

## White Paper

# Outdoor Air Quality

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## Abstract

This white paper covers generalities of Outdoor Air Quality (OAQ). It focuses on gases that significantly influence the outdoor air, especially nitrogen oxides (NO<sub>x</sub>) and ozone (O<sub>3</sub>). A description of gases related to outdoor air, the standards, and limits established by legislation and/or organizations, and the technologies for detecting, measuring, and cleaning outdoor air quality are discussed.

## Introduction

Outdoor air refers to the air outside buildings and interiors, and is essential for life on earth. In general, unpolluted outdoor air mainly consists of 78% nitrogen, 21% oxygen, and a mix of different trace gases as shown in figure 1. These trace gases usually occur in the range of parts per million (ppm) and parts per billion (ppb), which are considered at elevated levels as pollutants. The World Health Organization (WHO) distinguishes air pollutants in two groups: first, direct emitted into the atmosphere like sulfur dioxide (SO<sub>2</sub>), nitrogen oxides (NO<sub>x</sub>), carbon monoxide (CO), volatile organic compounds (VOCs), as well as particulate matter (PM, including carbonaceous and non-carbonaceous particles). Second, pollutants, which are formed inside the atmosphere caused by chemical reactions of primary pollutants. The most common secondary pollutants are ozone (O<sub>3</sub>), oxides of nitrogen (NO<sub>y</sub>), and secondary PM. Primary air pollutants concentrations are more convenient to measure because they always contribute under the same conditions to air quality. Unlike the primary pollutants, a measurement of secondary pollutants is more difficult due to their formation depending on environmental conditions, such as chemical precursors, temperature, sunlight, etc. [1, 2]

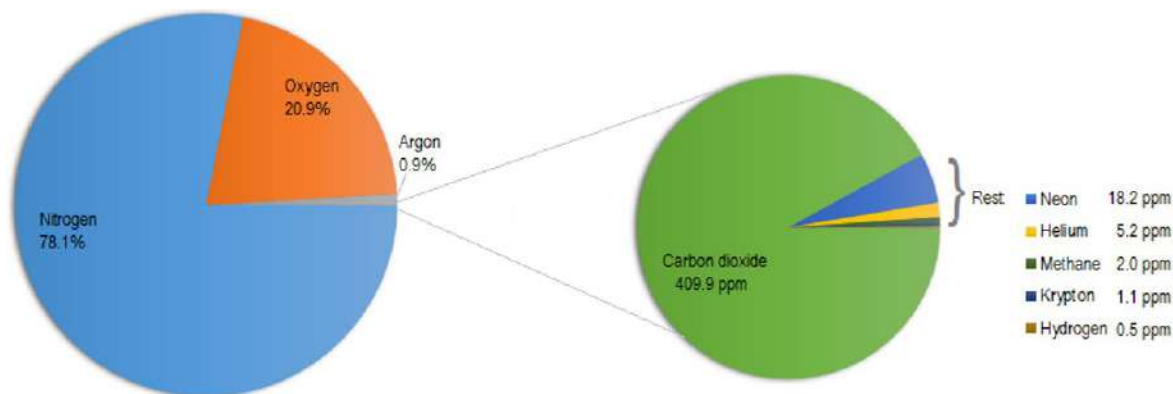


Figure 1. Composition of Earth's Atmosphere by Volume Percentage (Modified from [3])

Even if we spend most of our time indoors, everybody is influenced by outdoor air pollution. To measure the total personal exposure, it should be considered the proximity to the source, the amount of time spent exposed, and the multiple microenvironments, where someone spends their time. For example, people in buses and cars tend to be more exposed than cyclists and pedestrians, but increased breathing rates while bicycling and walking may mean that larger volumes of pollutants are inhaled. [2]

Examples of air quality monitoring were the programs of Baltimore and Lafayette (both in USA), parts of the Environmental Protection Agency’s Smart City Air Challenge. In 2017, the Lafayette Engagement and Research Network deployed about 300 air quality sensor across Lafayette city, mounting them largely on traffic signals, which were already wired with electric power and the city’s fiber communications network. Meanwhile in Baltimore, the Open Air Baltimore project, placed about 250 air monitors across the city, offering a window into air quality in each neighborhood [4]. It is a misconception to assume that contaminants only affect people on road traffic. For example, monitoring smoke in real-time from wildfires in warmer months and wood stoves and fireplaces in the winter was a decision taken by the Willamette Valley in Oregon (USA).

Also, more than 40 air quality sensors were installed at schools, parks, and other public places in the area around Eugene and Springfield, Oregon. In Springfield, sport practices in some schools were canceled or moved indoors in 2017 due to thick smoke and poor air quality. Another example is the new initiative to measure OAQ at schools across Europe that was proposed by the European Environment Agency (EEA) and the European Network of the Heads of Environmental Protection Agencies (EPAs). This project not only endorses nitrogen dioxide measurements, but also teaches children and parents about air pollution and its health effects. [5, 6]

Previous cases are just samples in which air quality measurement could be carried out. The final objective of monitoring is to preserve health and the environment. Table 1 summaries a study by the World Health Organization (WHO) about health effects of air pollution.

**Table 1. Health Effects of Air Pollution According to WHO**

Effects Attributed to Short-Term Exposure	Effects Attributed to Long-Term Exposure
<ul style="list-style-type: none"> <li>• Increased daily mortality</li> <li>• Respiratory and cardiovascular problems</li> <li>• Days of restricted activity, work, and school</li> <li>• Acute symptoms (wheezing, coughing, phlegm production, respiratory infections)</li> <li>• Physiological changes (e.g., lung function)</li> </ul>	<ul style="list-style-type: none"> <li>• Increased mortality due to cardiovascular and respiratory diseases</li> <li>• Chronic respiratory disease incidence and prevalence (asthma, COPD, chronic pathological changes)</li> <li>• Chronic changes in physiologic functions</li> <li>• Lung cancer</li> <li>• Chronic cardiovascular disease</li> <li>• Intrauterine growth restriction (low birth weight at term, intrauterine growth retardation, small for gestational age)</li> </ul>

To make concentration data comparable it is important to look at their unit. Usually, gas concentrations are given as either:

- Molar ratio: ppm (parts per million) or ppb (parts per billion), which is common for industrial and consumer use.
- Physical concentration: mg/m<sup>3</sup> or µg/m<sup>3</sup> (mass per volume), which is common for scientific and chemistry use.

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It is easy to convert from ppm to mg/m<sup>3</sup> as seen in equation 1:

$$c \text{ [ppm]} = \frac{V}{M} * c \left[ \frac{\text{mg}}{\text{m}^3} \right] * 10^3 \quad \text{Equation 1}$$

For an ideal gas at ambient temperature (25°C) and atmospheric pressure (1013 mbar), *c* is the concentration in ppm or mg/m<sup>3</sup>, *V* is the molar volume (0.024465 m<sup>3</sup>·mol<sup>-1</sup>), and *M* is the molecular mass of the compound in g·mol<sup>-1</sup>. Table 2 gives conversion examples for nitrogen dioxide and ozone. The conversion from ppm to ppb is more convenient since 1 ppm equals 1000 ppb.

**Table 2. Concentration Conversion for Nitrogen Dioxide and Ozone**

Compound	Chemical Formula	Molar Mass [g·mol <sup>-1</sup> ]	Molar Ratio [ppm]	Concentration [mg/m <sup>3</sup> ]
<b>Nitrogen Dioxide</b>	NO <sub>2</sub>	46.006	1	1.8805
			0.5318	1
<b>Ozone</b>	O <sub>3</sub>	47.998	1	1.9619
			0.5097	1

## Gases and Impacts of Outdoor Air Quality

Solid emissions from automobiles and industry, dust, pollen, and mold spores can be suspended as particles. Air pollution is in general considered as a mixture of gases and solid particles in the air. This section provides detailed information about nitrogen oxide pollutants, especially nitrogen dioxide and ozone, but also discusses sulfur dioxide, benzene, particulate matter, and smog.

All data of nitrogen dioxide and ozone concentrations shown are publically available from the BfUL (Staatliche Betriebsgesellschaft für Umwelt und Landwirtschaft), which is part of the environmental ministry of the state of Saxony in Germany. Exemplary, data from the city of Dresden and rural background levels were taken from Dresden-Bergstraße and Radebeul-Wahnsdorf air measuring stations, respectively (figure 2). These BfUL stations are approximately 10 km away, have high-end reference instrumentation, and are maintained and calibrated regularly [7].



**Figure 2. Dresden-City (left) and Radebeul (right) Air Monitoring Stations (Germany)**

## Nitrogen Oxides (NO<sub>x</sub>)

Nitrogen oxides are formed by the combination of oxygen (O<sub>2</sub>) and nitrogen (N<sub>2</sub>). According to the atomic valence of nitrogen, the different compounds could be NO, NO<sub>2</sub>, N<sub>2</sub>O, N<sub>2</sub>O<sub>3</sub>, among others. Nitrogen Oxide (NO) and Nitrogen Dioxide (NO<sub>2</sub>) are considered to be Nitrogen Oxides (NO<sub>x</sub>), and are important due to the formation of acid rain, production of photochemical smog, decomposition of tropospheric ozone, and their boost of PM<sub>2.5</sub> levels. Nitrogen dioxide is the representative compound of the group and the one that is used as the emission indicator of most of them. In atmospheric science commonly used is the term NO<sub>y</sub>, which refers to NO<sub>x</sub> (NO + NO<sub>2</sub>) and in addition all other nitrogen compounds with oxidizing state more than two (+II).

Nitrogen dioxide is a reddish-brown gas with an acrid odor. About 1% of the total amount of NO<sub>2</sub> found in the air result from natural sources such as lightning, plants, soil, and water. The primary source is a by-product from the burning of fuel such as emissions from vehicles, power plants, and off-road equipment. [8, 9, 10]

The reaction of nitrogen and oxygen is possible at high temperatures, as the conditions generated inside internal combustions engines, as product is formed nitric oxide (NO), see reaction 1, which reacts rapidly with ambient oxygen to produce nitrogen dioxide, see reaction 2: [11]



Another way in which NO<sub>2</sub> is produced is due to the action of peroxide radicals (HO<sub>2</sub> and RO<sub>2</sub>) by the direct oxidation of NO, see reaction 3. Hydrocarbons, and to a lesser extent CO, produce the peroxide radicals. [12]



In reaction 3, R stands for Rest and represents a hydrocarbon radical or a hydrogen atom.

Figure 3 shows the levels of nitrogen dioxide in urban areas (red line) on June 3<sup>rd</sup>, 2019, in the city of Dresden (Germany), comparing them with a rural background measurement (gray line) some kilometers outside the city [7]. Urban areas can be characterized as having the highest concentration of NO<sub>x</sub> because of traffic. For example, in figure 3 the two highest peaks in the urban area in the afternoon correlate with the first and second group of people returning home, respectively. The third highest peak occurs in the morning coinciding with people travel to work.

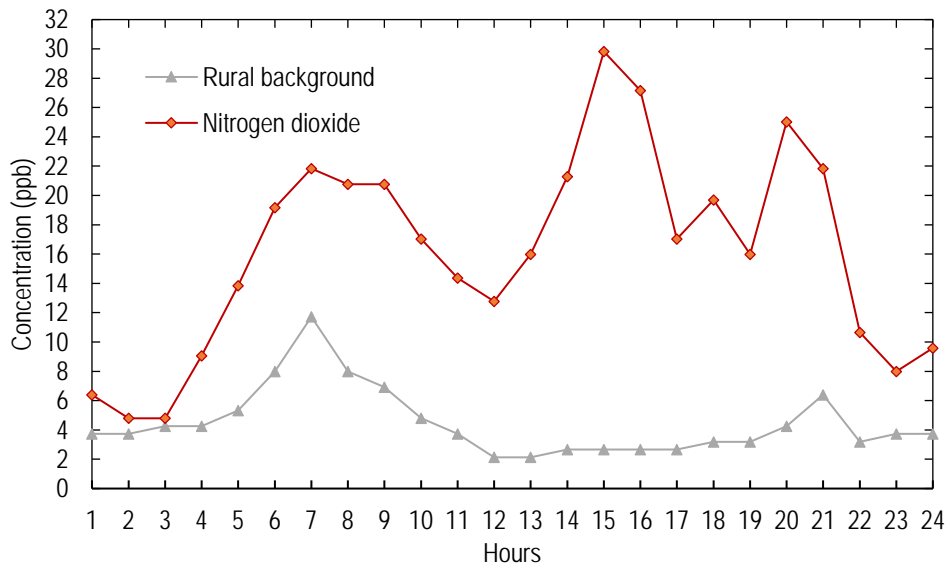


Figure 3. Nitrogen Dioxide Concentrations on June 3<sup>rd</sup>, 2019 in Dresden City

### Health and Environmental Effects

Nitrogen dioxide is related to some respiratory diseases (e.g., acute bronchitis) and the decrease in lung capacity. Some effects associated with NO<sub>2</sub> pollution are summarized in figure 4. Statistics of the German Environmental Agency (UBA) attribute in 2014 about 6000 premature deaths due to cardiovascular diseases linked with background NO<sub>2</sub> concentrations. They also support that NO<sub>2</sub> pollution is associated with diseases such as diabetes mellitus, hypertension, stroke, chronic obstructive pulmonary disease (COPD), and asthma. Toxicological data supported by the WHO indicates that NO<sub>2</sub> can reduce host defenses against microbiological agents and enhanced bronchial hyperresponsiveness in asthmatics to allergen and irritant stimuli. Additionally, a 2017 study by the Institute of Global Health among 2700 children in Barcelona (Spain), concluded that pollution, especially NO<sub>2</sub> and elemental carbon, affects the ability of children to attend school in the short term, delaying the speed of class responses. [13, 14]

There are also environmental effects associated with NO<sub>2</sub>. Since NO<sub>2</sub> contributes to the formation of acid rain, which is any form of precipitation with acidic components, aquatic environments are the most affected as acidic rainwater can leach aluminum from soil clay particles and then flow into streams and lakes. The more acid that is introduced in to the ecosystem, the more aluminum is released. At pH 5, most fish eggs cannot hatch, and at lower pH levels, some adult fish die. High levels of NO<sub>2</sub> can harm vegetation, including leaf damage and reduced growth. A study made on the habitat of Epping Forest (between Essex and Greater London, England) demonstrated that local traffic emissions contribute substantially to exceeding the critical levels and critical loads in the area, influencing ecosystem health in the forest. The term “Forest Dieback” has been used since 1983 to designate massive forest damage, after severe damage to the forests of Central Europe and parts of North America at the end of the 1970s. Forest damage in Germany lasted for 5 years affecting 50% of the trees. The main cause of the devastation is attributed mainly to acid rain, which is formed by Nitric Acid (HNO<sub>3</sub>). Also, NO<sub>2</sub> can react with other air pollutants to form peroxyacetyl nitrates (PANs) which serve as carriers for NO<sub>x</sub> for long distances. [15, 16, 17, 18]

## Uses and Applications

NO<sub>2</sub> is used in the industry as intermediate in nitric acid and sulfuric acid production, flour bleach, nitration of organic compounds and explosives, manufacture of oxidized cellulose compounds (hemostatic cotton), and was proposed as oxidizing agent in rocket propulsion. In general, NO<sub>x</sub> is used in the production of lacquers, dyes, and other chemical products. Also, several investigations of the late twentieth century discovered the beneficial effects of various organic nitrates used in the treatment of attacks of angina, chest pain, or arteriosclerosis. Similarly, other nitrogen oxide chemicals are applied in medicine (e.g., nitrous oxide (N<sub>2</sub>O) is used as a general anesthetic, best known as laughing gas. One of the standard devices to improve the diagnosis and management of asthma is NIOX<sup>®</sup> by Circassia AB. By measuring the concentration of nitric oxide (NO) in an exhaled breath, fractional exhaled nitric oxide of FeNO, clinicians can evaluate airway inflammation in patients with asthma. Other models of the medical NO trace gas detection for asthma are NIOX VERO<sup>®</sup> by Circassia AB, NIOX<sup>®</sup> Flex, and NIOX MINO<sup>®</sup> by Aerocrine AB. [19, 20, 21, 22]

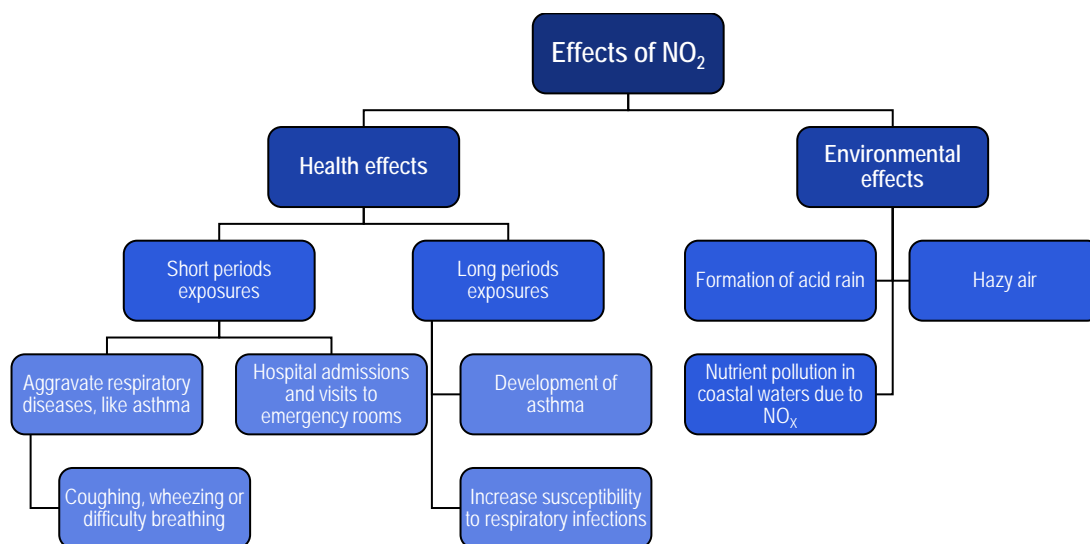
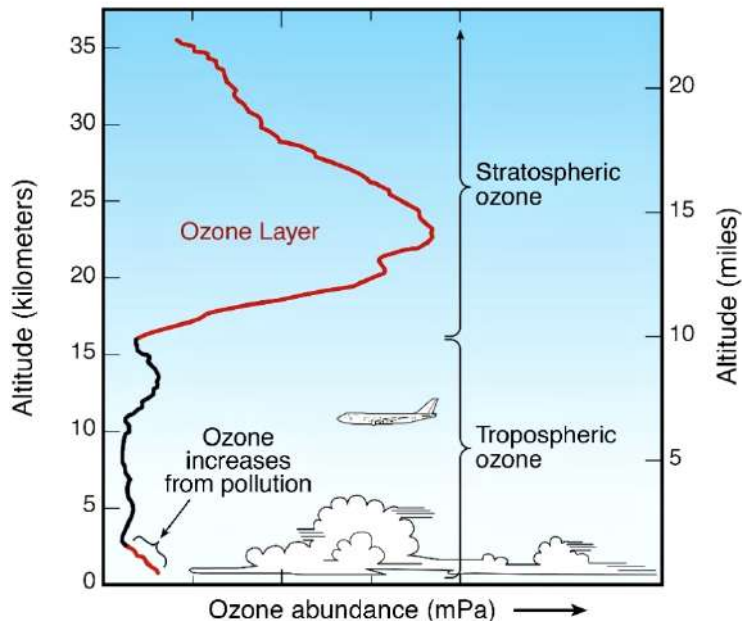


Figure 4. Effects of NO<sub>2</sub> in Human Health and the Environment

## Ozone (O<sub>3</sub>)

Ozone is a colorless to bluish gas with a pungent odor. It forms naturally in the stratosphere, second layer of the atmosphere between 15 and 50 km above the Earth's surface, and in the tropospheric as a result of photochemical reactions of man-made volatile organic compounds (VOC) and nitrogen oxides (NO<sub>x</sub>). Its maximum concentrations (given as partial pressure mPa) are found at ground level and at approximately 23 km altitude depending on time of the year and location, see figure 5. [23, 24]



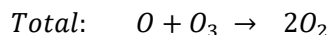
**Figure 5. Ozone Distribution in the Atmosphere [25]**

In the stratosphere, the photochemical steady-state model explains the formation of ozone in this layer of the atmosphere, see reaction 4 to reaction 8. [26]



Where M is an unreactive third molecule like N<sub>2</sub> and *hν* is sunlight. Reaction 5 becomes slower with increasing altitude in the stratosphere since M is decreasing; however, reaction 4 and reaction 6 become faster, as the intensity of radiation, particularly short wavelength radiation, is increasing. Therefore, O predominates at high altitudes and O<sub>3</sub> at lower stratospheric altitudes.

Figure 5 shows the maximum ozone concentration between 20 and 25 km, in the so-called low stratosphere (up to 25 km). Both O and O<sub>3</sub> are converted into each other very rapidly but to achieve the steady-state formation of O<sub>2</sub> must be formed. The species X in reaction 7 and reaction 8 are catalysts which destroy many ozone molecules typical examples of X are hydrogen (H), hydroxyl radicals (-OH), nitrogen monoxide (NO) and, chlorine (Cl) and bromine (Br), which typically occur in CFC (chlorofluorocarbons).

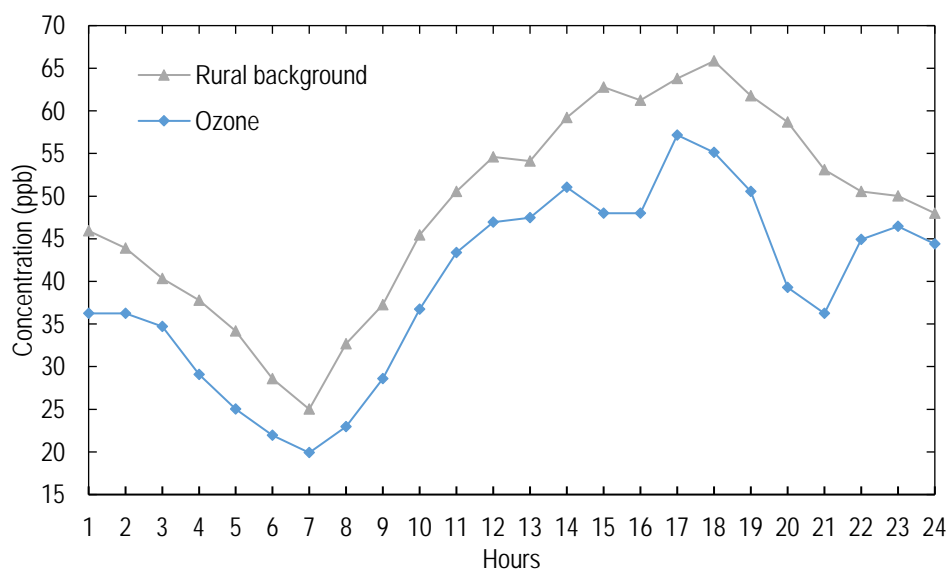


The direct reaction between O and O<sub>3</sub> is rarely possible due to the slow reaction rate without the catalysts and at the same time, the X/XO coupling is very fast, also concentrations of atomic oxygen are low in the low stratosphere.

In the troposphere, nitrogen dioxide and ozone are related by the *photostationary state*, which means they convert into each other if one of them is present. After NO is converted into NO<sub>2</sub> (reaction 2 and reaction 3), the photolysis of nitrogen dioxide (reaction 9), leads to ozone formation as shown in reaction 10. However, fresh emissions of NO may also lead to ozone removal by forming NO<sub>2</sub>, see reaction 11. [26]



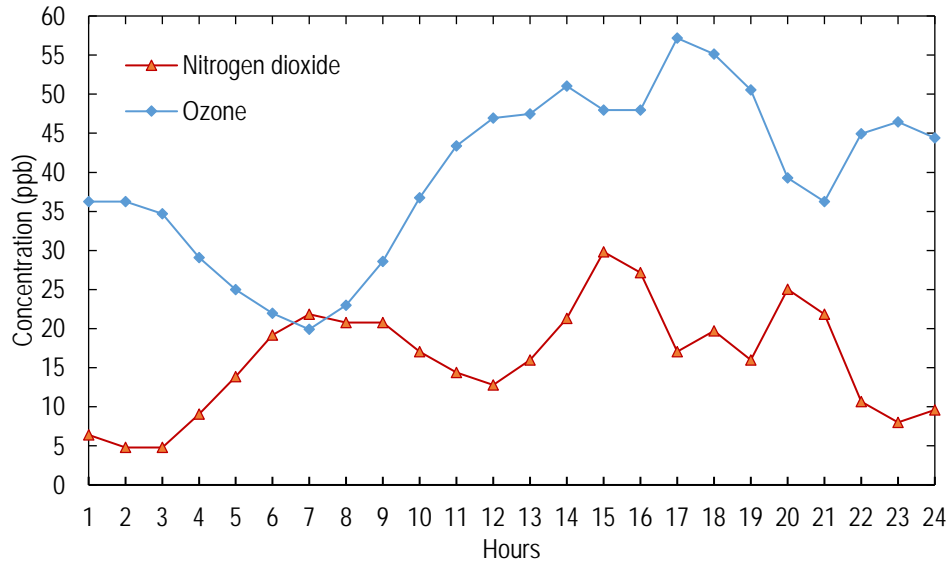
With  $O^*$  as an oxygen radical. The higher the sunlight intensity and the ratio of NO<sub>2</sub>/NO, the higher the concentration of ozone. As an example, figure 6 shows the behavior of ozone levels in urban areas (blue line) on June 3<sup>rd</sup>, 2019, in the city of Dresden, where the greatest sunlight intensity was evident in the afternoon hours, increasing ozone concentration between 2:00 and 5:00 pm. The figure also presents the rural background levels of ozone (gray line, some kilometers outside the city center) which is generally higher than urban levels due to ozone degradation by NO<sub>x</sub> and the downwind of O<sub>3</sub> precursors from urban areas. [7, 27]



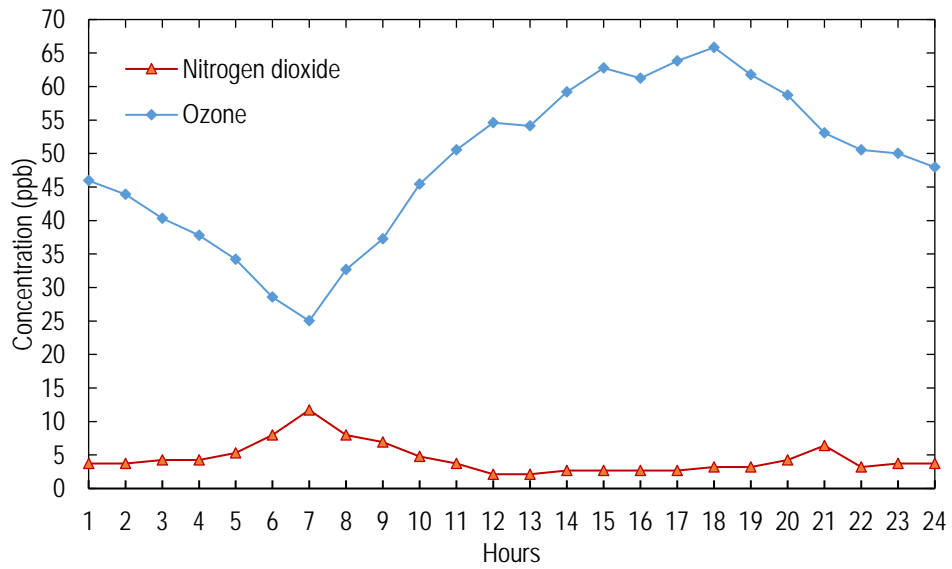
**Figure 6. Ozone Concentrations on June 3<sup>rd</sup>, 2019 in Dresden**

The *photostationary state* also explains why O<sub>3</sub> and NO<sub>2</sub> concentrations follow the opposite trend, as shown in figure 7 and figure 8, which represent the urban and rural background levels respectively of nitrogen dioxide and ozone on June 3<sup>rd</sup>, 2019 in Dresden. Especially in cities during daylight, a higher NO<sub>2</sub> concentration is found (emissions from vehicles), while in suburban areas the ozone concentrations are higher.



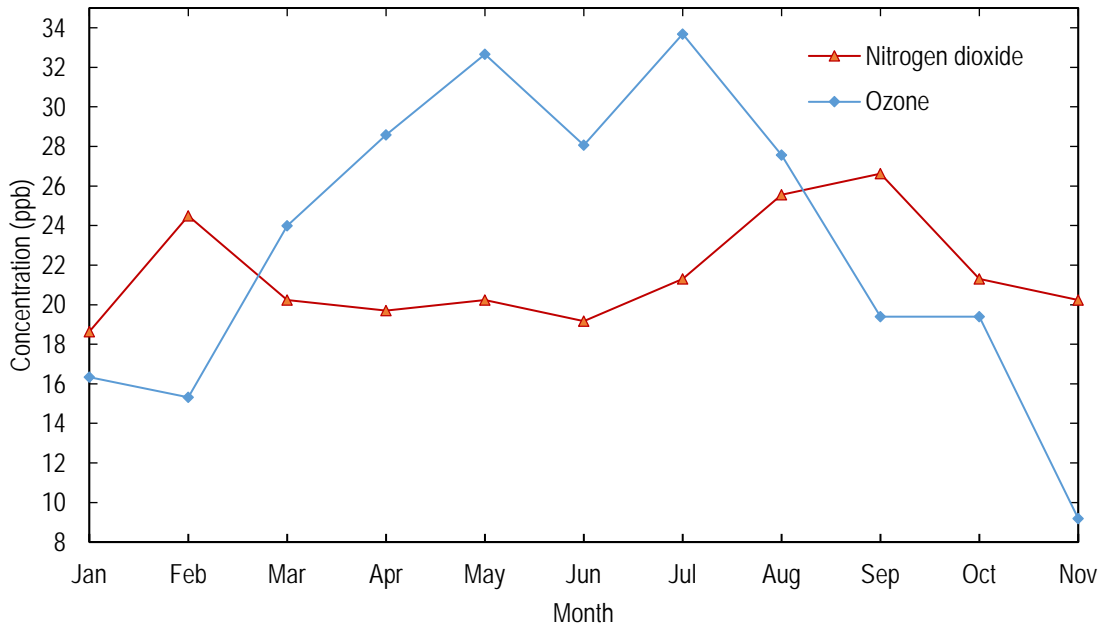


**Figure 7. Nitrogen Dioxide and Ozone Concentrations on June 3<sup>rd</sup>, 2019 in Dresden**



**Figure 8. Suburban Nitrogen Dioxide and Ozone Concentrations on June 3<sup>rd</sup>, 2019 Close to Dresden**

Figure 9 shows the behavior of the concentrations of NO<sub>2</sub> and O<sub>3</sub> during 2018 in Dresden. It shows that during the summer season, where the sunlight is higher, the ozone concentration increases while the concentration of nitrogen dioxide decreases, keeping the NO<sub>2</sub>-O<sub>3</sub> relation. During the winter season ozone decreases due to the lack of sunlight.



**Figure 9. Nitrogen Dioxide and Ozone Concentrations during 2018 in Dresden**

### Health and Environmental Effects

Ozone has a positive effect in the stratosphere since it absorbs UV light and reduces human exposure to harmful UV radiation that causes skin cancer and cataracts. Nevertheless, in the troposphere, it is a contaminant which acts like a powerful and aggressive oxidizing agent. On human health, respiratory problems caused by ozone include induction of respiratory symptoms, decrements in lung function and inflammation of airways. Figure 10 presents a summary relating the effects associated with O<sub>3</sub> pollution. The US Environmental Protection Agency (EPA) has observed in some studies that higher daily ozone concentrations are associated with increases of asthma attacks, hospital admissions, daily mortality, and other markers of morbidity. There is evidence of studies supporting the existence of an ozone-mortality relationship, even at short-term exposure, which is associated with premature mortality according to the National Research Council. The most representative study was made by Bell et al. throughout the years 1987 to 2000 in 95 US urban communities. These results had been inconclusive, but it has been observed that a 10ppb ozone increase causes a 0.52% increase in daily mortality and a 0.64% increase in cardiovascular and respiratory mortality. Other observations found that the ozone-mortality relationship is most prominent during the warm season, with few or smaller effects in the winter. [24, 28, 29]

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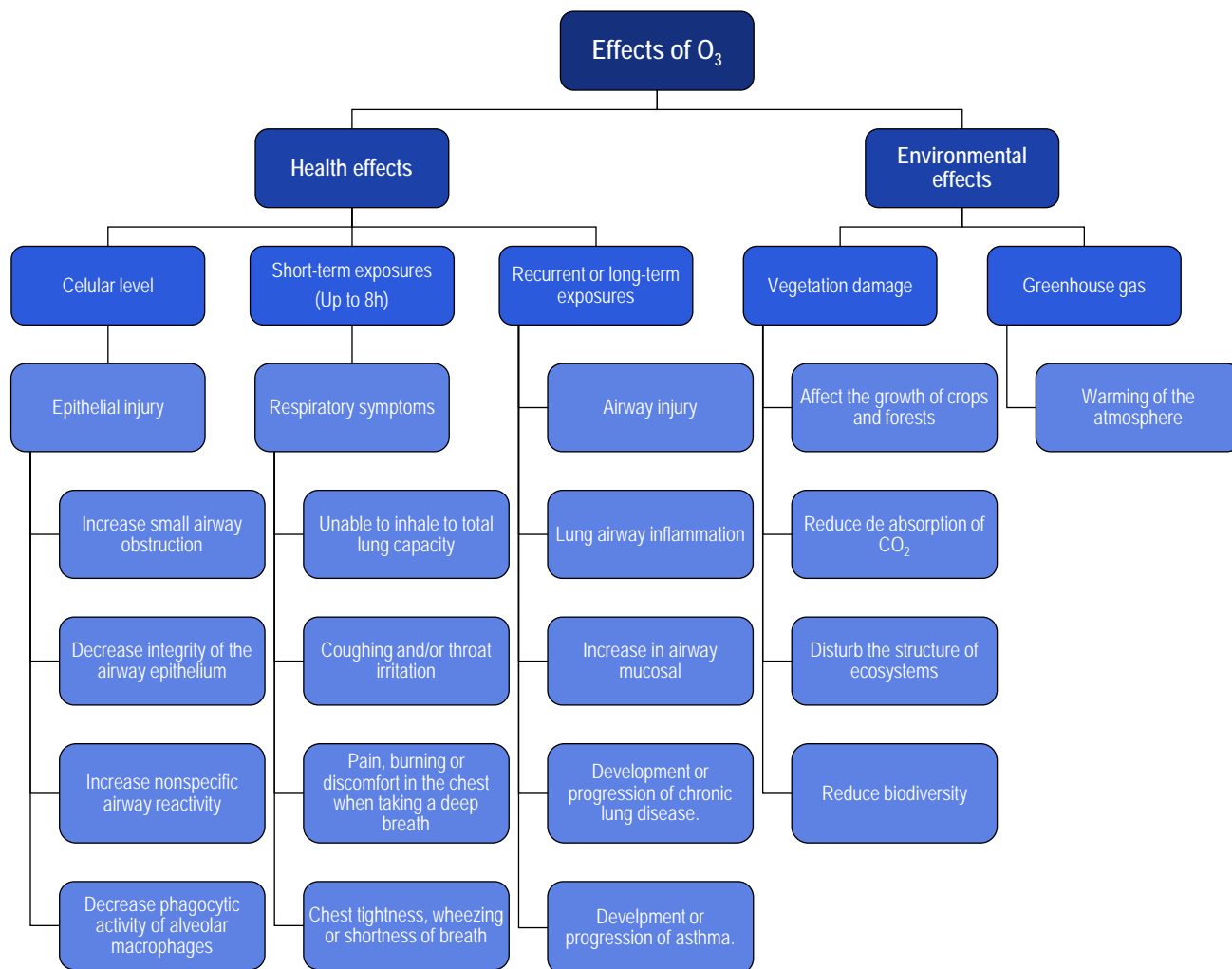
People most at risk from breathing air containing ozone include those with asthma, children, the elderly, and those who are active outdoors, especially for long periods of time, besides people with genetic characteristics or lack of nutrients, such as vitamins C and E. The level of sensitivity of the person and the dose delivered to the respiratory tract should be considered to detect the first effect of ozone. The more sensitive someone is, the lower concentration must be until the person experiences any effect. Although there is a large amount of variability among individuals' responses to ozone exposure, in the study made by Devlin et al. in 1997, a relation between age and body mass index (BMI), along with lung function and sensitivity to ozone exposure was observed. To short-term exposure, young adults (teens to thirties) and those with high BMI were much more sensitive than older adults (fifties to eighties) and those with low BMI. To long-term exposure, a decrease in lung function were higher in adults aged 20 years than in those aged 33 years. [29]

Environmental ozone effects can be divided in ozone pollution effects and ozone layer depletion effects. Firstly, ozone pollution affects sensitive vegetation and consequently ecosystems. For example, when ozone enters the leaves of a sensitive plant it can reduce photosynthesis, slow the plant's growth, or increase the plant's risk of disease, damage from insects, effects of other pollutants and harm from severe weather. When plants have been affected, the ecosystems have negative impacts related to loss of species diversity, changes to habitat quality, assortment of plants present in a forest, and water and nutrient cycles. [30]

Secondly, a decrease in stratospheric ozone concentration leaves an ozone layer depletion allowing more exposure to UVB radiation (sunlight with a wavelength of 280 to 315 nm) at the Earth's surface. UVB radiation affects the physiological and developmental processes of plants. On marine ecosystems, affects orientation and motility in phytoplankton, which is the foundation of aquatic food webs; causes damage to early developmental stages of fish, shrimp, crab, amphibians, and other marine animals; and decreases reproductive capacity and impaired larval development. UVB radiation could also disturb sources and sinks of greenhouse and chemically important trace gases like carbon dioxide (CO<sub>2</sub>), carbon monoxide (CO), carbonyl sulfide (COS), among others, mitigating or amplifying the atmospheric concentrations of these gases. [31]

## **Uses and Applications**

In the industry, ozone is used mainly as a disinfectant for air and water due to its oxidizing power. It is also used as a disinfectant for food in cold storage rooms, process certain perfumes, and treat industrial wastes, among other activities. In the chemical industry, cooling towers treated with ozone offer better heat transfer efficiency, lower blowdown volumes and decreased chemical usage. In the electronics industry, the use of ozone allows cleaning of process chambers and photoresist removal. Lately, it is used in the industrial laundries as disinfectant because of more efficient cost and energy, and environmentally friendly than conventional laundry methods. On the other hand, ozone is used in medicine as therapy to disinfect and treat diseases by limiting the effects of bacteria, viruses, fungi, yeast, and protozoa. [23, 32, 33, 34]



**Figure 10. Effects of Ozone in Human Health and the Environment**

## Other Relevant Outdoor Air Gases and Particulate Matter

This section presents a short summary of other relevant primary air pollutants with focus on sulfur compounds, volatile organic compounds (benzene) and particulate matter.

Sulfur dioxide is used as the indicator of all sulfur oxides (SO<sub>x</sub>). It is a colorless gas with a choking or suffocating odor, responsible for the smell of burnt matches. About 99% of the sulfur dioxide in air comes from human sources. In nature, volcanic eruptions can release sulfur dioxide into the air but the main source of this compound is industrial activity that processes materials containing sulfur as the generation of electricity from coal, oil, or gas that contains sulfur. Sulfur dioxide is also present in motor vehicle emissions, as the result of fuel combustion. In homes, sulfur dioxide gas can result from tobacco smoke, improperly or inadequately vented gas appliances, such as stoves, ranges, furnaces, or clothes dryers, gas or kerosene heaters, wood or coal stoves, automobile exhaust from attached garages, and malfunctioning chimneys. Some of the health effects of SO<sub>2</sub> are irritation of skin and mucous membranes of the eyes, nose, throat, and lungs causing coughing, wheezing, or shortness of breath. Short-term exposure to high levels can be life-threatening. Long-term exposure can cause changes in lung function and aggravate existing heart disease. [35, 36, 37, 38]

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Benzene is a clear, colorless, volatile, highly flammable liquid with a gasoline-like odor. Benzene in air exists predominantly in the vapor phase and is part of the volatile organic compounds (VOC). Naturally, benzene is released from volcanoes and forest fires, although the main sources of this compound are from vehicle exhaust, other combustion processes, and industrial processes as intermediary participant or final product. Benzene is a proven carcinogen and no safe concentration limited for an exposure is given by the WHO. However, exposure to normal environmental concentrations in air is thought unlikely to be dangerous in this respect. Short exposure to high levels of benzene in air can result in drowsiness, dizziness, rapid heart rate, headaches, tremors, confusion, and unconsciousness. At very high levels, even death may occur. With long-term exposure, the major effect of benzene is on the blood. It can cause a decrease in red blood cells leading to anemia, harmful effects on the bone marrow, and affect the immune system, increasing the chance for infection. For the environment, benzene is toxic for aquatic organisms when high concentrations arise from significant spills. [39, 40, 41]

Particulate matter (PM), also called particle pollution, is the term for a mixture of solid particles, including dust, dirt, soot, smoke, and liquid droplets found in the air. Particles are usually characterized by their size diameter. PM particles are those with a diameter between 0.001 $\mu\text{m}$  and 100 $\mu\text{m}$ . Particles less than about 0.001 $\mu\text{m}$  act more like gases, and particles greater than 100 $\mu\text{m}$  are easily removed and typically not inhaled. The EPA has classified PM particles in two groups:

- PM<sub>10</sub> are called “coarse” inhalable particles, with diameters greater than 2.5 $\mu\text{m}$  up to 10 $\mu\text{m}$ .
- PM<sub>2.5</sub> are called “fine” inhalable particles, with diameters that are generally 2.5 $\mu\text{m}$  and smaller.

Other terms used more commonly in industrial hygiene are inhalable, thoracic, and respirable particles, which describe where particles are likely to deposit in the lung. The smaller the particle, the more likely it will penetrate deeper in the lung, and for this reason, the size of particles is directly linked to their potential for causing health problems. Fine particles (PM<sub>2.5</sub>) pose the greatest health risk, getting deep into lungs and some may even into the bloodstream. Exposure to these particles can affect a person's lungs and heart. Generally PM health effects include premature death in people with heart or lung disease, nonfatal heart attacks, irregular heartbeat, aggravated asthma, decreased lung function and increased respiratory symptoms, such as irritation of the airways, coughing or difficulty breathing. People with heart or lung diseases, children and older adults are the most likely to be affected by particle pollution exposure. In 2013, particulate matter was classified as a cause of lung cancer by WHO's International Agency for Research on Cancer (IARC).

In 2016, there were an estimated 4.2 million premature deaths worldwide due to exposure of PM<sub>2.5</sub>. Environmental effects of particulate matter can be divided into three groups: visibility impairment, since visibility is reduced due to haze; environmental damage, as particles can be carried over long distances by wind; and materials damage. Depending on their chemical composition they can make lakes and streams acidic, change the nutrient balance in coastal waters and large river basins, deplete the nutrients in soil, damage sensitive forests and farm crops, affect the diversity of ecosystems or contribute to acid rain effects; and materials damage, staining and damaging stone and other materials. Particulate matter can also be classified into primary and secondary particles according to their formation mechanism. Primary particles come from sources like cars, trucks, buses, factories, construction sites, tilled fields, unpaved roads, stone crushing, and burning of wood. Secondary particles are formed indirectly by the chemical change of gases, when gases from burning fuels react with sunlight and water vapor. [42, 43, 44]

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## Smog

The term smog comes from the contraction of two words, smoke, and fog. It is a chemical mixture of both with high concentrations of sulfur oxides, nitrogen oxides, and hydrocarbons, and particles of lead, manganese, copper, nickel, zinc, and coal. [45]

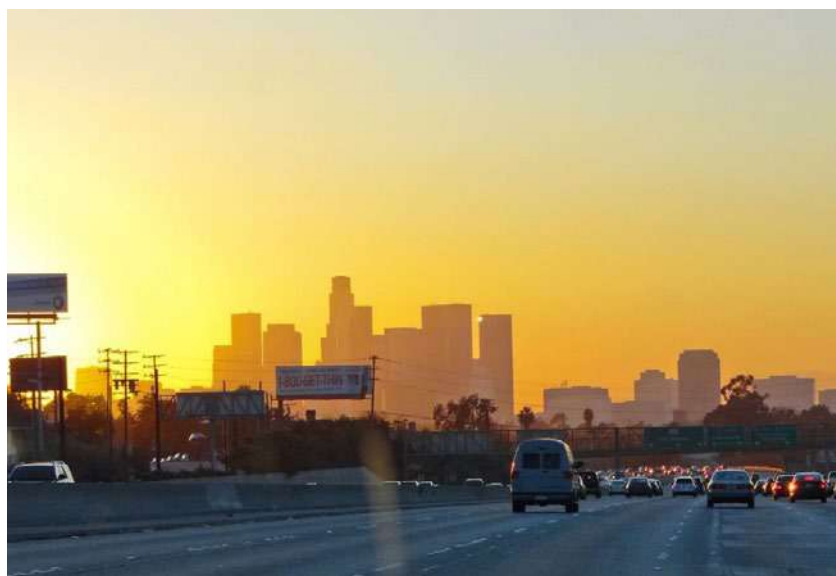
General health effects of smog are irritation of the respiratory tract, eyes and skin, anemia, influenza, tuberculosis, and heart problems. In addition, people with allergies can experience worse conditions. It can also cause premature death, and affect the brain of children causing concentration problems, delaying their learning and development. Furthermore, consequences on the environment are its impact on the landscape, for the absence of clouds, clear skies or starry nights, only a yellowish-gray veil; the changes in the climate like increased heat and altered rainfall, since pollutants and suspended carbon particles cause a decrease in rainfall levels; and damage to forests and crops, because metabolic functions and plant tissues are affected by various gaseous compounds with sulfur or fluoride.

There are two types of smog, photochemical smog and sulfurous smog, which are described in the following sections.

### Photochemical Smog

Nitrogen oxides and ozone are the main components of the mixture of pollutants known as “photochemical smog”. Photochemical smog, also known as “Los Angeles smog,” is formed when nitrogen oxides and volatile organic compounds (VOCs) react with sunlight producing ozone and peroxyacyl nitrate (PAN). Both, primary and secondary pollutants involved in photochemical smog result in a more or less dense fog with reddish-brown coloration that occurs during the day, mainly in the central hours. This type of smog is favored by anticyclone situations that are high-pressure atmospheric zone, great heat waves, and weak winds that hinder the dispersion of pollutants. [46]

Photochemical smog first occurred in Los Angeles (L.A.) on July 26<sup>th</sup>, 1943. In the middle of World War II, Los Angeles residents believed they were under attack with chemical warfare. Nevertheless, the fog was from their vehicles and factories, causing a bleach smell, eye irritation, and respiratory problems. At that time, L.A. had become the largest car market in the world. With the construction of more freeways and new industries, the smog became commonplace [47]. Figure 11 shows an example of photochemical smog; the picture was taken in Los Angeles on October 10<sup>th</sup>, 2011.



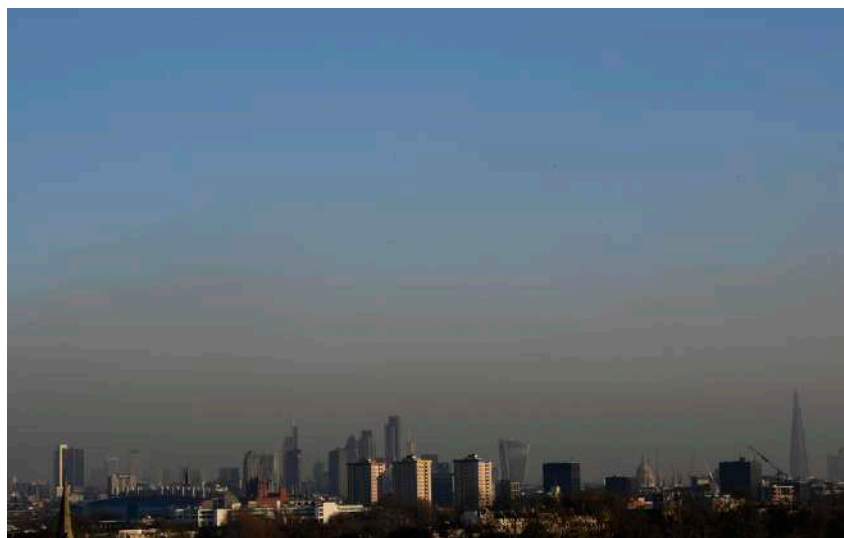
**Figure 11. Smog over Los Angeles (USA)**

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## Sulfurous Smog

Sulfurous smog better known as “London smog,” but also called industrial smog, acid smog, wet smog, or reducing smog, is due to pollution by sulfur oxides from the combustion particularly of coal, which reacts with water vapor from the atmosphere, forming sulfurous acid ( $\text{H}_2\text{SO}_3$ ) and a large variety of solid particles suspended in the air, and which are then precipitated in the form of acid rain. [45]

The name London smog was given after the worst case of urban smog happened in London from December 5<sup>th</sup> to 9<sup>th</sup>, 1952. Although 4000 deaths are attributed to it at first, many experts estimate that the Great Smog has caused up to 12000 deaths. Among many reasons, it was originated due to the low temperatures during that winter by the uncontrolled growth of the burning of fossil fuels in the industry and transport. Later, an anticyclone was installed in a windless London, which caused a temperature inversion and favored the formation and persistence of smog over the city. Figure 12 shows an example of sulfurous smog; the picture was taken in London on January 24<sup>th</sup>, 2017. [48, 49]



**Figure 12. Smog over London (Great Britain) [50]**

## Technologies for Outdoor Air Quality Detection

Instruments, techniques, and other tools to measure and monitor air quality have gained increasing importance to evaluate air emissions and to protect public health and the environment. Furthermore, air pollution data is needed by air regulators, organizations, and institutions, to develop effective preventive and mitigation strategies to protect air quality.

A multitude of measurement technologies for outdoor gases has been developed within the last decades. Figure 13 gives an overview focusing on nitrogen oxides and ozone for the most significant techniques: Cavity attenuated phase shift (CAPS), Cavity ring-down spectroscopy (CRDS), Chemiluminescence (CL), Electrochemical sensors (EC), Fourier transform infrared (FTIR), Gas Chromatography-Mass Spectrometry (GC-MS), Laser induced fluorescence (LIF), Non-dispersive infrared (NDIR), Photoacoustic spectroscopy (PAS), Quantum cascade laser (QCL), Ultraviolet spectroscopy (UV), Differential optical absorption spectroscopy (DOAS), Light detection and ranging (LIDAR), Differential absorption LIDAR (DIAL), and Resonance-enhanced multiphoton ionization (REMPI).

These techniques can also be differentiated within direct and indirect measurements. A direct measurement means that the concentration of the target gas is determined directly from the sample, such as DOAS. An indirect method, like chemiluminescence, indicates the modification of the target compound by, for example a chemical reaction, measuring a related parameter, and inferring from there. The technologies mentioned above are briefly introduced below. Except for sensor technologies, all other technologies are complex in continuous operation, large in size, and very expensive. The demand of inexpensive, miniaturized, portable, and highly sensitive instrumentation is driving the current sensor development.

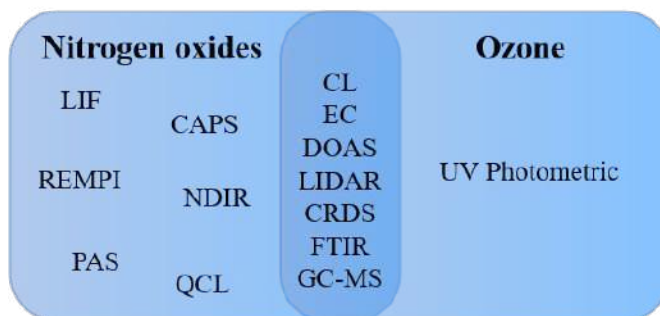


Figure 13. Overview of the Outdoor Air Sensing Technologies with focus on Nitrogen Oxides and Ozone

## In Situ Methods

The methods mentioned below are those that need a gas sample for analysis inside the instrument, or have a direct contact with the sensing area in order to do the concentration measurement of the target gas.

### Cavity Attenuated Phase Shift (CAPS)

The Cavity Attenuated Phase Shift (CAPS) spectroscopy technique is a direct and continuous measurement based on the principle of optical absorption. The CAPS technology measures NO<sub>2</sub> at 450nm in the blue region of the electromagnetic spectrum. The CAPS NO<sub>2</sub> system contains three major parts including a blue light emitting diode (LED) as the light source, a sample cell with two high reflexivity (R > 99,99%) mirrors centered at 450nm, and a vacuum photodiode detector. The square wave modulated LED light is input into the first reflected mirror, after passing through the absorption cell, the light appears to be a distorted waveform which is characterized by a phase shift in comparison to the initial modulation. By measuring the amount of the phase shift, the concentration of NO<sub>2</sub> is determined by the function of fixed instrument properties. [51, 52]

### Cavity Ring-Down Spectroscopy (CRDS)

The Cavity Ring-Down Spectroscopy (CRDS) is a sensitive technique that is based on measurements of the rate of attenuation. CRDS takes into account the specific wavelengths of the gaseous samples that absorb the light. In CRDS, the beam from a light source that could be blue or violet LEDs, a diode lasers or broadband supercontinuum, enters a cavity defined by two or more high reflectivity mirrors. When the light source is on, the cavity quickly fills with circulating light which is sensed by a photodetector. When the photodetector signal reaches a threshold level, the continuous light wave source is abruptly turned off. The light already within the cavity continues to bounce between the mirrors, but because the mirrors have a 99.99% reflectivity, the light intensity inside the cavity steadily exponentially decays to zero. This decay or "ring down", is measured in real-time by the photodetector. In the case a gas that absorbs light is introduced into the cavity, the ring-down process accelerates compared to a gasless cavity. [53]



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## Chemiluminescence (CL)

The chemiluminescence technique is the standard reference method for the measurement of nitrogen oxides and ozone. It is based on the reaction of nitric oxide (NO) with ozone (O<sub>3</sub>) to form electronically excited NO<sub>2</sub>\* molecules. The excited NO<sub>2</sub>\* molecules return to their fundamental state by emitting a light radiation ( $h\nu$ ), measured by the instrument. The light level in the reaction chamber is proportional to the concentration of NO<sub>2</sub> in the gas sample. [54]

In the NO<sub>x</sub> detection, NO<sub>2</sub> measurement is the result of a calculation process cycle. First, the reaction of NO with O<sub>3</sub> gives the “NO measure”. Second, NO<sub>2</sub> will be catalytically reduced to NO, which react later with O<sub>3</sub> giving the “NO<sub>x</sub> measure”. Finally, the NO<sub>2</sub> concentration is the difference between NO<sub>x</sub> and NO, while NO in air reacts directly. On the other hand, for the O<sub>3</sub> detection, NO is the reagent added in large excess to the flow of ambient air containing the O<sub>3</sub> concentration to be determined [55].

## Electrochemical (EC) Sensors

Electrochemical sensors are further classified into Chemiresistive Sensors, where a chemical reaction takes place on the catalytic surface and leads to a change in resistance, and Electro-Chemical Electrolyte Detector, where an electric current can be measured based on the ion transportation through the electrolyte, respectively. For the detection of nitrogen dioxide and ozone, both types of EC sensors are available.

A typical Electro-Chemical Electrolyte Detector consists of a sensing electrode, a counter electrode, an electrolyte, and usually a reference electrode. Gas diffuses into the sensor through a hydrophobic barrier, which prevents liquid electrolyte from leaking out, and eventually reaches the electrode surface. When the gas reaches the sensing electrode, an electrochemical reaction occurs, involving either an oxidation or reduction depending on the type of gas. A flow of ions through the solid or liquid electrolyte together with the necessary electronic charge constitute an electric current, which can be measured at the electrodes and is proportional to the gas concentration. However, all electrochemical sensors up to date have strong cross sensitivities and react to multiple gases. A truly selective measurement for ozone and NO<sub>2</sub> is not given. [56]

Chemiresistive Sensors, also called Metal Oxide sensors, use a metal oxide material (MO<sub>x</sub>) deposited onto a ceramic or alumina substrate. Typical MOX materials are doped semiconducting materials such as SnO<sub>2</sub>, WO<sub>3</sub>, and TiO<sub>2</sub>, etc. At elevated temperatures, gas molecules can adsorb onto the MO<sub>x</sub> surface and generate free-charge carriers. The consequential resistance change can be measured at two electrodes. Therefore, the sensor raw signal strongly depends on the ambient atmosphere, materials used, production technology, time, and temperature. All chemical target gases will catalytically react on the MO<sub>x</sub> surface and cause a resistance decrease or increase, depending on the gas oxidizing or reducing behavior. Modern MO<sub>x</sub> sensors take advantage of silicon micromachining to create a robust but thermally isolated micro-hotplate (MHP), resulting in extremely low power consumption, miniature size, and low prices due to their small dimension and high volume production. By running different sequences in operation temperature, heating slopes, and delays, a semi-selective gas measurement is possible with modern MO<sub>x</sub> sensor devices.

## Fourier Transform Infrared (FTIR)

Fourier Transform Infrared (FTIR) technique uses the absorption of infrared radiation to determine a gas concentration. FTIR relies on the “fingerprint” of the gas due to the unique infrared (IR) spectrum of each gas. Instrumentation is available for either in situ or remote deployment. Remote instruments are used for open-path monitoring where there is an open atmospheric path between the infrared source and the detector.

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Radiation in the IR region of the electromagnetic spectrum is passed through a beam-splitter, which divides the incoming IR beam into two optical beams. One beam is reflected to a stationary mirror and the other one to a movable mirror, and then reflected back, from the mirrors to the splitter. This process is taking place in the interferometer, resulting in a signal call interferogram due to the two beams interfering with each other. The interferogram has information about every infrared frequency that comes from the source, which is a function of the moving mirror position. As the interferogram is measured, all frequencies are being measured simultaneously. The beam reflected back to the beam-splitter is transmitted to a gas cell with windows, where is the sample gas. The IR beam passes multiple times through the sample before exiting the cell. After the cell, the beam is measured by the IR detector. Finally, the Fourier transformation (FT), a mathematical technique, is performed by the computer to decode the individual frequencies by comparison with an internal library. As a result, an infrared spectrum with peaks sizes is indicating the concentration of the target gas. [57]

### **Gas Chromatography - Mass Spectrometry (GC-MS)**

Gas chromatography is based on the difference in diffusion velocity of gases through a separation tube (chromatography column). A sample of the test gas is injected into the chromatography column together with a continuous flow of carrier gas.

Inside this column, the individual components of the test gas are bounded in different ways (e.g., physisorption and chemisorption) to the column filling material and column walls. There is some reaction (bonding) between the gas and the inside of the column, depending on the gas species, carrier gas, temperature, and the column material itself. Thus, stronger-bound molecules are slowed. This leads to a separation in time of the individual gas components at the exit of the chromatography column, where they can be measured individually. A very common method for collecting gas samples in the field is the use of polymer adsorbents. This sample gas tube is then analyzed by thermodesorption to release the adsorpt NO<sub>2</sub> or O<sub>3</sub> into the GC instrument.

Mass spectrometry is a technique relying on the mass and charge separation of ion beams in an analyzing magnetic field. For this, an electron beam ionizes a fraction of the test gas in a high vacuum environment. The resulting cloud of ionized gas is accelerated in an electric field and is passed through a strong magnetic field. Within this analyzer field, the ionized gas beam splits into its various components depending on the ratio of molecular mass and charge ( $m/z$  ratio). Here, the lightest and most heavily charged ions are deflected primarily due to the Lorenz force. The intensity of the resulting fan of sub-beams is measured in an angular array of Faraday cups. Each Faraday cup corresponds to a certain mass-to-charge ratio, and these ratios are specific to chemical compounds and molecules. By measuring the mass spectrum, it is possible to infer the occurrence and concentration of chemical compounds within the test gas. Due to its highly sensitive and fundamental working principle, MS can be applied to almost any gas, and can detect the smallest amounts of gases, even at sub-ppb levels. [58]

The combination of GC and MS allowed a highly selective measurement of all gases in lowest concentration.

### **Laser Induced Fluorescence (LIF)**

The LIF technique relies on the excitation on NO<sub>2</sub> molecules by a narrow band laser and the red-shifted fluorescence detection during laser-off periods. The molecules absorb the laser light (photon) in the visible region and ground-level electron is excited to a second level. Then the excited electrons in the molecules relax to lower states with spontaneous emission of light, red-shifted fluorescence. In this scheme, the number of photons emitted is proportional to the initial concentration of NO<sub>2</sub>. Thus, the NO<sub>2</sub> concentration can be determined by detection of this fluorescence. [59]

The method is extrapolated to other gases by the absorption of radiation by the sample gas, like NO, in the sampled air and the subsequent re-radiation at different wavelengths.

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## Non-Dispersive Infrared (NDIR)

The non-dispersive infrared (NDIR) technique is normally used when the target gases are already known but the concentration is requested. Similar to the FTIR technique, NDIR relies on the “fingerprint” of the gas due to a unique infrared spectrum for each chemical compound. The components of NDIR analyzers are a wavelength filter, a source of infrared radiation, an irradiated tube with the gas to be analyzed, and an infrared detector.

The sample gas is pumped into the analyzer. The wavelength filter or band-pass filter ensures the sensor responds only to the desire gas, restricting the wavelength range to that of the target gas. The infrared source directs waves of light through the tube with the sample gas toward an optical filter in front of an IR light detector. Ideally, only the target gas absorbs light of this wavelength and the IR light detector measures the amount of IR light that passes through the optical filter. [60]

## Photoacoustic Spectroscopy (PAS)

The photoacoustic spectroscopy (PAS) is a spectroscopic method that uses the photoacoustic effect. Parts of PAS analyzers are a parabolic mirror, an IR source, a chopper wheel, an optical filter, a measurement chamber with an optical window, and a microphone. The parabolic mirror focuses the light on the optical window of the measurement chamber that the IR source provides, first going through the chopper and the optical filter. The chopper is a slotted disk that rotates and switches the light on and off. When the sample is irradiated with modulated light of a predefined wavelength and the frequency of the light coincides with an absorption band of the gas in the cell, the gas molecule will absorb part of the light. As the gas absorbs energy, it is converted into heat creating a pressure rise. As the light is chopped, the pressure will alternately increase and decrease. Therefore, an acoustic signal is generated which is detected by a microphone and then evaluated. [61]

## Quantum Cascade Laser (QCL)

Quantum Cascade Lasers (QCL) are semiconductor lasers that emit in the mid- and long-IR light. QCL converts electrical energy into electromagnetic radiation at very specific wavelengths in the IR region, allowing the concentration measurement of the nitrogen compounds which exhibit high sensitivity in this wavelength region. With conventional diode lasers, only one photon is released from an energy gap existing between the valence and the conduction band, while a QCL element has several thin layers of semiconductors which create a multi-level band structure consisting of separate quantum wells. This results in the electrons “cascading” down through the layers while several photons are released. By analyzing the absorbed wavelength spectrum in a narrow region it is possible to detect the target gas, such as ozone or nitrogen dioxide. [62]

## Ultraviolet (UV) Spectroscopy

The UV photometric spectral analyzers are the most widely used methods for ozone compliance measurement using the principle of Lambert-Beer’s law. This law states that the absorption of radiation at a given wavelength is directly proportional to the concentration of the analyte and the sample thickness through a constant of proportionality that is called absorptivity.

UV photometric analyzers’ procedure starts when ambient air is drawn through the device by a vacuum pump. Upon entering the analyzer, the sample splits into two flow paths. One path incorporates a scrubber which selectively removes ozone, the outflow without ozone is used as the reference gas stream. A solenoid valve switches at a fixed interval allowing either the sample or the reference gas stream to flow through a quartz tube of accurately known length. A mercury-vapor lamp at one end of the quartz cell produces a monochromatic beam of UV light at 254nm, a wavelength at which ozone absorbs very strongly. A vacuum diode at the opposite end of the cell measures the intensity of transmitted light. Finally, the O<sub>3</sub> concentration is calculated based on Lambert-Beer’s law. [63]

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## Remote Sensing Methods

This section provides a short description of methods that measure the average concentration on a large area; the sample gas does not enter the device. These instrumentations are often used for a monitoring path in the atmosphere.

### Differential Optical Absorption Spectroscopy (DOAS)

The Differential Optical Absorption Spectroscopy (DOAS) is a direct method to determine the concentrations of atmospheric trace gases from remote sensing measurements. DOAS relies on the absorption spectrum of the species of interest. Light at ultraviolet, visible, or near infrared (NIR) wavelengths can be used. DOAS method involves artificial light sources, solar or lunar light, by pointing the instrument towards the ground, light scattered from the surface or the atmosphere is detected, providing information of trace species in the atmosphere [64]. As same as UV photometric method, DOAS technique is described by Lambert-Beer's law but with some modifications, most of the terms are a function of the wavelength and all terms are variable.

### Light Detection and Ranging (LIDAR)

The Light Detection and Ranging (LIDAR) also known as Laser Detection and Ranging (LADAR) is a radar-related, "radio wave detection and ranging" method to remotely measure atmospheric parameters. LIDAR is based on the interaction of optical radiation with the atmosphere. A LIDAR system consists of three main subsystems: an optical transmitter; an optical receiver or detector and ranging, timing, and control electronics. A pulsed laser beam is sent into the atmosphere, hits air molecules, and particles, and is scattered by them. Only a small part of the scattered light is reflected back towards its origin. The backscattered light is then collected by telescopes and conducted into a detection unit, which transforms the irradiance into electronic signals, and recorded with temporal resolution. Depending on the laser wavelength used, different gas molecules or particles will be detected [65].

DIAL (Differential Absorption Lidar) is an optical remote sensing technique based on LIDAR technology. The difference are the two laser pulses at different wavelengths are emitted into the atmosphere. One of these, the "on-resonant wavelength" ( $\lambda_{on}$ ), is chosen to be at a wavelength that is absorbed by the target species. The other, the "off-resonant wavelength" ( $\lambda_{off}$ ), is chosen to be at a nearby wavelength that is not absorbed significantly by the target species. The intensities of the two backscattered light are compared to determine the optical attenuation by the target gas. This technology is used for high precision measurements of local ozone concentration in the upper atmosphere. [66]

### Resonance-Enhanced Multiphoton Ionization (REMPI)

The resonance-enhanced multiphoton ionization (REMPI) technique allows efficient ionization of atoms and molecules using high power laser radiation in the range of visible (VIS) or near-ultraviolet (UV). REMPI occurs in two steps: excitation to intermediate states of the molecule and then absorption until the ionization potential is reached. Normally the REMPI process has a special notation, the name must be accompanied by two numbers in the form  $(n + m)$ , where "n" is the number of photons necessary to reach to a resonant level, and "m" is the subsequent number of photons required to reach the ionization potential of the atom or molecule. [67]

## Air Quality Standards and Target Values

Limits and standards of chemical compounds in the air are defined for the protection of human health and environment. The World Health Organization (WHO) proposed establishing political actions related to outdoor sources, including an international air quality definition and guidelines, and to make a source control and dilution control. At present, there is no global standard that defines allowable concentrations for outdoor air components. Organizations like the WHO and the EPA have given recommended and mandatory concentrations values, respectively, for the safety of human health and besides each country defined their standards.

## Target Values

Table 3 presents target concentration values, which are standard for nitrogen dioxide and ozone for different countries. All levels are expressed in parts per billion (ppb) with exposure times of 1 hour, 8 hours, 24 hours, and 1 year. The blank spaces indicate that there is no information available on a target value.

**Table 3. Nitrogen Dioxide and Ozone Target Concentration Standards in ppb**

Country / Organization	Specification	Nitrogen Dioxide (NO <sub>2</sub> )			Ozone (O <sub>3</sub> )		Reference
		1 hour	24 hours	1 year	1 hour	8 hours	
<b>WHO</b>		106		21		51	[68]
<b>Australia</b>		120		30	100	80	[69]
<b>Brazil</b>	Primary	170		53	82		[70]
	Secondary	101		53	82		[70]
<b>Canada</b>	Effective since 2015					63	[71]
	Effective in 2020	60		17		62	[71]
	Effective in 2025	42		12		60	[71]
<b>China</b>	Class 1	106	43	21	82	51	[72]
	Class 2	106	43	21	102	82	[72]
<b>Colombia</b>		106		32		51	[73]
<b>USA</b>	Primary	100		53		70	[74]
	Secondary			53		70	[74]
<b>EU</b>		106*		21		61 <sup>‡</sup>	[75]
<b>Germany</b>		106*		21		61 <sup>‡</sup>	[76, 77]
<b>Great Britain</b>		106*		21		51***	[78]
<b>India</b>	Class 1		43	21	92	51	[79]
	Class 2		43	16	92	51	[79]
<b>Japan</b>		40 - 60			60		[80, 81]
<b>Mexico</b>		210**			95	70	[82]

\*Not to be exceeded more than 18 times/year

\*\* Not to be exceeded more than 1 time/year

\*\*\*Not to be exceeded more than 10 times/year

<sup>‡</sup>25 days averaged over 3 years

The WHO Air Quality Guidelines (AQG) offer guidance on threshold limits for key air pollutants that pose health risks and provide a reference for setting air pollution targets at regional and national levels to improve air quality. Some epidemiological investigations indicate adverse health effects even at concentrations below the guideline value. and for this reason, some countries have decided to adopt lower concentrations than the WHO guideline values as their national air quality standards. In addition, some countries have established thresholds and long-term objectives. For example, 92 ppb and 123 ppb are the “information-to-public” threshold and the public alert thresholds for ozone, respectively as given by the German Environment Agency (Umweltbundesamt, UBA).

## Workplace Values

Occupational Exposure Limits (OELs) are a measure for minimizing worker exposure to hazardous substances in the workplace. These upper limit concentrations are not expected to generate acute or chronic harmful effects on employees' health. It is typically set by national authorities and enforced by legislation.

The OELs are normally classified into two groups:

- First group – The long-term exposure limit which refers to the Time-weighted average (TWA), this value is measured in a workplace by sampling a worker's breathing zone for the whole workday. Then, add up all the exposure and divide by 8 hours.
- Second group – The short-term exposure limit, which mainly refers to the Short term exposure limit (STEL) that is the TWA concentration taken over 15 minutes (instead of 8 hours).

For proper safety in the workplace, the set exposure level cannot be exceeded during that 15-minute test period. If a test shows that a STEL has been exceeded; this means that the employee has been exposed to a heavy dose exposure of that hazardous substance during that 15-minute test period. In some cases, the reference is also the Ceiling limit value (C), which indicates the gas concentration should not exceed at any time during the workday.

Table 4 summarizes the nitrogen dioxide and ozone limit values for some countries. All levels are expressed in parts per billion (ppb) with an exposure time of 8 hours (TWA) and short term, which in most cases is STEL (15 min) value. If the limit has a (C) indicator it refers to the ceiling limit value. The blank spaces indicate there is no information available on the limit value at the moment. Because the maximum workplace concentration is calculated for a limited exposure time, the threshold values are much higher than for the outdoor air target concentrations (see Target Values).

**Table 4. Nitrogen Dioxide and Ozone Limit Values Expressed in ppb**

Country / Organization	Nitrogen Dioxide (NO <sub>2</sub> )		Ozone (O <sub>3</sub> )		Reference
	8 hours	Short term	8 hours	Short term	
<b>Australia</b>	3000	5000		100 (C)	[83]
<b>Brazil</b>	4000*		100*		[84]
<b>Canada - Ontario</b>	3000	5000 (C)	100	300	[83]
<b>Canada - Québec</b>	3000			100 (C)	[83]
<b>China</b>	3000	5000		200 (C)	[83]
<b>EU</b>	500	1000			[83]
<b>Germany (DFG)</b>	500	500			[83]
<b>Japan (JSOH)</b>			100		[83]
<b>Mexico</b>	200			100 (C)	[85]
<b>UK (HSE)</b>	0.5	1		0.2	[83]
<b>USA (OSHA)</b>		5 (C)	0.1		[83]

## Air Quality Standards

The Air Quality Index (AQI) is a guide that says how clean or polluted the air is, and the associated health effect. Different countries define its air quality index corresponding to different national air quality standards.

### US Air Quality Index (AQI)

EPA calculates the AQI for five major air pollutants regulated by The Clean Air Act: ground-level ozone, particle matter, carbon monoxide, sulfur dioxide, and nitrogen dioxide. Table 5 contains the EPA's AQI with exposure times of 1 hour, 8 hours, and 24 hours, as indicated in each pollutant. An AQI value of 100 generally corresponds to the national air quality standard for the pollutant, which is the level the EPA has set to protect public health. AQI values below 100 are generally satisfactory, while above 100 are considered to be unhealthy at first for sensitive groups. The Clean Air Act requires the EPA to review its NAAQS every five years, thus the AQI is adjusted periodically according to the evolution of health effects information. [86]

**Table 5. EPA's Air Quality Index (AQI)**

AQI	Category	NO <sub>2</sub> [ppb] (1 hr)	O <sub>3</sub> [ppb] (8 hr)	O <sub>3</sub> [ppb] (1 hr)	PM <sub>2.5</sub> [µg/m <sup>3</sup> ] (24 hr)	PM <sub>10</sub> [µg/m <sup>3</sup> ] (24 hr)	CO [ppm] (8 hr)	SO <sub>2</sub> [ppb] (1 hr)
0 to 50	Good	0 to 53	0 to 54	-	0.0 to 12.0	0 to 54	0.0 to 4.4	0 to 35
51 to 100	Moderate	54 to 100	55 to 70	-	12.1 to 35.4	55 to 154	4.5 to 9.4	36 to 75
101 to 150	Unhealthy for Sensitive Groups	101 to 360	71 to 85	125 to 164	35.5 to 55.4	155 to 254	9.5 to 12.4	76 to 185
151 to 200	Unhealthy	361 to 649	86 to 105	165 to 204	55.5 to 150.4	255 to 354	12.5 to 15.4	186 to 304
201 to 300	Very Unhealthy	650 to 1249	106 to 200	205 to 404	150.5 to 250.4	355 to 424	15.5 to 30.4	305 to 604
301 to 400	Hazardous	1250 to 1649	-	405 to 504	250.5 to 350.4	425 to 504	30.5 to 40.4	605 to 804
401 to 500	Hazardous	1650 to 2049	-	505 to 604	350.5 to 500.4	505 to 604	40.5 to 50.4	805 to 1004

### World Air Quality Index Project

The World Air Quality Index project started in 2007 in Beijing, China. Its mission is to promote air pollution awareness for citizens, providing a unified and world-wide air quality information. Nowadays, it includes data of more than 88 countries, covering more than 11000 stations in 1000 major cities via websites. The data published on the World Air Quality Index project comes from each country, is real-time, and is displayed in the US EPA Index scale that means it is based on EPA standards. Figure 14 shows an example of the World Air Quality Index project presentation to the public. [87]

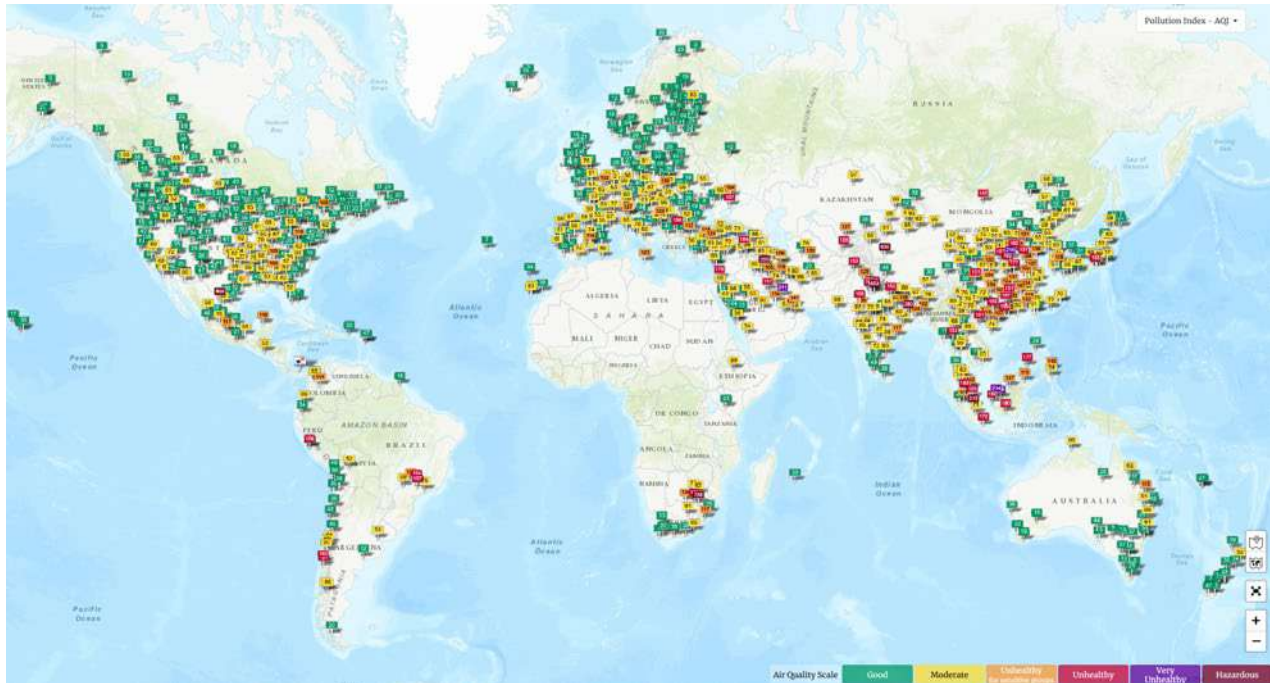


Figure 14. World Air Quality Index Project on September 16<sup>th</sup>, 2019

### European Common Air Quality Index (CAQI)

The Common Air Quality Index (CAQI) was first developed in 2006 during the CITEAIR project with the purpose of easily comparing the air quality in European cities in real-time. CAQI was launched on November 16<sup>th</sup>, 2017 as the new European Air Quality Index by the European Environment Agency (EEA) and the European Commission. The CAQI is calculated for hourly, daily, and yearly averaged data. The hourly and daily indices have a scale from 0 (very low) to > 100 (very high). They are based on three pollutants of major concern in Europe: PM<sub>10</sub>, NO<sub>2</sub>, and O<sub>3</sub>, but also take into account CO, PM<sub>2.5</sub>, and SO<sub>2</sub>. In order to make cities more comparable, it is calculated for city background and traffic situations. Table 6 presents the European Common Air Quality Index for hourly averaged data, except for CO that is given in 8 hours moving average. On the other hand, the yearly average common air quality index provides a relative measure of the annual average air quality in relation to the European limit values. It is presented as a distance to a target index. [88, 89]

Table 6. European Air Quality Index

Index Class	Grid	Traffic				City Background					
		Core Pollutants		Pollutants		Core Pollutants			Pollutants		
		NO <sub>2</sub> [ppb] (1 hr)	PM <sub>10</sub> [µg/m <sup>3</sup> ] (1 hr)	PM <sub>2.5</sub> [µg/m <sup>3</sup> ] (1 hr)	CO [ppm] (8 hr)	NO <sub>2</sub> [ppb] (1 hr)	PM <sub>10</sub> [µg/m <sup>3</sup> ] (1 hr)	O <sub>3</sub> [ppb] (1 hr)	PM <sub>2.5</sub> [µg/m <sup>3</sup> ] (1 hr)	CO [ppm] (8 hr)	SO <sub>2</sub> [ppb] (1 hr)
Very low	0 to 25	0 to 27	0 to 25	0 to 15	0 to 4.4	0 to 27	0 to 25	0 to 31	0 to 15	0 to 4.4	0 to 19
Low	25 to 50	27 to 53	25 to 50	15 to 30	4.4 to 6.6	27 to 53	26 to 50	31 to 61	15 to 30	4.4 to 6.6	19 to 38
Medium	50 to 75	53 to 107	50 to 90	30 to 55	6.6 to 8.7	53 to 107	50 to 90	61 to 92	30 to 55	6.6 to 8.7	38 to 134
High	75 to 100	107 to 213	90 to 180	55 to 110	8.7 to 17.5	107 to 213	90 to 180	92 to 123	55 to 110	8.7 to 17.5	134 to 191
Very High*	> 100	> 213	> 180	> 110	> 17.5	> 213	> 180	> 123	> 110	> 17.5	> 191



## BreezoMeter Air Quality Index (BAQI)

The BreezoMeter Air Quality Index (BAQI) is the first global air quality index developed by the company BreezoMeter in 2012. Due to the wide variety of air quality indexes around the globe, and in an attempt to unify air quality information, the company created the BreezoMeter Global AQI. The BAQI scale ranges from 0, indicating poor air quality, to 100, excellent air quality, with 5 color-coded categories of equal lengths as seen in figure 15. BAQI has a big data infrastructure of more than 60 countries, however, air pollution concentrations are calculated by dispersion algorithms, not taken at the exact point at which the value is reported. As a result, not only can an inaccurate concentration be reported due to an estimated calculation but it also makes people think they know the air quality everywhere even when the next measuring station is far away and air pollution changes very quickly between places. One the other hand, BAQI is driven by one company and therefore information on algorithms and internal calculations for the unification method are not available to public. [90]

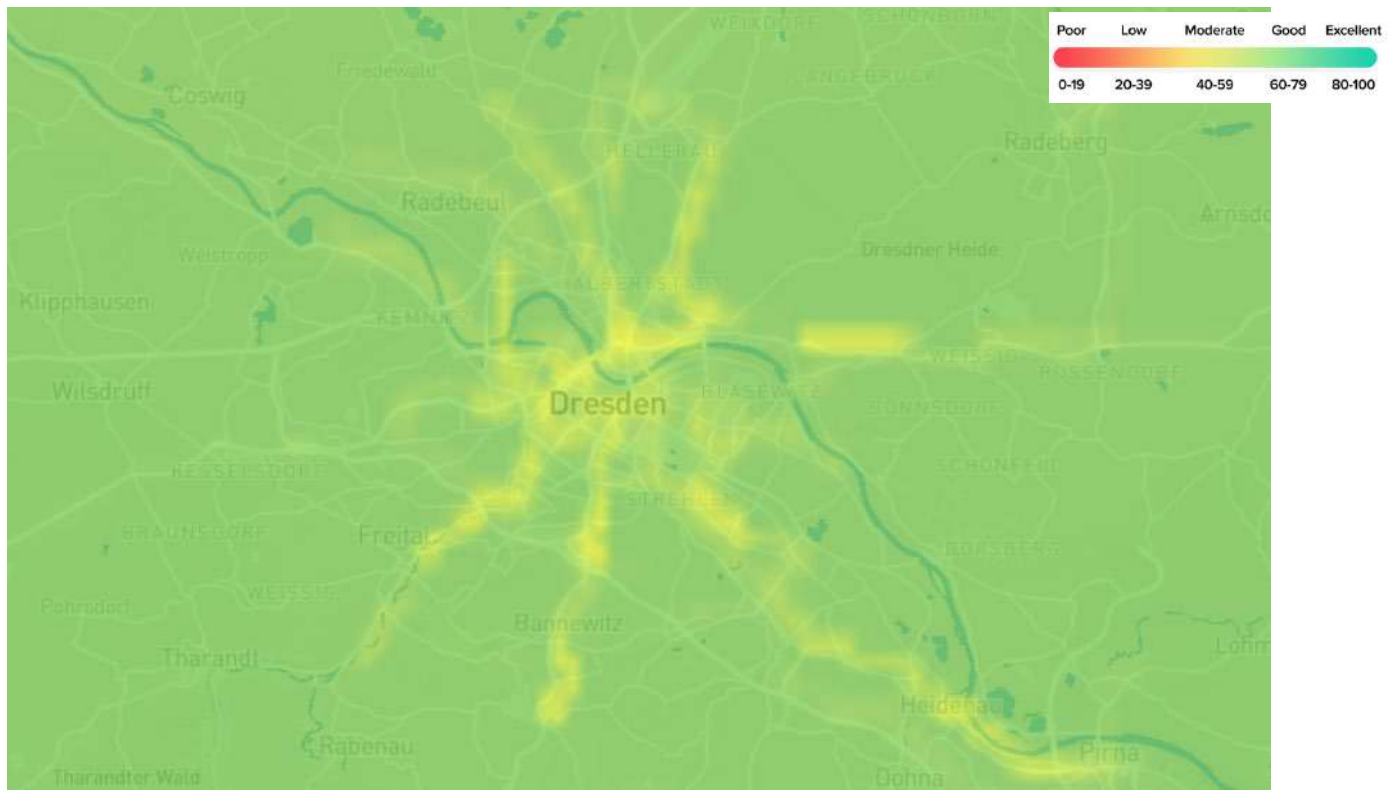


Figure 15. BreezoMeter's Air Quality Index (BAQI) for Dresden on September 16<sup>th</sup>, 2019 [90]

## Abbreviations

Abbreviation	Meaning	Abbreviation	Meaning
AQG	Air Quality Guidelines	O <sub>2</sub>	Oxygen Molecule
AQI	Air Quality Index	O <sub>3</sub>	Ozone
BfUL	Staatliche Betriebsgesellschaft für Umwelt und Landwirtschaft in Saxony (Germany)	OAQ	Outdoor Air Quality
BMI	Body Mass Index	OEL	Occupational Exposure Limit
CAPS	Cavity Attenuated Phase Shift	-OH	Hydroxyl Radicals
CL	Chemiluminescence	OSHA	Occupational Safety and Health Administration (USA)
CO	Carbon Monoxide	PAN	Peroxyacetyl Nitrates
CO <sub>2</sub>	Carbon Dioxide	PAS	Photoacoustic Spectroscopy
CRDS	Cavity Ring-Down Spectroscopy	PM	Particulate Matter
DFG	German Research Foundation (Germany)	ppb	Parts per billion
DIAL	Differential Absorption LIDAR	ppm	Parts per million
DOAS	Differential Optical Absorption Spectroscopy	QCL	Quantum Cascade Laser
EC	Electrochemical	REL	Recommended Exposure Limit
EEA	European Environment Agency (EU)	REMPI	Resonance-Enhanced Multiphoton Ionization
EPA	Environmental Protection Agency (USA)	SO <sub>2</sub>	Sulfur Dioxide
EU	European Union	SO <sub>x</sub>	Sulfur Oxides
FTIR	Fourier Transform Infrared	STEL	Short Term Exposure Limit
H <sub>2</sub> O <sub>2</sub>	Hydrogen Peroxide	TWA	Time-Weighted Average
H <sub>2</sub> SO <sub>4</sub>	Sulfuric Acid	UBA	German Environmental Agency (Germany)
HNO <sub>3</sub>	Nitric Acid	UV	Ultraviolet
IARC	International Agency for Research on Cancer (WHO)	VOC	Volatile Organic Compound
IR	Infrared	WHO	World Health Organization
JSOH	Japan Society for Occupational Health (Japan)		
LIDAR	Light Detection and Ranging		
LIF	Laser Induced Fluorescence		
MO <sub>x</sub>	Metal Oxide		
N <sub>2</sub> O	Nitrous Oxide		
N <sub>2</sub> O <sub>3</sub>	Dinitrogen Trioxide		
NDIR	Non-Dispersive Infrared		
NO	Nitrogen Monoxide		
NO <sub>2</sub>	Nitrogen Dioxide		
NO <sub>x</sub>	Nitrogen Oxides		
NO <sub>Y</sub>	Oxides of Nitrogen with oxidation state ≥ +II		
O	Atomic Oxygen		

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