towards the troposphere and then back to the equator. The result is the so-called Brewer-Dobson circulation. The background colours indicate the local mean ozone density in Dobson Units per vertical kilometre. It can be seen that the highest concentrations are reached in the lower stratosphere between some 80° and 60° North and South latitudes. (Credit: Old Dominion University, Center for Coastal Physical Oceanography, Virginia, USA)

Both upper panels, however, prove the contrary: the largest ozone amounts are rather found at the high latitudes. We conclude therefore that an additional process must take place that reduces ozone values at the tropics and increases them at the winter/spring pole. It was again G. M. B. Dobson, preceded by A. W. Brewer, who was able to find a slow circulation bringing air masses from the equatorial troposphere up into the stratosphere. There, it is enriched in ozone by the strong solar radiation. These air masses then split and flow pole-wards, whereby the ozone enrichment of the middle and polar latitudes takes place. Then, the ozone-rich air sinks down to the troposphere and flows back to the tropics. We now expect the highest values of total ozone at the polar latitudes just outside of the polar vortex. **Fig. 12** illustrates the results of this mechanism, confirming the existence of the so-called Brewer-Dobson circulation as shown in **Fig. 13.**

Arctic Total Ozone Maps

The situation in the northern hemisphere is shown in **Fig. 12** (middle tables) for the same two days as above. At the end of the arctic winter, on 29 March 2007, the total ozone values reached very high values (up to 500 DU, left table). Due to its much lower dynamic stability, the northern polar vortex often gives rise to an attenuated polar ozone hole as compared with its southern counterpart. However, lower ozone concentrations corresponding to the northern ozone hole can still be observed in the left-side panel at about 60°N and longitudes between 30 and 120°E. Obviously, the northern polar vortex was weak and perturbed enough during the winter 2006/2007 to allow the supply of tropical, ozone-rich air to the polar stratosphere even within the vortex. At the end of the arctic summer, on 3 October 2007, the values were between 300 and 350 DU, which is close to normal.

As the majority of humans live under the tropical and northern middle latitudes, the danger for the world's population caused by the depletion of the arctic polar ozone layer has been relatively low over the past 40 years. However, excursions of the polar vortexes towards the equator, induced by perturbed atmospheric dynamics, could lead to direct threats to the populations, such as for instance during winter 1996/97. At that time, an outright arctic vortex together with a large ozone hole developed. The latter spread down well towards densely inhabited parts of Europe and the United States, as indicated by **Fig. 14.** The question of the stability of the northern (and to a lesser extent the southern) polar vortex is still the object of investigations. Relationships have been demonstrated with other global-scale dynamic patterns, such as the equatorial quasi-biennial oscillation (QBO).

Antarctic Total Ozone Maps

In **Fig. 12**, the antarctic total ozone concentration is shown again for the same two days. The left table presents the values on 29 March 2007, at the end of the antarctic summer. Total ozone reached values even in excess of those found in the tropics

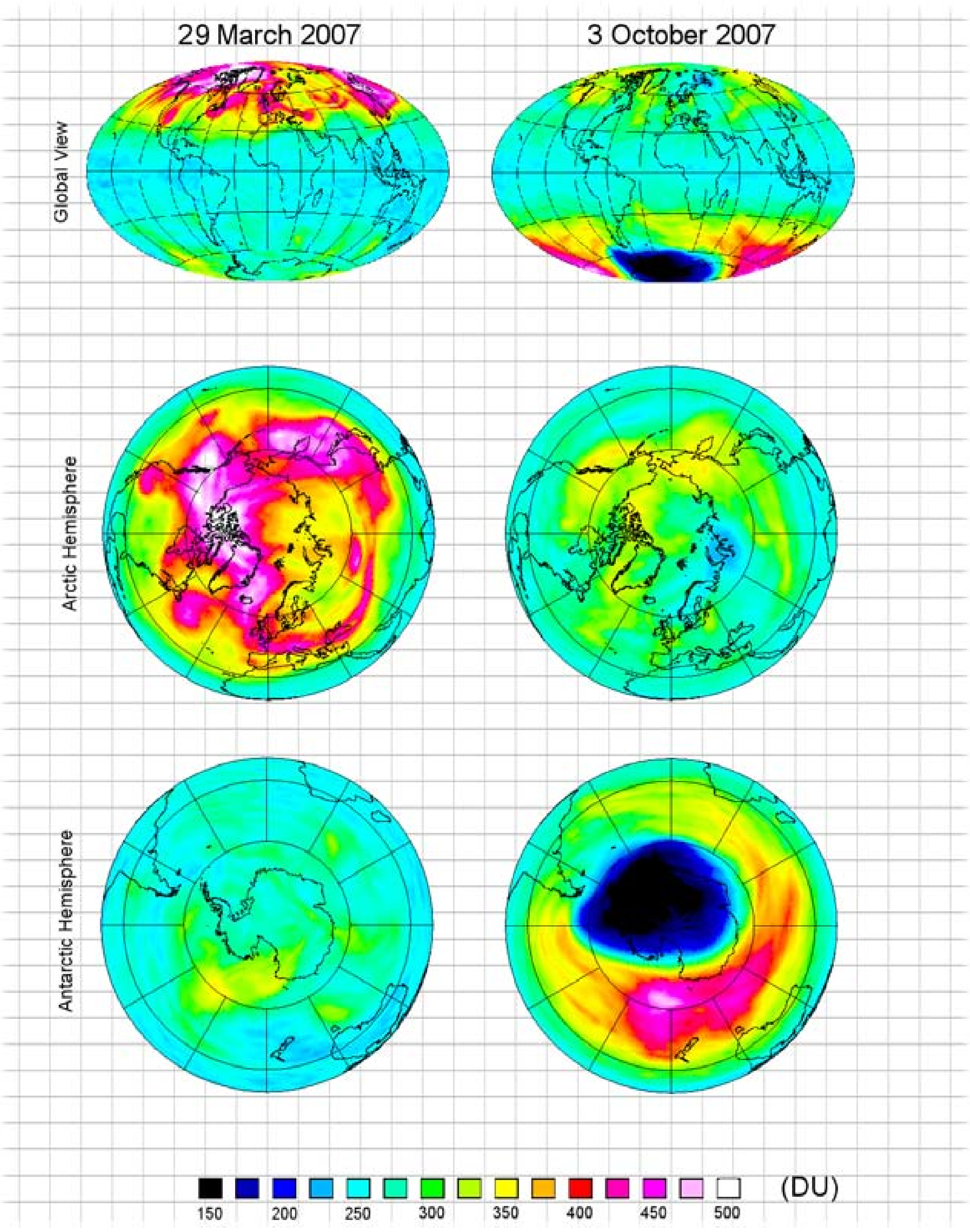

Fig. 12: Assimilated total ozone distributions on 29 March and 3 October 2007. (Credit: TEMIS)

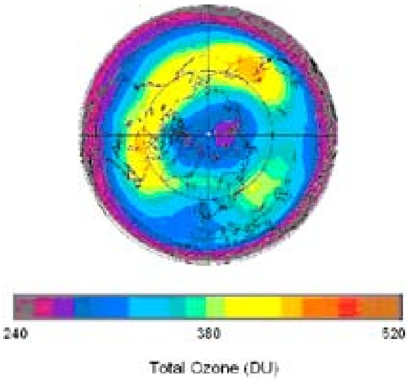

Fig. 14: Arctic total ozone distribution 1997, March average. This image shows the arctic ozone hole that developed at the end of winter 1996/97. In that period, the longest lasting polar vortex on record built-up over the Arctic and in March 1997, the average ozone column over the Arctic fell down to 354 DU, the lowest in the 20 years of observations. (Credit: NASA/GSFC)

thanks to the Brewer-Dobson circulation. The contrast to the right-hand panel, however, could not be more dramatic: here, at the end of the antarctic winter, the ozone destruction process confined within the stable polar vortex during the last few months destroyed some 50% of the ozone as compared to the summer values. Today, the antarctic ozone hole can reach a size exceeding the area of the United States of America.

It is important to understand why the situation is much more dramatic in Antarctica than in the Arctic. The large landmass constituting Antarctica is almost perfectly centred on the pole, allowing a strong circumpolar circulation of the jet stream building the polar vortex during the southern winter. This gives rise to the strongest polar vortex and the coldest temperatures within the vortex, allowing in turn the development of polar stratospheric clouds and consequently the largest ozone holes on Earth.

Local Ozone Data

While satellite views provide an excellent record of the Earth's ozone layer on a global scale, local data remain attractive for their (generally) higher temporal and spatial resolution. They also allow for comparison with series that were taken before the space age that were exclusively local data. In addition, such measurements play the role of "ground truth" data supporting the concurrent calibration of data from spacecraft.

In Switzerland, the Swiss Federal Office of Meteorology and Climatology (MeteoSwiss) is responsible for monitoring the status of the ozone layer over Switzerland. The data is supplied via their Internet site[13], from where the following data have been retrieved.

Total Ozone Over Arosa

It has already been mentioned that the Arosa time series represent the

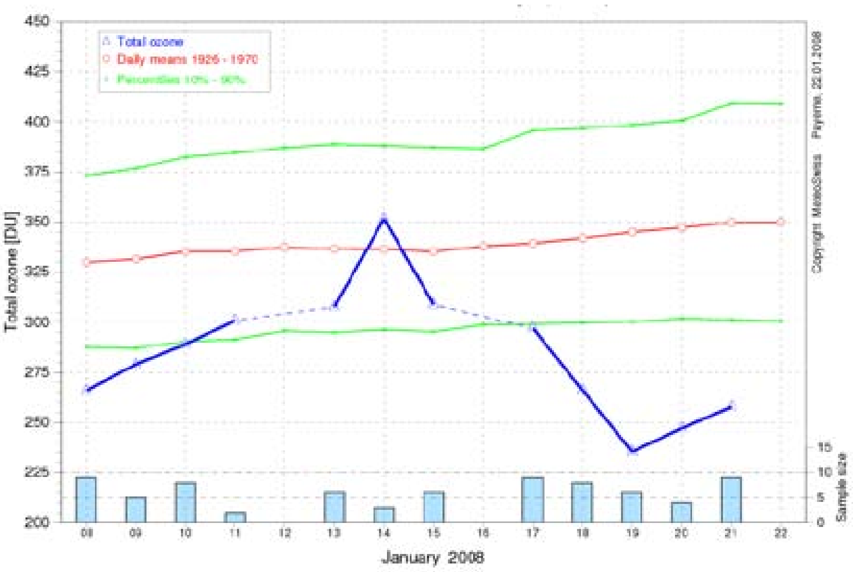

Fig. 15: Excerpt from a recent Arosa total ozone time series. This table shows the mean daily total ozone values over Arosa from 8–22 January 2008. The blue line segments represent actual daily mean values, while the red line shows mean values between 1926 and 1970, that is to say, before the ozone layer's degradation became measurable. The green lines mark the band around the mean values that contain 90% of the values measured from 1926-1970. The table shows a significant loss of ozone towards the end of the observation period that can be attributed to large-scale meteorological activities. As the total ozone measurement requires clear sky, some data from cloudy days are missing. Therefore, some parts in the actual blue curve were interpolated as indicated with dashed blue line segments. (Credit: Bundesamt für Meteorologie und Klimatologie MeteoSchweiz, 2007)

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[13] http://www.meteoschweiz.admin.ch/web/de/wetter/ozone_layer.htm

longest traceable total ozone record worldwide. This station continues to take daily measurements and to compare actual with former values **(Fig. 15).**

As a result of large-scale meteorological activities and of the previously noted relationship between synoptic-scale weather system and total ozone, local ozone values can fluctuate considerably from day to day. This means that assessments of the status of the ozone layer from daily values are not feasible. To this end, long-term time series are required, and this is why the long Arosa record is of such a high scientific value.

Vertical Ozone Profiles

The total ozone values measure the sum of ozone gas from the surface up to the top of the atmosphere. In contrast, the distribution along the vertical axis shows where the ozone resides in the atmosphere. In Switzerland, this data is gathered by means of balloon probes that are launched regularly thrice per week from the MeteoSwiss aerological station in Payerne. As an example, **Fig. 16** shows the partial pressure[14] (in nbar) of ozone, a measure for the ozone particle density per volume, over height. The altitude distribution of ozone is represented for the different seasons of the year 2006. The seasonal maxima of ozone concentrations are situated somewhere between 20 and 25 km. Daily measurements, however, show major displacements of the maximum as well as significant changes over relative small altitude differences as was the case on 3 March 2006.

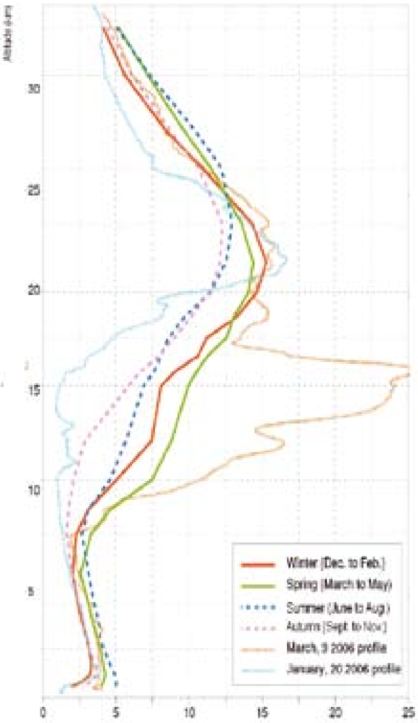

Fig. 16: The vertical ozone profile over Payerne, Switzerland. (Credit: Bundesamt für Meteorologie und Klimatologie MeteoSchweiz, 2007)

Outlook

We do not know the global stratospheric ozone concentrations in earlier times, specifically not before global industrialization with its ever-increasing discharge of CFC's. Nevertheless, we know for sure that the antarctic ozone hole will continue for decades as the relevant pollutants have lifetimes that can reach hundreds of years in the stratosphere. Still, many pieces of the ozone puzzle remain missing, and the science community is challenged by open questions such as how safe the CFC substitutes are, or whether other compounds exist that significantly deplete the ozone layer.

The Montreal Protocol provides a striking example of science at the service of humankind. By quickly piecing together the ozone puzzle, atmospheric researchers revealed the true danger of halocarbons even before the discovery of the Antarctic ozone hole, and urged the community to take decisive actions protecting the Earth's ozone layer. While this agreement represents a critical step toward saving the ozone layer, it has taught scientists and policy makers an invaluable lesson about addressing environmental problems. Beyond all differences that divide humanity there is one common vision to safeguard planet Earth as the home for our future generations.

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[14] The partial pressure is defined as the absolute pressure exerted by one component of a mixture of gases. It is thus a measure of the absolute number of molecules of the gas of interest. If related to the pressure of the entire mixture of gases, the partial pressure allows computing the relative fraction of the gas particles respective to the total air molecules.

The Author

Yasmine Calisesi, is both a Swiss and an Italian citizen; she studied physics at Geneva University and received her diploma in 1996. During her studies, her interest in atmospheric science was aroused by the reading of a book: "Gaia: a new look at life on Earth", by James Lovelock. Besides displaying a quite pessimistic view of Earth's future, Lovelock was also one of the first scientists to demonstrate the influence of mankind on its environment even at the most remote locations on Earth, forcing one's awareness of the proper responsibility in this issue, and triggering the willingness to contribute to a solution…

At the University of Bern, she studied the variations of stratospheric and mesospheric ozone by means of ground-based microwave instruments. She received her Ph.D. degree in Atmospheric Physics in 2000. Ozone was also the subject of her post-doctoral activities in the frame of a joint project of the University of Bern and MeteoSwiss, the Swiss national weather service.

When the International Space Science Institute decided to study its possible involvement in Earth Sciences in 2004, Yasmine Calisesi was asked to prepare the scientific and programmatic issues and to help assessing projects proposed by the international Earth Science community. She organized the workshop on Solar Variability and Planetary Climates in 2005 and co-edited the related subsequent volume i n ISSI's Space Science Series, volume 23. In 2006, she was awarded the Atmospheric Chemistry and Physics Award of the Swiss Academy of Sciences for her work on the continuous monitoring of ozone using microwave radiometry.

In 2007, Yasmine Calisesi received a call from the Swiss Federal Office for Energy to co-ordinate public energy research and education activities in Switzerland. She is now in charge of knowledge and technology transfer within the Swiss Federal Office of Energy.

In her free time (whenever work permits!), she loves to run in the "Bremgartenwald", to go for long hikes (recommended: the Swiss National Park in Graubünden), or to explore Bern's surroundings by bicycle with her husband. Of course, she does not own a car, as this is far from necessary in Switzerland…