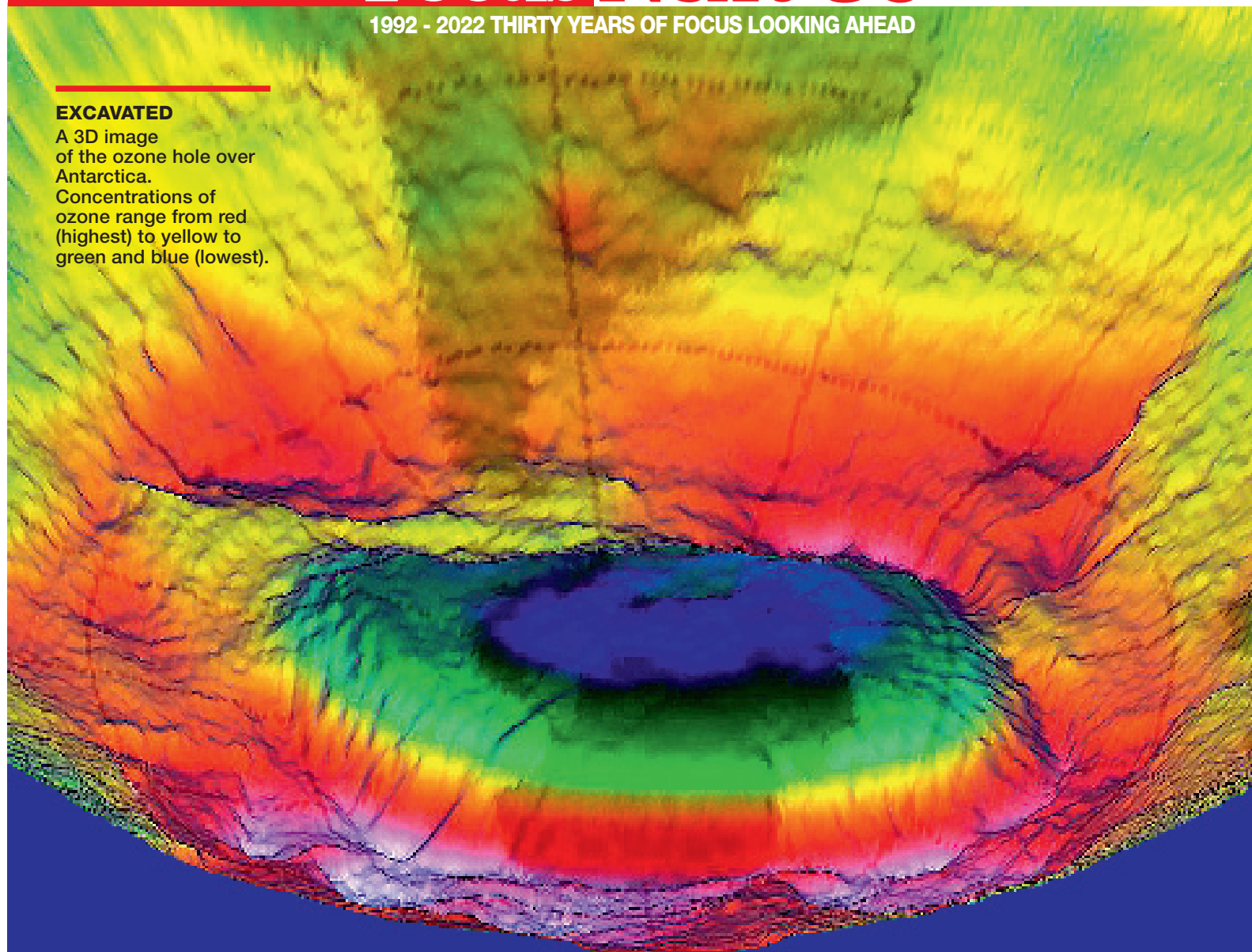


EXCAVATED

A 3D image of the ozone hole over Antarctica. Concentrations of ozone range from red (highest) to yellow to green and blue (lowest).



33 years after the Montreal Protocol, the layer of gas that protects us from ultraviolet rays is being **recovered**. But we must not let our **guard down**.

by Vito Tartamella

How is the OZONE

The discovery of “hole”

The alarm was raised in **1976**. Scientists and activists mobilized. And harmful substances were banned. Before you even find the **evidence**.

It was 1974 when Professor Frank Sherwood Rowland, professor of chemistry at the University of California, and his research fellow Mario Molina published an alarming study in Nature: some artificial gases, chlorofluorocarbons (CFCs) risked destroying the ozone layer at high altitudes. The then CEO of DuPont – the company that had patented those gases under the name “freon” in 1930 – objected that theory was “a science fiction story, a load of garbage, a total absurdity”. The fight against the ozone hole therefore began uphill, opposed by strong economic interests. How did you get there? And what happened next?

A MURDERER ALWAYS FREE

When, at the end of 1992, Focus wrote an article on this topic, the fight against the ozone hole had already begun. The Montreal Protocol, which banned CFCs, had been in force for 3 years, providing for a two-speed accession: immediate for developed countries, deferred for others. At that time there were still 40 companies – including one in Italy, the Ausimont of the Ferruzzi-Montedison group – that produced these dangerous substances. They could have gone on until 1995; from 2010 the call would have had a planetary adhesion.

Science had discovered that a CFC molecule takes 6 years to pass from ground level to the upper atmosphere, where it then remains for about 100 years destroying up to 100 thousand ozone molecules: chlorine binds to an ozone molecule, breaking its bonds, and then binds to another molecule, in an endless cycle (see diagram). “It is like a murderer who, after a crime, returns free to strike again,” explains Ugo Cortesi, of the Institute of Applied Physics Nello Carrara of the CNR in Sesto

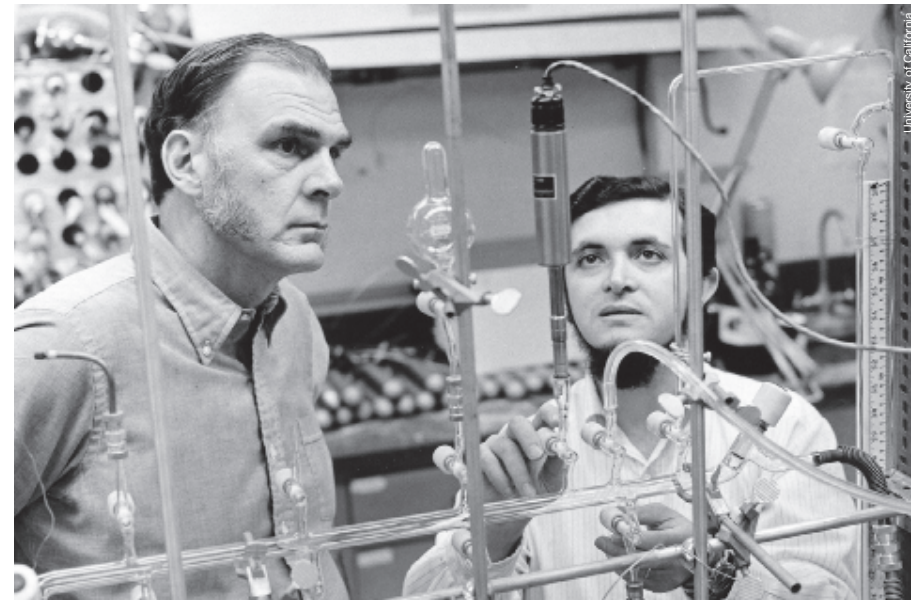
Fiorentino. A real trouble: without ozone, which filters ultraviolet rays, we would risk developing melanomas and cataracts. Even if it is a very thin shield: if the entire atmosphere were concentrated at the temperature of 0 °C and the pressure of 1 atmosphere, the ozone would form a layer of 3 mm on a total atmospheric height of 8 km.

DEFECTIVE TOOLS? NO: THE HOLE IS THERE

The discovery of this planetary threat had happened almost by chance. Professor Rowland had set out to study CFCs – used as refrigerant gases in refrigerators and air conditioners because they are non-flammable, stable and non-toxic – thanks to an invention by James Lovelock, a doctor at the University of Reading, of the electron capture detector. With this instrument Rowland had found traces of CFCs in the atmosphere. A few years earlier, chemist Paul Crutzen of the University of Oxford had discovered that nitrous oxide, produced by soil bacteria and aircraft, thinned the ozone layer: Rowland wanted to test whether CFCs had a similar effect. Studies confirmed this.

In 1976 the U.S. National Academy of Sciences confirmed the credibility of Rowland and Molina’s hypotheses, and in 1978 – despite strong industry pressure – the U.S. banned the use of CFCs. It was an act of trust towards science: the observations that confirmed the hypothesis of the two scientists came only in the following years. The stakes, moreover, namely the health of humanity, were high:

Greenpeace activists organized sweeping demonstrations to keep the world’s attention on the threat. And they did well: in 1985, 11 years after Rowland’s research, British Antarctic Survey scientists Joseph Farman, Brian Gardiner and Jonathan



Shanklin discovered a recurrent ozone hole in the spring on the South Pole. An event never observed: so much so that, at first, they thought that their instruments were defective. Even the measurements made by the satellites had been discarded by the automatic algorithms because they were considered too low to be trusted.

The “normal” ozone layer measures 300 Dobson Units (DU), equal to the 3 mm mentioned above. Before 1979, researchers had never observed concentrations below 220 DU. Now, during the cold season, the layer became very thin. Too much: in 1991 it would have fallen below 100 DU for the first time; in 1994 there was a negative record (fortunately never equaled again) with 73 DU.

In addition, researcher Susan Solomon of NOAA (National Oceanic and Atmospheric Administration) discovered an additional mechanism of ozone destruction in polar clouds: they

form at very low temperatures (-80 °C) and contain inactive chlorine compounds; when the sun’s rays hit them in spring, they activate chemical reactions that form active chlorine molecules (chlorine monoxide) that destroy ozone. And scientists also discovered that volcanic eruptions thin ozone because they produce hydrochloric acid and chlorine: the eruption of Pinatubo in 1991 helped reduce the ozone layer for years.

All the research, in short, converged on a common point: large areas of the Earth risked being deprived of the protective ozone shield. In 1987 the first 90 nations signed the Montreal Protocol (today there are 197, all UN countries) which sanctioned the ban on CFCs. Just in that year, in fact, the “smoking gun” had been found: the NASA planes that took off from Chile had taken air samples in the upper atmosphere at the South Pole, finding traces of the chlorine emitted by the industry.

However, an environmentally friendly alternative to CFCs ▶



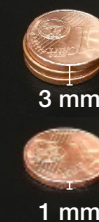
OZONE: WHERE IT IS, HOW MUCH IT IS

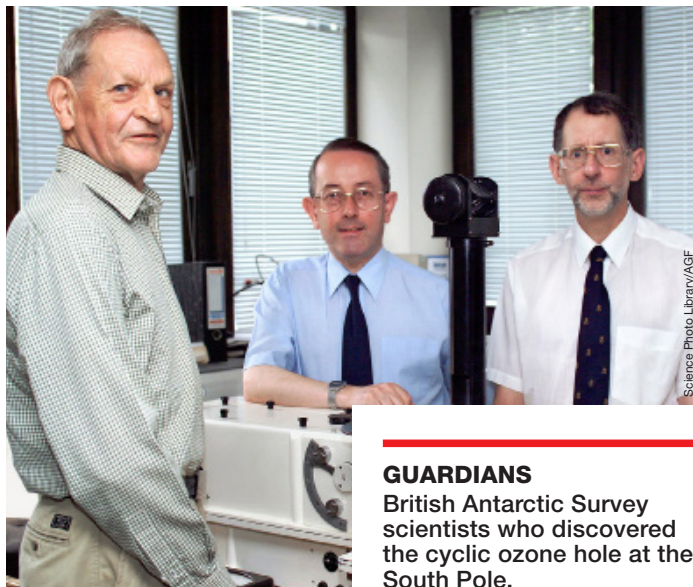
Ozone is a gas composed of 3 oxygen atoms (O₃). It is present in small quantities throughout the atmosphere, where it is formed naturally through chemical reactions triggered by solar radiation. 90% of ozone is formed in the stratosphere, between 18-28 km of altitude; the rest in the troposphere (under 10 km). Ozone is formed mainly in the Tropics, from where atmospheric circulation transports it to the middle latitudes and to the Poles.

Ozone can form at ground level as a by-product of pollutant emissions (although 1/4 of the ozone in the troposphere comes from the stratosphere). Causes irritation to the respiratory tract.

The total mass of ozone in the atmosphere is 3 billion tons. It may sound like a lot, but it’s only 0.00006% of the atmosphere. This proportion can be represented in a more direct way: if we imagine compressing the whole atmosphere (at 0 °C and at a pressure of 1 atmosphere), it would form a layer of 8 km. The ozone, in that layer, would be 3 mm thick, equal to 300 Dobson Units (the unit of measurement of ozone, DU). What we call the “ozone hole” corresponds to 100 Dobson Units, equal to 1 mm thick, like a 1 euro cent coin.

Global average ozone: 300 DU
Average ozone hole: 100 DU





GUARDIANS
British Antarctic Survey scientists who discovered the cyclic ozone hole at the South Pole.

for refrigeration systems remained to be found. In 1992, as the Focus article reported, the world focused on hydrofluorocarbons (HFCs): in the following years, however, research discovered that they are powerful greenhouse gases. In 2016 they were blacklisted in an amendment to the Montreal Protocol.

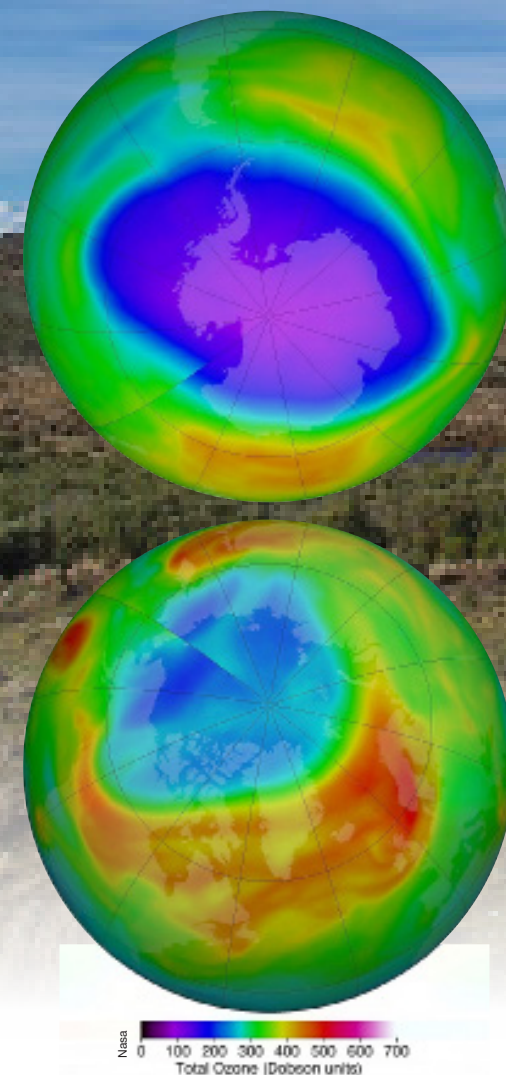
GREENPEACE FREEZER

Fortunately, however, a greener solution had emerged. At the Institute of Hygiene in Dortmund, Germany, researchers were studying natural hydrocarbon-based refrigerants used in the 30s, before the advent of CFCs. They found that isobutane was safe for ozone and the greenhouse effect. The molecule, called GreenFreeze, won the environmental award organized by the Institute. A GreenPeace activist, Wolfgang Lohbeck, learned the news and looked for a fridge factory willing to use it, but found only closed doors: hydrocarbons were in fact perceived as flammable, even if technology had eliminated this risk. The only company willing to produce the new refrigerators was DKK Scharfenstein, an old Factory in East Germany.

Refrigerator manufacturers with HFCs campaigned for delegitimization, saying greenfreezes were “electricity eaters” and “potential bombs” in kitchens. But GreenFreeze gained the support of the government and scientists. And in 1993, a few months after the release of Focus, the first 70,000 GreenFreezes came out of german plants. To conquer the world: greenFreeze technology was not patented to promote its planetary industrial diffusion.

“It was the demonstration,” recalls Giuseppe Onufrio, director of GreenPeace, “that the struggles for the environment serve to keep attention on the problems; but they are won only if they are supported by trade and technological cooperation agreements. By the time of the Montreal Protocol, patents for the production of CFCs had expired: China and India could have manufactured them without hindrance. With GreenFreeze they had a convenient alternative.”

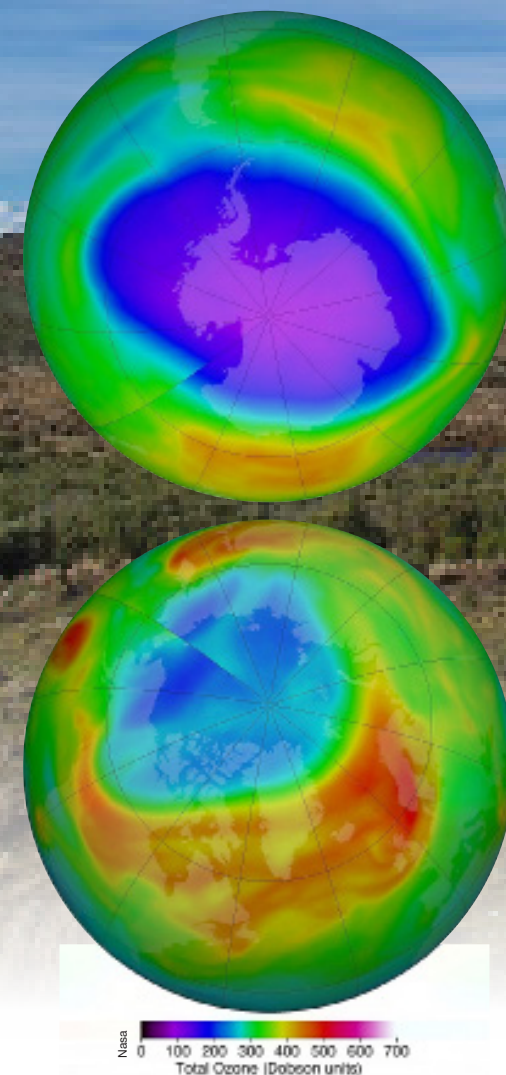
So the battle against the ozone hole took a virtuous path: in 1995, the discoverers of ozone-depleting substances, Crutzen, Molina and Rowland, received the Nobel Prize in Chemistry. On Molina’s certificate there is the design of an umbrella: the symbol of the protection of the ozone layer. But the fight to keep that umbrella intact is not over yet. **F**



THE TWO HOLES

The latest images of the hole in 2021. Above, the one on Antarctica, below, the hole on the Arctic, which forms less often and is less deep and wide. In the large photo, launch of a probe to measure ozone from Ushuaia, Argentina.

Ozone is healing, but...



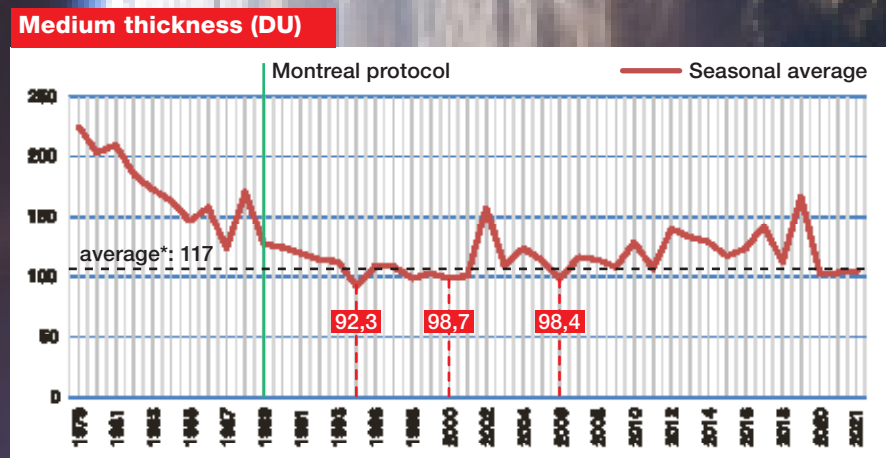
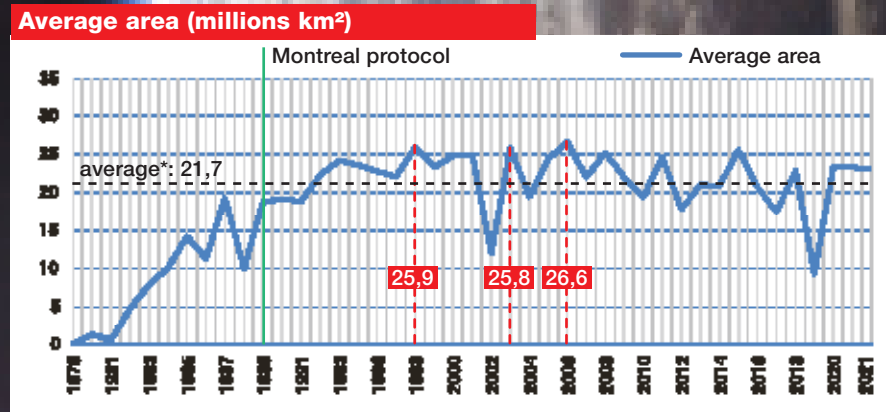
The latest alarm is from 2018. A researcher from NOAA (National Oceanic and Atmospheric Administration), Stephen Montzka, denounces from the columns of *Nature* an increase in emissions of CFC-11: trichlorofluoromethane, a gas of the family of chlorofluorocarbons banned by the Montreal Protocol. The research is mobilized, and the smoking gun is discovered: those emissions, recorded between 2014 and 2017, came from China. In more detail, from the data collected by air monitoring stations in South Korea and Japan, it turns out that 7 thousand tons of that gas came from plants in Shandong province, in Eastern China. The study, published in *Nature* and signed by researchers at Peking University, has raised great concerns: those abusive emissions risked lengthening the full recovery of the ozone hole by 6 years, estimated in a study a researcher at MIT, Megan Lickley. But the reaction of the Chinese authorities was immediate: at

regular meetings on the implementation of the Montreal Protocol, representatives of the Asian state reported that they had demolished the “rogue factories”, seized the materials and arrested those responsible. In fact, already in 2019 CFC-11 emissions were gone, canceling the risk of delay in the roadmap towards the full recovery of the ozone layer.

“We need to keep in mind that any unreported emission of harmful substances will have a lasting environmental impact,” says Matt Rigby, an atmospheric scientist at the University of Bristol. “Unfortunately, it is likely that only a part of the gases produced has been released into the atmosphere: the rest could still be imprisoned in the foam of buildings (CFC-11 is also used as an insulator, ed) and spread in the air in the coming decades.” The fight against the ozone hole, in short, is far from over. Also because in the last 30 years research has made many discoveries in this regard: that the “hole” can form seasonally even over the Arctic. **►**

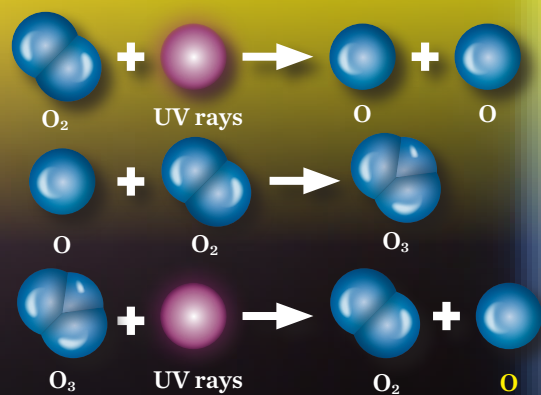
The ozone hole, 1979-2021

The size and concentration of the ozone hole over Antarctica varies from year to year. In these graphs, the average trend from 1979 to 2021: the 3 years with the worst-case scenarios are highlighted, in terms of extent and thickness of ozone. In 2000, the maximum width of the “hole” was recorded for a few days: 29.6 million km²; in some days of 2006 the thinnest level was reached, 84 Dobson Units (DU). The best values, in recent times, were recorded in 2012, 2017 and 2019. 2021 ended with a wide “hole” on average 23.3 million km² and with 103.3 DU thick. The Montreal Protocol, signed in 1987, has entered into force since 1989, the year from which the arithmetic average* of the values in the two graphs is calculated. Given that chlorine molecules remain active in the atmosphere for a century, the gradual depletion of the ozone hole will be more evident in the coming decades.



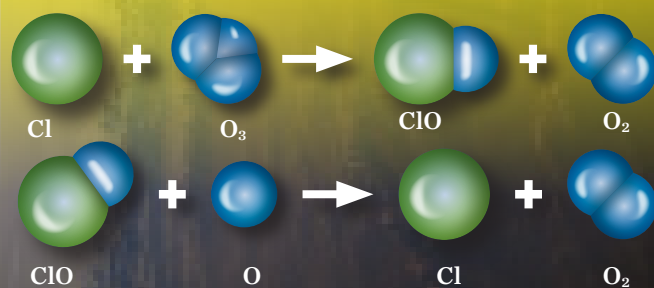
How it is formed

When UV light from the Sun hits an oxygen molecule (O₂), it breaks its bond, releasing two oxygen atoms (O). These, by binding to an oxygen molecule O₂, form ozone (O₃), which in turn, hit by the rays, breaks down into a molecule and an oxygen atom, restarting the cycle. These chemical reactions absorb ultraviolet light, converting it into heat. To be precise: the first reaction absorbs all short-wave UV radiation (UV-C, the most energetic), the third reaction absorbs 90% of the average ones (UV-B), letting the long ones pass (UV-A). The first two are harmful to humans (they cause skin cancers and cataracts), while the third is important for producing the vitamin D essential to the bones.



And so it breaks

The ozone layer shrank by 4% per decade from 1980 to the 2000s. The cause was the introduction of chlorofluorocarbons into the atmosphere: these compounds, which contain chlorine, fluorine and carbon, rise to the stratosphere, where ultraviolet light breaks down the molecules releasing chlorine: this steals an oxygen atom from the ozone, forming chlorine monoxide (ClO) and an oxygen molecule (O₂); then the chlorine monoxide reacts with an oxygen atom, thus releasing chlorine for a cyclic reaction. A single molecule of CFCs can last 20 to 100 years in the atmosphere and can destroy 100,000 ozone molecules. With the ban on chlorofluorocarbons, established by the Montreal Protocol (1987), the hole is healing: it should return intact by 2060.



Volcanoes, pesticides and the greenhouse effect can erode ozone. So it is necessary to be vigilant

That other substances so far neglected contribute to affecting the thin ozone layer. And that climate change can also have negative effects on ozone.

IT HAS DROPPED BY 4 MILLION KM²

But before telling all this, 33 years after the entry into force of the Montreal Protocol, a question arises: is the ozone layer healing? By when will it return intact? Looking at the graphs since 1979 it would not seem that it is recovering: the “holes” that formed in 2020 and 2021, among other things, were among the most durable measured to date.

“The latest scientific assessment by the World Meteorological Organization indicates that full recovery in Antarctica should take place by 2060,” says Vincent-Henri Peuch, director of the Copernicus Atmosphere Monitoring Service, the European atmospheric monitoring programme. “An update of this forecast is planned for the end of the year: recent projections may change this date slightly, but not substantially.”

Already in 2016 a study in Science conducted by Susan Solomon, atmospheric chemist at MIT in Boston, had shown that in the last 15 years the size of the ozone hole over Antarctica has been reduced by about 4 million km², like the surface of the European Union.

“The ozone layer is recovering and the levels of substances harmful to ozone are decreasing”, confirms Ugo Cortesi of the CNR. “The ban on CFCs has been fundamental to stop a phenomenon that could have reached dramatic dimensions. The signs of containment are undeniable, but the thinning of ozone has not disappeared: it must be remembered, moreover, that the CFC molecules remain in the stratosphere for up to 100 years, during which they continue to exert their destructive action».

An action made possible and enhanced by the very cold temperatures that reaching -80 ° C allow the formation of polar stratospheric clouds. When the sun arrives in spring, light breaks down chlorine compounds into active molecules that destroy ozone. For this reason, the hole is formed mostly over Antarctica, where the currents favor the achievement of colder temperatures.

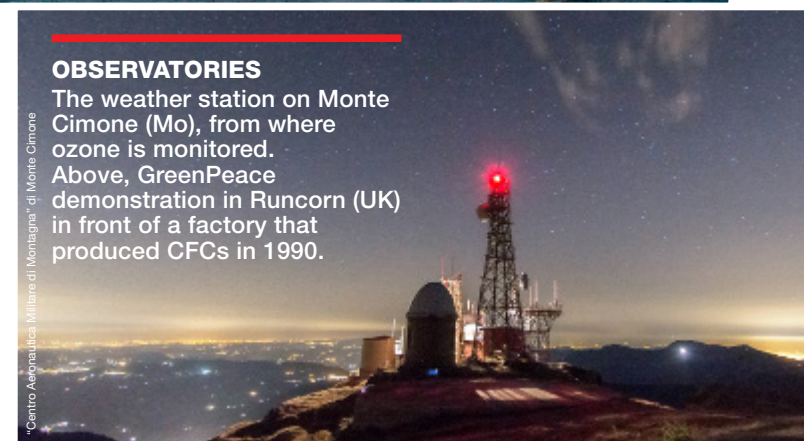
NORTH POLE, SMALLER BUT INSIDIOUS HOLE

But, occasionally, a hole also forms over the Arctic, when cold air currents remain longer around the Pole during the boreal winter: it formed in 1997, in 2004, in 2011. The last one dates back to 2020, and was the largest ever recorded: 23 million km². “The hole above the Arctic is rarer, less durable and shallower, but it raises more concerns than the one over Antarctica,” Cortesi said.



OBSERVATORIES

The weather station on Monte Cimone (Mo), from where ozone is monitored. Above, GreenPeace demonstration in Runcorn (UK) in front of a factory that produced CFCs in 1990.



Why? “Because it comes to touch more densely inhabited lands than what happens in the opposite hemisphere. The hole above Antarctica, in its maximum extension, touches the tip of South America and Australia; but the one on the Arctic goes as far as Scandinavia, Russia, Alaska and Canada. There are many more people potentially at risk of receiving more ultraviolet rays in the Northern Hemisphere.”

A scenario, this, made even more complex by climate change: while temperatures on the surface of the planet increase due to the action of greenhouse gases, those in the stratosphere, where ozone is concentrated, are falling more and more. Favoring the formation of stratospheric clouds at the Poles, where ozone-depleting substances are concentrated. In short, a vicious circle that gives one more reason not to lower the guard in the monitoring of ozone.

NEW SOURCES OF HARMFUL SUBSTANCES

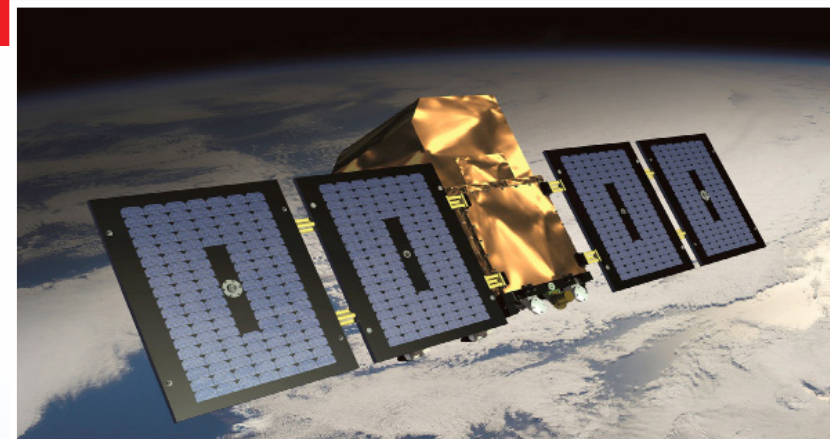
And, as if that were not enough, new sources of substances that threaten ozone are always being discovered: in a research published in early 2022 in *Nature Communications*, researchers at the University of California have discovered that bromide and methyl chloride, two compounds known to destroy ozone, have many sources that have not been taken into account until now: copper-based compounds released into the environment by fungicides, brake pads, paints, pesticides.

“About a third of the bromide and methyl chloride in the atmosphere comes from unknown sources,” said Robert Rhew, a professor of environmental science. “The use of copper in the environment is expected to increase rapidly in the coming years and will have to be taken into account for the recovery of the ozone layer.”

“The risk of other emissions of ozone-depleting substances cannot be excluded,” Peuch concludes. “Therefore, it is important to keep the efforts to monitor the atmosphere high.”

... it remains under special surveillance

More capillary **ground stations**, new **research** and more sensitive **satellites**: with these instruments we'll control the healing of the ozone layer.



ACCURATE

Above, the Altius satellite that ESA will send into orbit in 2025. On the opposite page, the Neumayer station at the South Pole, from which ozone is monitored.



From the earth, from sky

The ozone in the stratosphere is monitored by a dozen satellites, probe balloons (which reach up to 40 km of altitude), aircraft. The Global Atmosphere Watch of the World Meteorological Organization (WMO) manages a network of 30 ground stations (one in Italy, on Monte Cimone, Modena, at 2,165 m altitude): they use lasers and microwave radiometers to determine the amount of ozone.

Increasingly precise and capillary observations. And new research on the chemistry of the atmosphere. These are the weapons with which we will save ozone in the coming decades. Starting from the instruments that first confirmed the ozone depletion: satellites. Today those who observe the concentration are many: they deduce the amount going, for example, to measure how many ultraviolet rays are absorbed by the atmosphere. The more UV light passes, the less ozone is present. In this way the satellites can measure the total amount of ozone and its vertical distribution.

In the coming years, new space missions will provide ozone data "in unprecedented quantity and quality", announces the European Space Agency (ESA).

From 2024, Copernicus Sentinel-5, the largest Earth observation program ever implemented, will be operational. And in 2025, ESA will launch Altius, an ozone measurement mission funded by Belgium with contributions from Canada, Luxembourg and Romania. "It will fly in low orbit," explains Ugo Cortesi, a member of the Advisory Group of the Sentinel-4/-5 missions. "Its observation geometry will allow it to look in directions tangent to different layers of the atmosphere. In this

way it will be possible to establish the concentrations of ozone at the various altitudes. He will do a sort of CT scan of the atmosphere."

THE RISKS OF A NUCLEAR WAR

The satellites will be flanked by the monitoring done by the ground stations: the Global Atmosphere Watch of the World Meteorological Organization (WMO). The network consists of 30 control centers scattered all over the planet: thanks to them it was possible to discover the "rogue factories" that, in China, emitted substances harmful to ozone.

"In the coming years it will be important to expand the existing network to make controls more widespread and timely," adds Vincent-Henri Peuch, director of the Copernicus Atmosphere Monitoring Service.

Also, as the latest research on emissions of bromide and methyl chloride shows, there is still much to learn about substances that damage ozone. Recent research by the UCAR (University Corporation for Atmospheric Research) has established that if a global nuclear war broke out it would erase 3/4 of the world's ozone in 15 years; a regional nuclear war would lose 1/4 globally.

Just to reiterate how fragile that layer is.

35 years after the signing of the Montreal Protocol, what lessons have we learned from the ozone hole?

The world has managed to foil a planetary environmental threat by finding and respecting a global agreement.

The history of the ozone hole has shown that trust in science is well placed: when scientists Frank Sherwood Rowland and Mario Molina hypothesized the destructive action of CFC molecules on ozone, the scientific world gave them credit even though they still lacked the field evidence, which arrived in the following years. And satellite observations have been instrumental in monitoring this complex atmospheric phenomenon in real time.

AN EXAMPLE TO FOLLOW

The GreenPeace demonstrations have lit the spotlight on the emergency thanks to an imprecise metaphor that has made inroads into the collective imagination: the "hole" in the ozone. Over Antarctica and the Arctic, in fact, a real crack has never opened: the ozone layer has actually thinned.

All these factors, in short, have worked synergistically to ar-

rive at the Montreal Protocol, "the single most successful international agreement", as former UN Secretary-General Kofi Annan called it. Can this formula also be applied to the fight against greenhouse gases and climate change?

"The starting point is the same as ozone: we know which molecules are responsible for it (CO₂, methane, etc.) and we know that they are emitted by man," Peuch replies. "But reducing CO₂ emissions is much more difficult than ozone-depleting substances. Lowering CO₂ emissions involves reducing some human activities (from intensive farming and agriculture to the use of coal, ed), developing renewable energy sources, reducing the energy needs of homes and means of transport, and finding solutions to store excess carbon in the atmosphere. Substances that threaten ozone have been easily replaced with other harmless ones: it is a global problem but influenced by a limited number of sectors. To reduce greenhouse gases, however, much deeper changes are needed that will impact all people. Therefore, discussions, agreements, technological solutions take longer. But the Montreal Protocol has shown us that science can help solve the environmental problems that threaten the planet." **F**