WEATHER CLIMATE WATER

WORLD METEOROLOGICAL ORGANIZATION

GLOBAL ATMOSPHERE WATCH

WMO REACTIVE GASES BULLETIN

Highlights from the Global Atmosphere Watch Programme

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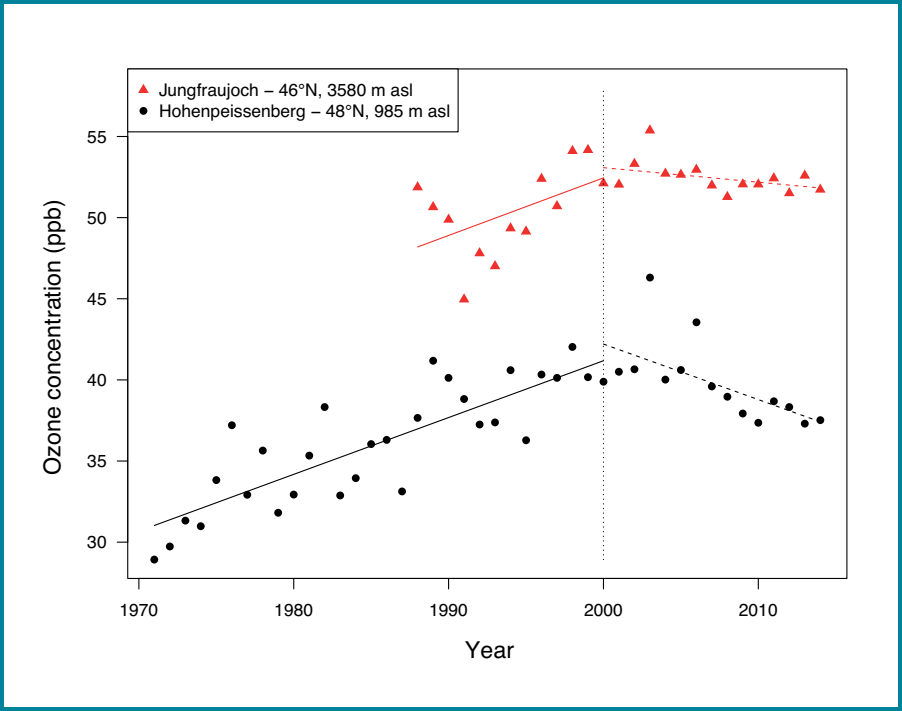

Figure 1. Annual average surface ozone concentrations from two European stations. Both stations are part of the Global Atmosphere Watch Programme and participated in the Tropospheric Ozone Assessment Report. Trend lines are fitted separately for the periods before and after the year 2000. The years 2003 and 2006 are outstanding because of the European heatwaves. Ozone concentration levels are higher at Jungfraujoch than at Hohenpeissenberg as they increase with altitude.

Air quality regulations and pollution mitigation actions in Europe and North America have had remarkably positive impacts on the quality of the air. Since the year 2000, both mean and peak concentrations of surface ozone in Europe and North America have levelled off and have even started to decrease in some locations, after having increased throughout the twentieth century (Figure 1). In contrast, at the few available surface stations in East Asia, a continuous increase in surface ozone has been observed since the year 2000. Moreover, due to the atmospheric transport of ozone and its chemical precursors(1) over long distances, some surface sites on the west coast of North America also show a continued increase. While severe ozone impacts on health and vegetation have become less prevalent in many regions of the world, long-term effects, which are caused by background ozone concentration,(2) remain a concern.

The identification of changes in background concentration levels requires systematic long-term measurements at locations not directly influenced by local emissions. This is in addition to urban monitoring, which is necessary to investigate episodes of high ozone levels and to verify compliance with air quality regulations. While there have been systematic observations of surface ozone concentration in Europe and North America since the 1970s, such observations are sparse or completely lacking in many parts of the world. The Tropospheric Ozone Assessment Report (TOAR), a recent international research activity with a major contribution from the Global Atmosphere Watch (GAW) Programme, has analysed changes in the global distribution of surface ozone concentration and released an assessment of the tropospheric(3) ozone burden [1].

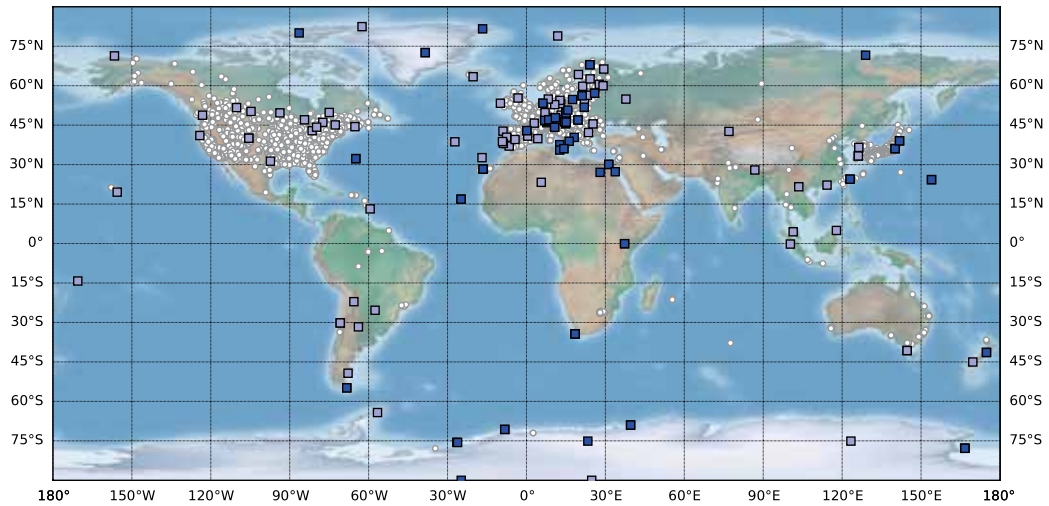

Figure 2. Global coverage of surface ozone observing stations. Dark squares (data recently updated in the World Data Centre for Reactive Gases) and light-blue squares denote stations from the GAW network; small white circles show stations from other networks included in the TOAR database.

Ozone in the troposphere

Tropospheric ozone (O_3) is a secondary air pollutant and greenhouse gas, which is detrimental to human health, crops and ecosystem productivity. It is formed by the chemical reactions of so-called ozone precursors in the presence of sunlight. The main precursors are nitrogen oxides (NO_x = NO + NO_2), carbon monoxide (CO), methane (CH_4) and non-methane volatile organic compounds (VOCs, see also *WMO Reactive Gases Bulletin* No. 1). Although these precursors also occur naturally, contributions from anthropogenic[4] sources, such as industry or internal combustion engines, are mainly responsible for high ozone concentration levels. Ozone, as well as many of its precursors, is highly chemically reactive and oxidizing. Ozone also plays an important role in atmospheric chemistry by facilitating the removal of other pollutants from the atmosphere. For instance, ozone is the primary tropospheric source of the hydroxyl (OH) radical, which acts as the "detergent" of the atmosphere by initiating the oxidation reaction of a range of pollutants and chemically reactive greenhouse gases. In order to understand these complex chemical interactions, assess the impact of emission changes on pollution levels, verify numerical model simulations[5] [2], and quantify the interactions between short-lived reactive compounds and climate change, long-term observations of reactive gases in the troposphere must be made [3].

In this issue of the *WMO Reactive Gases Bulletin*, impacts of tropospheric ozone on human health, vegetation and climate are presented. This information is based on recent globally-harmonized insights derived from the observational network.

Global network of long-term observations

Surface ozone was first observed in the nineteenth century. Measurement techniques have evolved considerably since the semi-quantitative method used at that time, and the portion of the globe being observed has increased [4]. Ongoing observations started at a very small number of sites in the early 1970s, including GAW Global Stations such as Hohenpeissenberg (Germany), Barrow (Alaska, United States) and Mauna Loa (Hawaii, United States). The world's longest continuous ozone record, which started in 1956, is from a combination of the two nearby sites of Arkona and Zingst (60 km apart) on the Baltic Sea coast in northern Germany. After the inception of GAW, in 1989, the number of stations in the global network of surface ozone measurements grew rapidly. In TOAR, several thousand hourly datasets were gathered from surface measurement sites around the world (both urban and non-urban), and ozone exposure statistics were made available in a globally consistent way [5]. The current GAW measurement network for surface ozone and the network of stations contributing to TOAR are shown in Figure 2.

Although tropospheric ozone observations have evolved from sporadic measurements at a few locations to extensive, well-calibrated national networks with formal international collaboration, and have been supplemented by ozonesondes,[6] aircraft-based measurements and global satellite observations, surface observations are still neither comprehensive nor evenly distributed [5].

Impacts of tropospheric ozone

Direct and indirect impacts of surface ozone on human health, vegetation and climate are explained below. The Tropospheric Ozone Assessment Report provides information and maps tailored to each of those impacts, in addition to the impact-based assessments in TOAR-Health [6], TOAR-Vegetation [7] and TOAR-Climate [8].

Human health

Life on Earth as we know it would not be possible without the stratospheric[7] ozone layer, which absorbs harmful ultraviolet (UV) radiation that could otherwise reach the Earth's surface. However, in the troposphere and particularly close to the surface, in the so-called planetary boundary

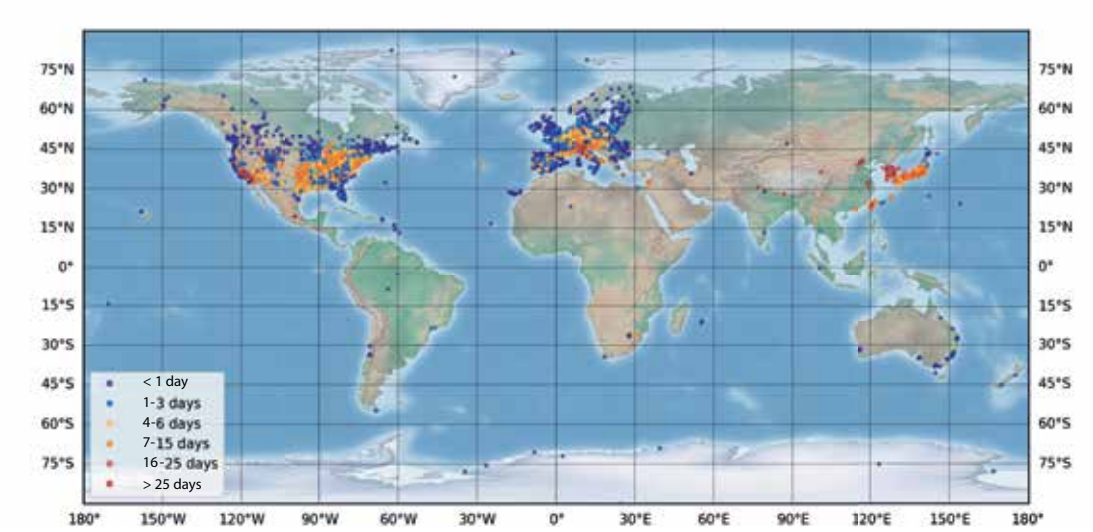

Figure 3. Peak short-term exposure expressed as number of days per year with ozone concentration levels greater than 70 ppb (US limit value), averaged over 2010–2014. Data from 4801 stations in the TOAR database were used for analysis. (*Source*: Adapted from Fleming et al., 2018 [6], Figure 4b)

layer,[8] ozone acts as a powerful oxidant, which can impair the functioning of the human respiratory and cardiovascular systems through its reaction with the lining of the lungs' tissue and other surfaces in the respiratory tract [9]. Hundreds of thousands of lives end prematurely each year due to the effects of anthropogenic ozone pollution [10]. Intensive air-quality control measures are required to prevent urban premature mortality which is expected to double by 2050, if population growth and economic development continue at the current pace [11].

Many countries have implemented ozone air quality standards for the protection of human health through an exposure limit based on the maximum 8-hour average ozone concentration. This is often combined with a number of exceedances of the limit that are allowed before violation of the ozone standard occurs. For example, the European threshold value is 60 ppb (Directive 2008/50/EU). In the United States, the threshold value is 70 ppb, in China it is 75 ppb and the one recommended by the World Health Organization (WHO) is 50 ppb.

High-peak short-term ozone exposure is, in relative terms, more frequent at urban sites than at non-urban sites. Among the areas where measurements are available, current summertime peak short-term exposure values (Figure 3) are highest in East Asia, southern Europe and the west coast of North America. Evaluation of the ozone peaks in other regions is limited due to lack of data.

Since the 1990s, anthropogenic ozone precursor emissions have gradually decreased in North America and Europe and increased in East Asia [12]. Accordingly, peak ozone concentrations and therefore human exposure have decreased in Europe and North America and increased in East Asia [13]. Established emission control measures (for example in China, in 2011) are too recent to have had a noticeable effect on the ozone trend. Apart from anthropogenic emissions of ozone precursors, changes in meteorology associated with inter-annual variability and climate change may also impact the ozone distribution [14].

In many locations across Europe, high ozone episodes show a clear downward trend even where the annual mean has not decreased since 1990 (Figure 4). This highlights the fact that peak ozone exposure values do not necessarily behave in the same way as the annual mean and should be investigated separately when human exposure to ozone is determined.

In the generally decreasing trend of high ozone episodes in Figure 4, two extreme years stand out. High ozone concentrations in these years are related to the European heatwaves in 2003 and 2006. During such episodes, ozone concentration levels can reach up to 200 ppb as was the case in France during the 2003 heatwave [15]. Mortality during heatwaves is higher due to heat stress. However, it is not only heat that affects people, but high levels of ozone as well; between 225 and 595 excess deaths were associated with high ozone episodes in the United Kingdom during the heatwave in August 2003 (see also the section entitled: Where and when is ozone exposure highest? Variability of tropospheric ozone). In the context of a changing climate, such heatwaves are projected to occur more frequently.

Vegetation

Ozone pollution can affect the main ecosystem services provided by terrestrial plants, such as biodiversity conservation, production of food and forest-based products, carbon sequestration and water regulation. At present, 85 million tonnes of wheat grain are lost annually due to ozone exposure [16], and ozone damage causes economic losses in the range of US$ 10–20 billion due to its effects on staple food crops such as wheat, soybean and maize [17]. Apart from this reduction in crop yields, high ozone levels reduce forest biomass and alter the species composition of grasslands and semi-natural vegetation [18].

Direct effects of ozone on plants are species-specific and include direct plant toxicity and cell damage [18]. Plants are especially vulnerable to ozone episodes when ozone levels are high on several consecutive days and when

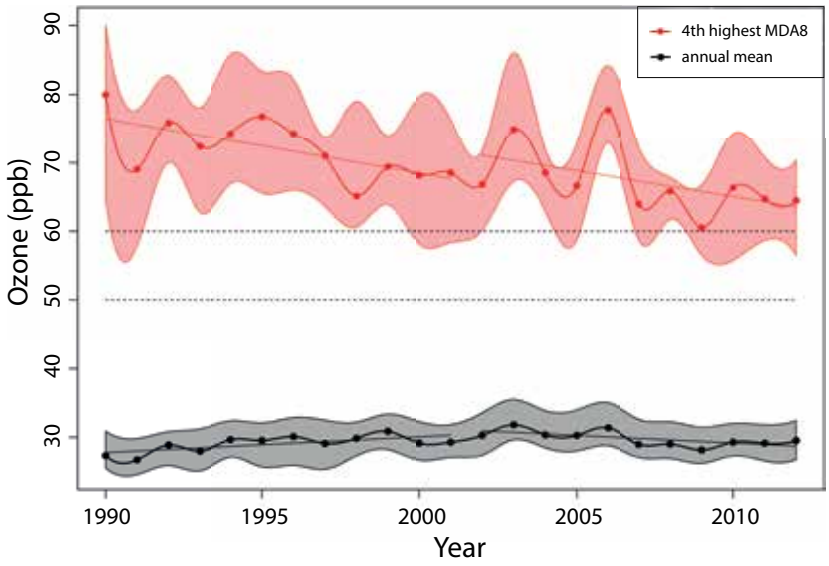

Figure 4. Annual mean (black) and peak (red) median ozone concentration at 55 rural monitoring sites from the European Monitoring and Evaluation Programme (EMEP). The maximum daily 8-hour average (MDA8) represents the fourth highest daily maximum of the 8-hour running mean. Dashed lines indicate the WHO air quality guideline (50 ppb) and the European Union long-term objective (60 ppb). The thick line is the network-wide annual median, and lower/higher bounds of the shaded areas are for the 25th and 75th percentiles. Thin straight lines show the linear trend over the 1990–2001 and 2002–2012 periods. (*Source*: Colette et al., 2016 [20], Figure 2.1)

long-term cumulative effects of absorbed ozone occur over one or several growing seasons [17]. An example of ozone-induced plant damage and how it gets worse over time is shown in Figure 5. Altered vegetation physiology also causes reduction of carbon dioxide uptake by plants, which is an indirect effect of ozone on climate [19].

Ozone exposure can be high in both moist and dry climates as well as in cool or warm climates. Lowest plant exposure to ozone is associated with unpolluted tropical conditions although sites in tropical regions are under-represented [17]. Apart from ambient ozone concentration, actual ozone uptake also depends on the degree of stomatal[9] opening. For instance, some of the highest ozone levels are in areas that have dry climates with low air and soil humidity (for example, the Great Plains in the United States). When exposed to these conditions, plants tend to close their stomata to limit water loss. This limits plant ozone uptake and protects the plant from ozone damage. However, ozone removal from the atmosphere is also reduced with consequent higher ambient ozone concentration levels.

When irrigation is used to overcome soil moisture deficit in dry climates, plants do no longer have to prevent water loss and open their stomata. Consequently, ozone is taken up and the plant is no longer protected from ozone damage [17]. In the case of wheat, as much as one third of the yield benefits of added irrigation could potentially be lost due to ozone pollution [16].

Climate

The impact of tropospheric ozone or any other greenhouse gas on climate is quantified by its contribution to radiative forcing.[10] With reference to the pre-industrial period (1750), the global average radiative forcing of ozone is similar to that of methane, and about one quarter of that due to carbon dioxide. In contrast to carbon dioxide and methane, the lifetime of ozone is much shorter and its impact on climate occurs primarily shortly after its formation. The evolution of ozone radiative forcing (Figure 6) reflects trends in anthropogenic precursor emissions, with a noticeable acceleration trend after 1950 and a deceleration trend starting in the 1990s [19]. For ozone, a recent systematic review of historic measurements indicates that pre-industrial ozone concentration levels were somewhat higher than hitherto assumed, and confirms trends that have been derived from numerical models [4].

In addition to its direct contribution to radiative forcing, ozone can also affect radiative forcing indirectly through damage to vegetation, which reduces plant productivity and thereby leads to decreased carbon dioxide uptake

Figure 5. Ozone injury to common bean leaves (Black Turtle). Damage increases when ozone exposure continues: initially, the level of damage is small (left), then symptoms get worse (centre and right).

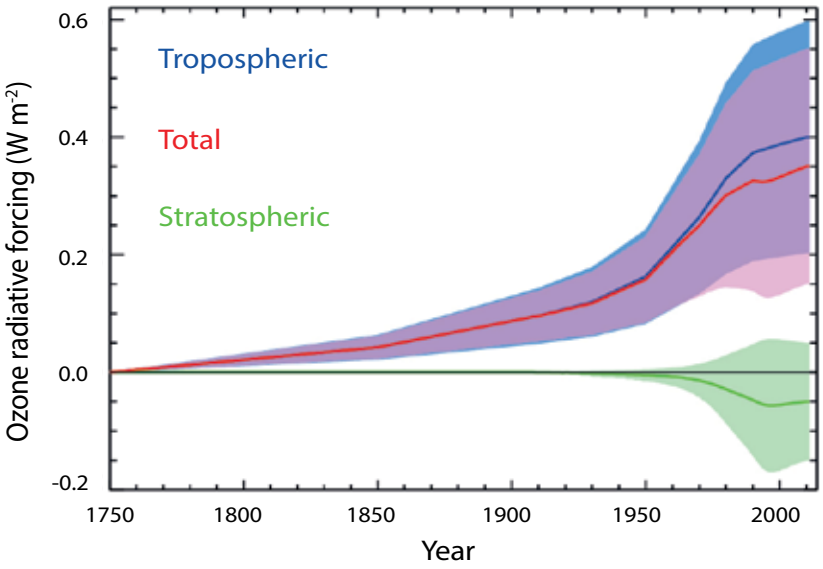

Figure 6. Evolution of the radiative forcing from tropospheric and stratospheric ozone (1750-2010). (*Source*: Intergovernmental Panel on Climate Change (2013) [19], Figure 8.7)

resulting in more carbon dioxide in the atmosphere [19]. Another indirect impact of ozone on radiative forcing has the opposite effect: with increasing ozone concentration the production of the hydroxyl radical increases as well, leading to a reduction of the lifetime of methane in the atmosphere (see section entitled: Ozone in the troposphere).

In contrast to human or plant exposure, ozone's impact on climate is more challenging to estimate as it is not restricted to the boundary layer but requires consideration of ozone in the whole atmosphere. To get as comprehensive a picture as possible, different data sources have to be combined. For a comprehensive analysis of different data sources, including their strengths and limitations, please refer to TOAR-Climate and the upcoming TOAR-Observations [4].

Ozone measurements taken at mountaintop stations, because of the sites' altitude above sea level, are used to understand ozone variation in the free troposphere while the vertical distribution of ozone is obtained from ozonesondes and aircraft-based measurements. Routine ozonesonde launches have been made typically weekly at fewer than 100 stations worldwide that are unevenly distributed (see World Ozone and Ultraviolet Radiation Data Centre (WOUDC), https://woudc.org/). A range of satellite instruments is used to retrieve the total ozone content in the troposphere though these retrivals are complicated by the presence of the stratospheric ozone layer [4]).

As all of the available data products have strengths and limitations, confidence in observed trends is ensured by analysing agreement amongst different data sources, as demonstrated in TOAR-Climate.

Where and when is ozone exposure highest? Variability of tropospheric ozone

In mid- and high-latitude regions, summer is considered the "ozone season". Exceedances of regulatory thresholds are most frequent in summer for several reasons. Warm temperatures, abundant sunlight, long days and the presence of ozone precursors, such as NOx and VOCs, favour ozone formation. While nitrogen oxides are largely emitted by the combustion of fossil fuels, a major source of VOCs, especially isoprene, are plants during their growing season. Air pollution is particularly persistent under stagnant high-pressure conditions as the lack of precipitation and light winds do not favour quick removal of air pollutants. An increase in temperature of 10°C was calculated to have given rise to a 5% increase in the peak ozone values during the heatwave in August 2003. The summer of 2003 can be regarded as a field example of the close link between

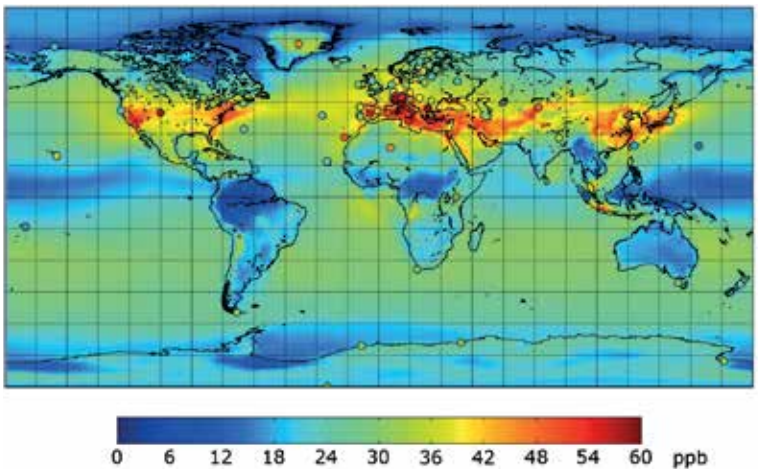

Figure 7. Global distribution of near-surface ozone concentration measured by the GAW network stations (2000–2009) superimposed on model-simulated ozone concentration from the Monitoring Atmospheric Composition and Climate reanalysis (2003–2010). Monthly mean for July. (*Source*: *GAW Report No. 209*, 2013 [26])

meteorological conditions and a secondary pollutant such as ozone [21]. The dry conditions associated with heatwaves may lead plants to protect themselves from water loss. This prevents ozone uptake by plants (for details, see the section entitled: Vegetation) thereby turning off an important ozone removal process. During the August 2003 heatwave, this effect increased ozone concentration by approximately 20–35 ppb on most days in the United Kingdom [22]. Volatile organic compound emissions from plants generally increase with temperature. Since VOCs play a role in ozone production, increased emissions can foster ozone production in warm weather conditions, particularly in summer. For example, during the 2003 heatwave in Europe, isoprene concentrations of up to 1.2 ppb were measured in south-east England, which is 3–6 times higher than those typically observed [23].

Tropospheric ozone concentration levels are generally larger in the northern hemisphere than in the southern hemisphere (Figure 7), and larger over land than over the ocean, increasing with altitude [24] (see Figure 1 for an example of different altitudes). As its global average lifetime is relatively short (between 20 and 25 days [25]), and even shorter near the Earth's surface in summertime, tropospheric ozone is highly variable in both space and time. An example of the typical mean spatial ozone distribution based on numerical modelling for the month of July in the period 2000–2009 is given below (Figure 7). The high ozone concentration associated with urban/industrial emissions in the northern hemisphere and tropical biomass burning regions in Africa and Indonesia is clearly visible. Over the remote oceans, ozone levels are typically low.

Tropospheric ozone and the Global Atmosphere Watch

Quantifying and understanding changes in tropospheric ozone and its precursors, and the environmental consequences of such changes, are priority tasks identified by the Scientific Advisory Group on Reactive Gases within the GAW Programme of the World Meteorological Organization. Global networks that include agreements on standardization and compatibility of data from different observational platforms and sites are of crucial importance for the early detection of regional and global changes in the composition of the atmosphere, especially in connection with changing anthropogenic emissions and climate change.

Detailed guidelines for tropospheric ozone measurements are provided in the *GAW Report No. 209* [26]. As shown in this Bulletin, large gaps exist in the global observational network of troposheric ozone. To fill these gaps, existing GAW stations without reactive gas measurements are encouraged to add ozone and its precursors to their observational suite. Installing new sites in data-sparse regions that join the GAW network would improve understanding of ozone, its precursors and other gases covered within the GAW Programme.

Acknowledgements and links

Data provided to the GAW Programme by WMO Members and contributing networks are submitted to the World Data Centre for Reactive Gases (WDCRG, https://www.gaw-wdcrg.org), hosted and maintained by the Norwegian Institute for Air Research (NILU). The Global Atmosphere Watch stations are described in the GAW Station Information System (GAWSIS, https://gawsis.meteoswiss.ch) supported by MeteoSwiss. The results from the Tropospheric Ozone Assessment Report (TOAR) cited in this Bulletin are published as a special issue of Elementa (https://collections.elementascience.org/toar/). Data from TOAR [27] is also available on PANGAEA (https://doi.org/10.1594/PANGAEA.876108). The live database can be accessed via the interactive web interface of the Jülich Open Web Services Interface (JOIN, https://join.fz-juelich.de).

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(1) In chemistry, a **precursor** is a compound that participates in a chemical reaction that produces another compound.

(2) The **background concentration** of a trace gas is its concentration that is not attributed to local emission sources but representative of a larger area. Note that, even though using the term concentration for the mixing ratio unit parts per billion (ppb) is technically incorrect without specifying atmospheric conditions, the word concentration is used throughout this Bulletin to facilitate uderstanding of the information it contains.

(3) The **troposphere** is the lowest part of the atmosphere, from the surface of the Earth to 6–15 km altitude depending on the latitude.

(4) **Anthropogenic** means caused by or related to human activities.

(5) In a **numerical model simulation,** the physical laws of the Earth system (or in principle of any other system) are approximated through mathematical modelling on a computer.

(6) An **ozonesonde** is a balloon-borne instrument that measures ozone and meteorological quantities at different altitudes while the balloon is ascending, until it bursts (roughly at 25 km altitude).

(7) The **stratosphere** is the second lowest layer of the Earth's atmosphere, situated just above the troposphere and below the mesosphere (altitude range ~10–65 km).

(8) The **planetary boundary layer** is the lowest part of the troposphere and strongly influenced by surface turbulence.

(9) **Stomata** are the pores, for example on the undersurface of plant leaves, which facilitate gas exchange. Through the stomata air for respiration and photosynthesis gets in and water vapour leaves the plant.

(10) **Radiative forcing** or climate forcing is the difference between insolation (sunlight) absorbed by the Earth and energy radiated back into space. To analyse the impact of a greenhouse gas on climate change during a certain period, radiative forcing due to concentration changes between a pre-industrial (here 1750) and a chosen later year is estimated for this greenhouse gas [20].

Selected GAW stations carrying out observations of reactive gases


Alfred Wegener Institute

Neumayer Station III, named after the geophysicist Georg von Neumayer, is Germany's Antarctic research station operated by the Alfred Wegener Institute (AWI) Helmholtz Centre for Polar and Marine Research. It is located on the approximately 200 m-thick Ekstrom Ice Shelf (70.7°S, 8.3°W, 42 m asl). Researchers live and work on Neumayer III all-year round, with a wintering team of nine crew members. Neumayer III and previous Neumayer stations have been the centre of continuous research in atmospheric chemistry, meteorology and geophysics since 1981. In the video (https://youtu.be/HtjzTRWfBRU) the meteorologist is starting an ozonesonde, to measure ozone and meteorological variables at different altitudes as the sonde ascends, until the balloon bursts.

The Assekrem GAW Global Station is located on the summit (plateau) of the second highest point of the Hoggar mountain range in the Saharan desert, in Algeria (23.3°N, 5.6°E, 2710 m asl). The site is very remote at a distance of 50 km from Tamanrasset. Touristic activities in the area are limited to a few dozen visitors per day due to difficult access. Vegetation is extremely sparse. In the foreground of the photo, the air intake for the ozone gas analyser is visible. The instrument itself is inside the building and has recently been refurbished. In the background, there are meteorological measurement devices. The station is also part of the National Oceanic and Atmospheric Administration (NOAA) Global Monitoring Division flask-sampling network.


Météo Algérie


Servicio Meteorológico Nacional, Argentina

The Ushuaia GAW Global Station is located on a cliff on the Isla Grande de Tierra del Fuego, Argentina (54.8°S, 68.3°W, 18 m asl), roughly 10 km south-west of the city of Ushuaia in a remote part of the sub-Antarctic coast. Steady winds blow prevalently from the clean air sector (SW) down the Beagle Channel. Tierra del Fuego and its adjacent oceanic area are under the influence of westerlies. Attached to the building is the Dobson spectrophotometer. The air inlet and several radiation and meteorological instruments are mounted on the platform at the top of the roof. In addition to the main facility, a sampling site with a 12 m tower is located on a remote island called Isla Redonda, in the Beagle Channel, which can be used for special projects. The station's ozone time series starts in 1994 and facilitates the study of the atmospheric composition in a region with sparse coverage of monitoring stations (Figure 2).

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