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THE INTRICACIES OF PHOTOCHEMICAL SMOG: FROM MOLECULAR INTERACTIONS TO ENVIRONMENTAL IMPACT

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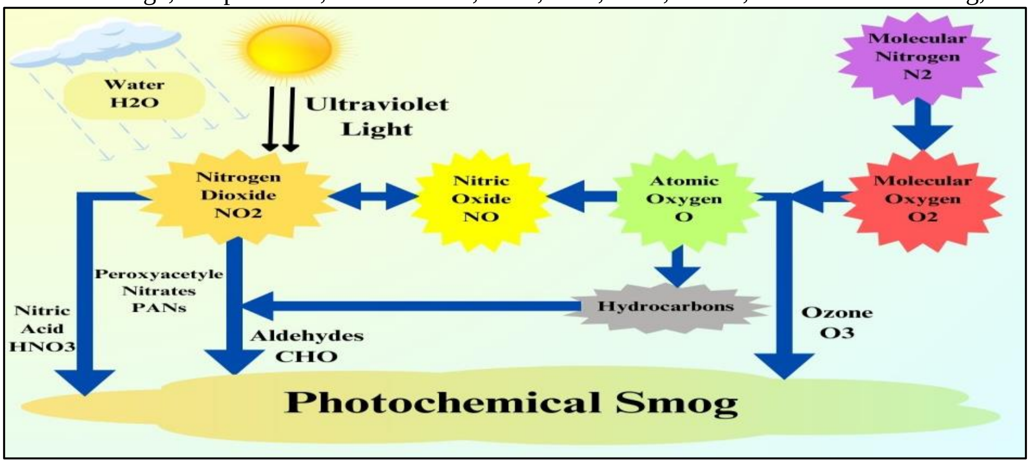
Abstract
Rapid urbanization and industry can lead to an increase the air pollution. Through 1964 the, photochemical aspects of air pollution are studied. In this review article, we have compiled data about the major processes that cause photochemical smog, tropospheric ozone (O3), and other oxidants. Besides this natural and anthropogenic activities that contribute to the formation of photochemical smog are also discussed so that mitigation and adaptation strategies can be done in a better way. Photochemical smog is formed when sunlight reacts with volatile organic compounds and nitrogen oxides. Due to these reactions, ozone and other pollutants are formed. Nowadays photochemical smog is a major problem in urban areas during the summer. Sunlight acts as a major precursor in the formation of photochemical smog. Photochemical air pollution is an emerging issue therefore we must implement strategies to reduce the emissions from industries, vehicles, and power plants. The use of electric vehicles as compared to other vehicles can help to reduce photochemical air pollution.

Keywords: Climate change, Air pollution, Urbanization, NH3, SO2, NOx, VOCs, Photochemical smog, Ozone



Graphical abstract

1. INTRODUCTION

Climate change and air pollution are included in some of the most serious environmental issues. Air pollution has adverse effects on the environment (Komolafe et al., 2014). Therefore, it is very necessary to understand the mechanisms and processes involved in air pollution for better policymaking and scientific research related to air pollution control. Urbanization is a major cause of emissions in cities because automobiles, coal combustion, exhaust, and industries are included in one of the major sources that increase emissions. Therefore, the fine particles like NH3, SO2, NOx, and volatile organic compounds are increased. Proper mitigation and adaptation strategies are needed to minimize the rapidly increasing level of air pollution. Air Pollution is defined release of harmful contaminants into the atmosphere by natural processes or anthropogenic activity (Kemp et al., 2011). There are two kinds of air pollutants: primary and secondary. When a hazardous substance is released directly into the atmosphere, it produces primary air pollutants. On the other hand, secondary air pollutants are harmful substances produced in the atmosphere when primary air pollutants combine with naturally occurring substances or other air pollutants (Sonwani et al., 2016). Besides this, there are also major sources of pollutants such as fire, dust and soil, sea spray, volcanic eruptions, and lightning. Fire releases harmful pollutants into the atmosphere, such as carbon monoxide, nitrogen oxides, and volatile organic compounds. Dust particles from agriculture activities are included in one of the leading causes of pollution. Seaspray is also a major contributor to pollution. Volcanic eruptions release harmful substances such as sulfur dioxide, ash, and others which are harmful to the environment.

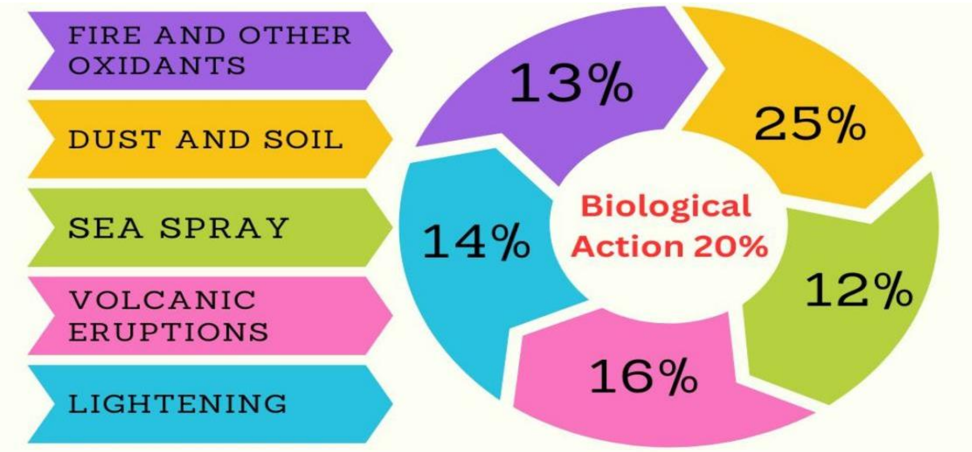


Fig 1. Represents the air pollutants other than primary and secondary air pollutants, and their ratio.

During the summer high oxidation reactions occur. These reactions occur due to the large amounts of pollution that come from vehicles such as motorcycles buses, and cars. In more populated areas of the world photochemical air pollution is included in one of the major problems that affect human health. High levels of ozone (O3) and other secondary pollutants are the major contributors to photochemical smog. Therefore, the reactions of nitrogen oxides (NOx), volatile organic compounds (VOC), and other pollutants can occur more frequently. These reactions can cause photochemical air pollution (Leighton et al., 2012). When nitrogen oxides and hydrocarbons react photochemically in the atmosphere, they form photochemical oxidants. These oxidants can undergo physical and chemical processes. These oxidants have severe impacts on humans and plants. Proper mitigation and adaptation strategies are necessary to minimize the effect of these pollutants (Narumi et al., 2009).

Photochemical smog is formed as a result of photochemical reactions from automobile and stationary sources (Haagen-Smit et al., 2013). Thus it is very important to understand the mechanism of photochemical smog. A lot of reviews have been written about the air pollution and photochemical smog. This paper contains previously published data about photochemical smog. Sunlight acts as a precursor in the formation of photochemical smog, when it combines with nitrogen oxides and volatile organic compounds (VOCs), a mixture of pollutants known as photochemical smog is produced (Rani et al., 2011). It can also occur when anthropogenic air pollutants like nitric acid, ozone, and organic compounds are trapped due to temperature inversion. These contaminants have harmful effects on humans as well as on plants (Ma et al., 2012). Nitrogen oxides are released into the atmosphere from the internal combustion engines of the vehicles. When nitric oxide (NO) absorbs sunlight it releases oxygen atoms. These oxygen atoms (O) combine with molecules of oxygen (O2) to form ozone (O3) (Sillman et al., 2003). The most harmful components of photochemical smog are ozone, PAN (peroxyacetylnitrate), nitrogen dioxide (NO2), and CHO-containing chemical compounds (aldehydes). VOCs can also cause photochemical smog because they can lead to the formation of photochemical ozone (Muilwijk et al., 2016).

Photochemical pollution has severe impacts on human health, and the environment (Zhang et al., 2002). Sources and mechanisms of photochemical air pollution are complicated and there are knowledge gaps. Understanding the mechanism and the environmental impact of air pollution is necessary for policymaking and scientific research in reducing pollution. In the past few years, the population and economic growth have led to increased pollution levels. This pollution comes from coal burning, car exhaust, and other sources. Frequent haze pollution events have been caused by the high concentrations of these contaminants. In this review article, the photochemical mechanisms such as (how different reactions occur and contribute to the formation of photochemical smog) are discussed.

Smog Components	Source	Effects	Mitigation strategies	References
SO2	• Industries • Use of fossil fuels Power plants • Volcano eruptions	• Irritation, inflammation • infection of the respiratory tract. • Asthma and poor lung function. • Obstructive pulmonary disease • Arrhythmias, and hemorrhagic stroke	Use low-sulfur fuel. Natural gas low sulphur gasoline	4, 25, 55
Hydrocarbons	Automobile exhaust	• Carcinogenic • leukemia • lung cancer	Replace the least efficient fuel with clear and efficient fuel.	10
PAN1	• Hydrocarbon • Nitrogen oxide Photochemical reaction	• Itching in the eyes. • Nose and throat problems • Breathing difficulties • Protein damage	Reduce emissions from industries and vehicles.	57
Nitrogen oxide	• Fossil fuel combustion Volcanic activity • Lightning • Forest fires	• Effects the liver • Kidney cancer • Prostate cancer • Brain cancer	Utilize low nitrogen fuels, Flow gas treatment techniques	31
Tropospheric ozone	By-product of photochemical smog	• Eye and respiratory irritation • Cardiovascular disease • Heart failure • Breast cancer • Bladder cancer	Vapour recovery nozzles can help improve vehicle inspection processes.	22, 39, 58
PM 2	• Industries • Vehicles	• Particles enter the lungs deeply • Disrupt the reproductive system • Promote Parkinson's disease	Replace the old engine with a new one, and quit smoking	30

Table 1. Represents the different components of photochemical smog their sources, effects and mitigation strategies

2. Photochemical Smog & Smog difference

Photochemical smog and smog are types of air pollution, however, there are some slight differences between them. When sunlight combines with harmful contaminants such as nitrogen oxides and volatile organic compounds photochemical smog is produced. This reaction contains a variety of hazardous compounds, including ozone, which is harmful to the plants and environment. Photochemical smog is mostly occurred in cities, due to excessive emissions from the automobile. Human health is negatively affected by the photochemical smog. Ozone and Particulate matter found in photochemical smog can hurt breathing, especially for people who already have respiratory diseases like asthma (Wang et al., 2020).

However, smog is a mixture of pollutants, including particulate matter, and gas that combine with fog to form visible air pollution. Industrial pollutants, vehicles, and the combustion of fossil fuels can lead to the formation of photochemical smog. Meteorological circumstances have varying compositions depending on the sources of pollution. Smog can affect the air quality, contributing to respiratory disorders and other health issues. Smog can lead to the formation of acid rain, which is harmful to forests, and affects the water bodies, and soil quality including nitrogen oxides and volatile organic compounds. Plants are also affected by smog, which reduces the growth and decrease the crop yields. Furthermore, smog can also cause photochemical degradation of buildings (Raza et al., 2021).

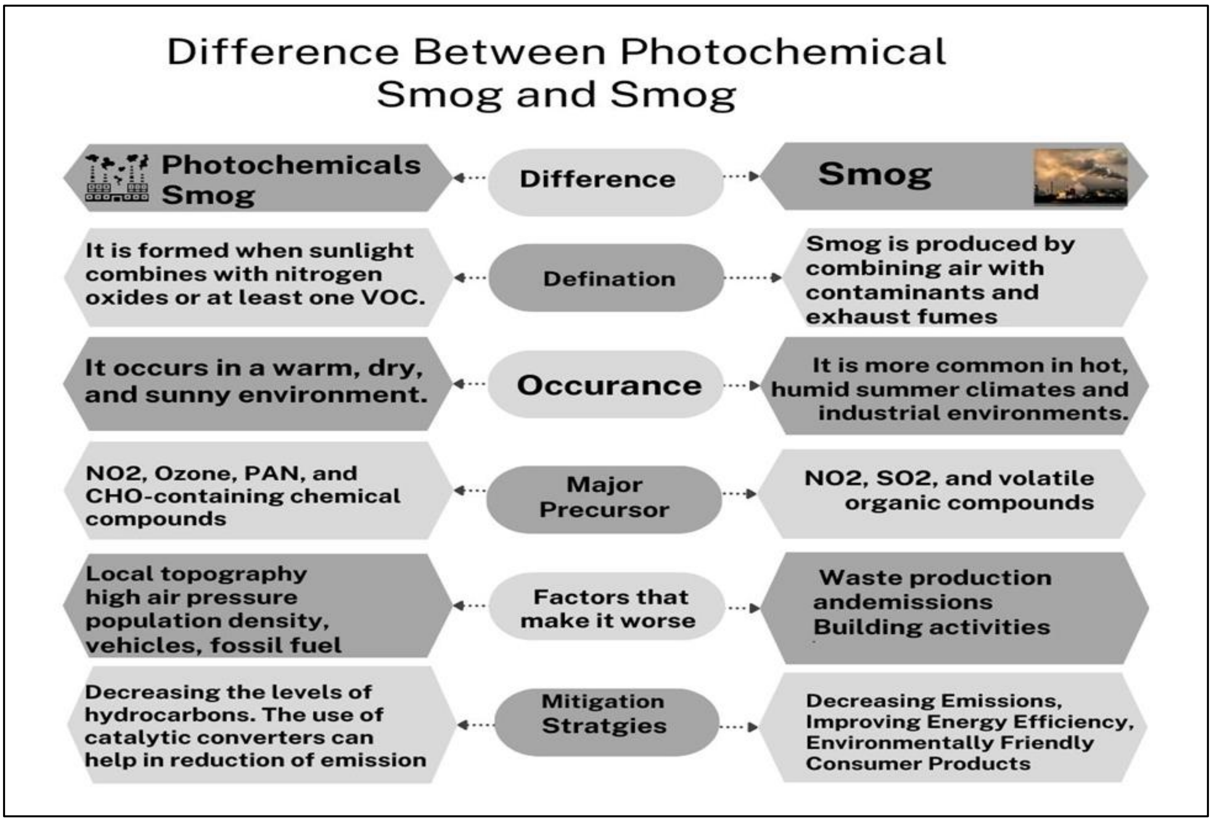


Fig 2. Represents the difference between photochemical smog and smog.

3. The photochemical mechanism in smog formation

3.1. Causes of Photochemical smog

Nitrogen oxides (NOx) and volatile organic compounds (VOCs) react in the presence of sunlight to form photochemical smog. Pollutants, including ground-level ozone, particulate matter, and other harmful substances are produced by these reactions. Vehicle emissions are the main sources of NOx and VOCs in the cities. Indeed, emissions from power plants and other sources of VOCs and NOx can cause photochemical smog (Mohan Kumar K 2002).

3.2. Formation of photochemical smog

Various processes are involved in the formation of photochemical smog. Nitrogen oxides (NOx) and volatile organic compounds (VOCs) are released into the atmosphere from various sources, including vehicles, and industrial emissions. NOx and VOCs undergo chemical reactions that form secondary pollutants like ozone in the presence of sunlight. These reactions can cause smog. These pollutants are have harmful affects on the plants, and humans. These pollutants can affects the respiratory system, can cause irritation of eyes. Indeed it can also affects the ecosystem. Photochemical smog can only happen under certain circumstances:

(a) UV light; (b) hydrocarbons; (c) nitrogen oxides

In the morning, an oxidation step produces nitric oxide by burning or oxidizing nitrogen that is released from cars.

- Nitric oxide (NO) and additional oxygen combine in a subsequent oxidation reaction to form nitrogen dioxide in a matter of hours.
- In a reduction reaction, nitrogen dioxide breaks down when it absorbs sunlight and forms nitric oxide (NO) and oxygen radical (O).
- Oxygen radicals react to atmospheric oxygen (O_2) to form ground-level ozone (O_3). Ozone is a major component of photochemical smog and contributes to its hazy appearance.
- Nitric oxide breaks down ozone to produce oxygen and nitrogen dioxide. This response can be reversed.
- PAN and other hazardous compounds are created when nitrogen dioxide combines with various hydrocarbons (R), which are compounds made of carbon, hydrogen, and other elements. The VOCs are the primary source of these hydrocarbons. Similarly, nitric oxide and oxygenated organic and inorganic compounds (ROx) combine to form more nitrogen oxides.
- (ISA Ground, 2003). The photochemical reactions also lead to the formation of particulate matter, such as fine particles which can be harmful to human health.

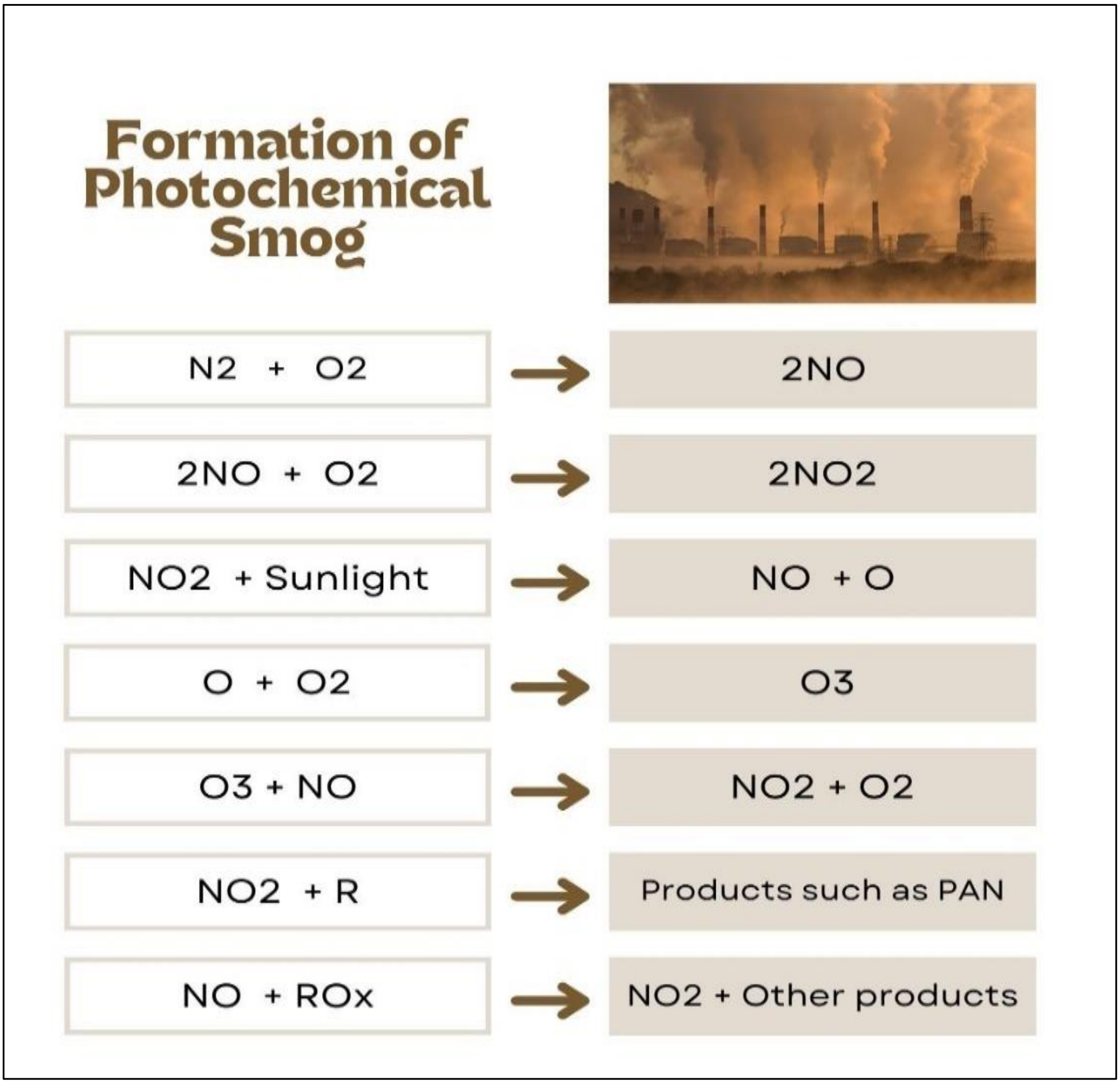


Fig 3. Represents the chemical reaction involved in photochemical smog formation.

3.3. Other circumstances include

Nitrogen oxides and methane hydrocarbons are released into the atmosphere when people go to work in the morning. Methane hydrocarbon is a volatile organic compound that can cause smog. Nitrogen oxides and volatile organic compounds start to react with each other to form nitrogen dioxide. Nitrogen dioxide byproducts increase the amount of ozone in the air (Mohan Kumar K 2002). Some of the nitrogen dioxides can react with the volatile organic compounds to make poisonous chemicals. In the evening the formation of ozone becomes slow down. (Roberts et al., 2007). Various meteorological parameters affect the photochemical smog formation (Fatima et al., 2024). These circumstances are as follows

3.3.1. Rainfall

Rainfall can reduce photochemical smog because it can help to remove contaminants from the air (Dam et al., 2008). During the rain, the contaminants in the air get spread over large distances, therefore can help to minimize the pollutants. Rainfall can also help in reducing the humidity and temperature, which can delay the chemical reactions that can cause photochemical smog. Smog levels are also decreased by the rainfall.

3.3.2. Wind

Wind can also help to disperse the chemicals of the photochemical smog. Indeed, pollutants can also be transported over long distances by winds, thus it can help to minimize the harmful effects of environmental pollution (Safavi Y et al., 2006). In certain conditions, such as when temperature increases with height pollutants are trapped close to the ground, leading to the accumulation of smog (Ullah et al., 2024).

3.3.3. Temperature inversions

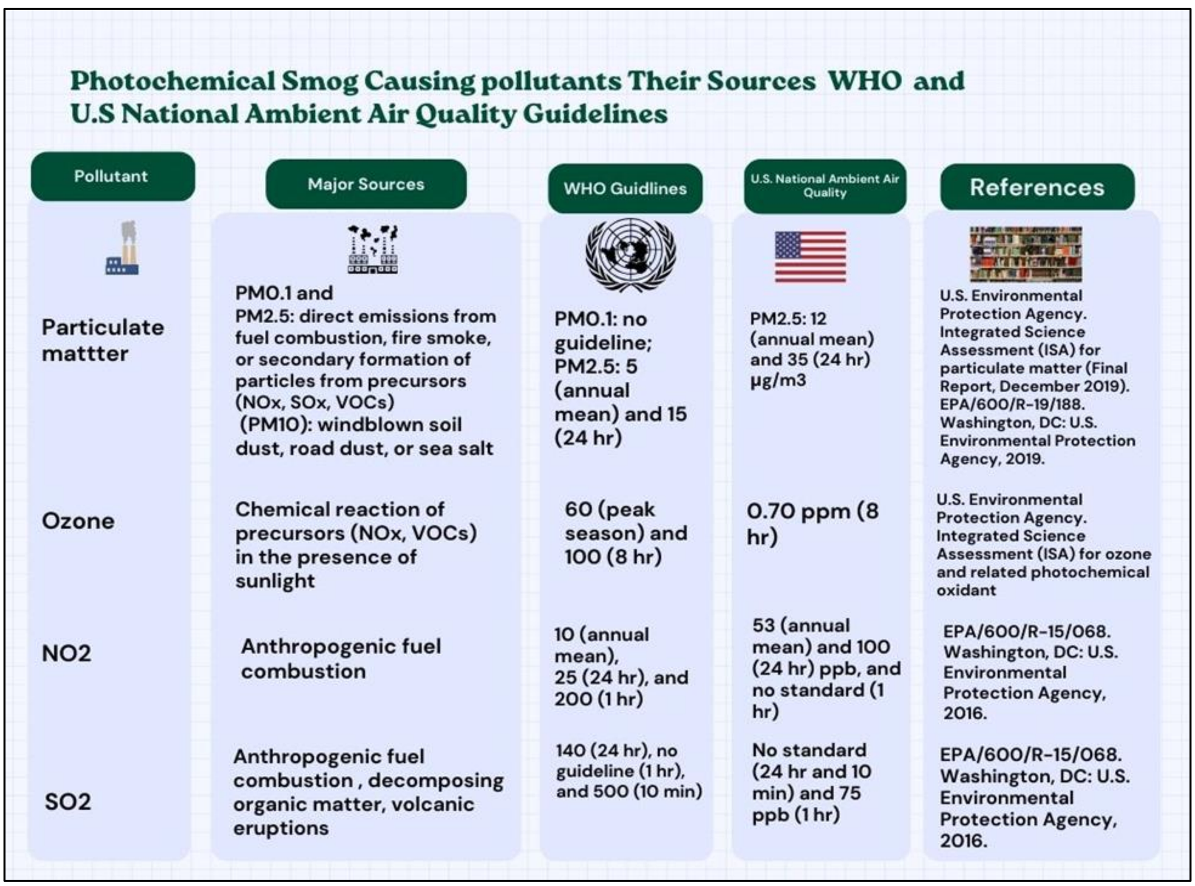
Temperature inversions have severe consequences on the photochemical smog. During a temperature inversion, the pollutants can stuck near the surface of the Earth. Inversions can last anywhere from a couple of days to a few weeks. The rates of reactions and emission rates are affected by the temperature of the atmosphere (Fritz BK et al., 2008).

3.3.4. Topography

Topography is also included as one of the major factors which affect the photochemical smog. People who live in valleys are more vulnerable to photochemical smog because hills and mountains can play a major role in blocking the flow of air and increasing the pollutant level. Valley also affects the photochemical smog because temperature inversions in valleys are high (Louka et al. 2003; Haidri et al., 2023; Agarwal SK 2005).

4. World Health Organization and U.S National Ambient Air Quality Guidelines

The World Health Organization (WHO) and the United States have developed strategies for maintaining air quality. These guidelines can help to improve the public health by reducing the harmful impacts of air pollution. The WHO states that ozone is a major component of photochemical smog. Indeed this guideline serves as a standard for countries developing their air quality standards and policies (Burki, et al 2021). The Environmental Protection Agency in the United States sets the National Ambient Air Quality Standards (NAAQS) to protect public health. Moreover, it plays an important role in maintaining the policies and measures to eliminate photochemical smog and improve air quality (U.S. Environmental Protection Agency, 2020). We must investigate the effective photochemical smog reduction strategies. Mitigation strategies for photochemical smog include implementing emission-reduction measures (Hussain et al., 2024). Some important strategies include the use of cleaner fuels and technologies, such as electric vehicles and renewable energy. Implementing emission standards for industries and vehicles can also help to minimize the pollutants. Increasing awareness about the effects of smog and implementing strict policies can help to maintain air quality standards. By implementing these measures, photochemical smog can be minimized (Zhu et al., 2020).



Photochemical Smog Causing pollutants Their Sources WHO and U.S National Ambient Air Quality Guidelines

Pollutant	Major Sources	WHO Guidlines	U.S. National Ambient Air Quality	References
Particulate mattter	PM0.1 and PM2.5: direct emissions from fuel combustion, fire smoke, or secondary formation of particles from precursors (NOx, SOx, VOCs) (PM10): windblown soil dust, road dust, or sea salt	PM0.1: no guideline; PM2.5: 5 (annual mean) and 15 (24 hr)	PM2.5: 12 (annual mean) and 35 (24 hr) µg/m3	U.S. Environmental Protection Agency. Integrated Science Assessment (ISA) for particulate matter (Final Report, December 2019). EPA/600/R-19/188. Washington, DC: U.S. Environmental Protection Agency, 2019.
Ozone	Chemical reaction of precursors (NOx, VOCs) in the presence of sunlight	60 (peak season) and 100 (8 hr)	0.70 ppm (8 hr)	U.S. Environmental Protection Agency. Integrated Science Assessment (ISA) for ozone and related photochemical oxidant
NO2	Anthropogenic fuel combustion	10 (annual mean), 25 (24 hr), and 200 (1 hr)	53 (annual mean) and 100 (24 hr) ppb, and no standard (1 hr)	EPA/600/R-15/068. Washington, DC: U.S. Environmental Protection Agency, 2016.
SO2	Anthropogenic fuel combustion , decomposing organic matter, volcanic eruptions	140 (24 hr), no guideline (1 hr), and 500 (10 min)	No standard (24 hr and 10 min) and 75 ppb (1 hr)	EPA/600/R-15/068. Washington, DC: U.S. Environmental Protection Agency, 2016.

Fig 4. Represents the photochemical smog-causing pollutants and their sources WHO and U.S National Air Quality guidelines.

Table 2. Represent the previous work on photochemical smog their findings and purpose of the study

Purpose of study	Year	Author	Findings
To study the Development of Photochemical Smog in the Santiago de Chile Metropolitan Area	2000	Rappenglück, B. et al	The urban plume plays a significant role in the formation of PAN (peroxyacetyl nitrate) and the highest levels of ozone during day time.
Evaluation of photochemical smog for environmental management	2001	Tirabassi, T. et al	Reducing primary pollutant emissions, such as NO2, does not always result in a decrease in secondary pollutants, such as ozone, or a reduction in photochemical smog.
To better understand the sources of gas-phase and particle-phase pollutants during a severe photochemical smog episode.	2002	Schauer, J.J. et al	A strong correlation exists between the concentrations of secondary organic aerosols and 1,2-benzenedicarboxylic acid in fine particles in the atmosphere.
This study focuses on measuring and analyzing a multi-day episode of photochemical smog that occurred in the Pearl River Delta of China.	2003	Wang, T. et al	The high concentrations of O3 and other pollutants were primarily a result of diffusion under light north-northeast winds
The main objective of this study is to evaluate the possible effects of various management approaches on air quality using photochemical smog modeling.	2004	Oanah, N.T.K. et al	The formation of O3 in Bangkok was more sensitive to volatile organic compounds (VOCs) than nitrogen oxides (NOx). This means that the presence and concentration of VOCs have a greater influence on O3 formation in the city.
The purpose of this study is to examine the role that motor vehicle emissions play in the development of photochemical smog in the Perth airshed.	2005	Todd, D.	The primary cause of photochemical smog formation in the Perth airshed is motor vehicles. The presence of aromatic compounds in vehicle emissions is one of the main causes of this smog.
The goal of this research is to explore the atmospheric photochemical reactions that give rise to secondary pollutants.	2006	Cuciureanu, R. and Dimitriu, G.	Plants play an important role in absorbing and interacting with ozone (O3), which can harm organic molecules in plant tissues, particularly during the day and peak vegetation period.
The purpose of this study was to determine the origin of the secondary organic aerosols (SOA) during an episode of photochemical smog.	2007	Kleeman, M.J. et al	When it comes to secondary organic aerosols (SOA), those associated with anthropogenic sources tend to have slightly lower concentrations during the day due to increased mixing depth. However, SOA concentrations linked to biogenic sources show higher levels of aqueous biogenic SOA at night.
The purpose of this study is to forecast the interactions between the main photochemical pollutants in Istanbul, Turkey.	2008	Im, U. et al	The highest concentrations of ozone were observed in the afternoon and the lowest concentrations during rush hours . This is due to the fact that nitrogen oxides (NOx) from traffic emissions, through a process known as titration, aid in the neutralization of ozone.
As Beijing, China experiences a severe photochemical smog episode, identify the source of ozone.	2009	Wang, X. et al	In Beijing's urban areas, volatile organic compounds (VOCs) restricted O3 formation, whereas in the suburbs and farther out, NO x levels were more sensitive.

To assess Melbourne's urban ventilation and photochemical smog in light of potential future climate conditions.	2010	Walsh, S. et al	Wind speed affected particle concentrations; at higher wind speeds, wind-blown dust becomes significant, and at lower wind speeds, pollutants build up. Over the next fifty years, Melbourne's air quality may get worse due to climate change.
Examine how relative humidity affects a photochemical smog chamber's characterization.	2011	Hu, G. et al	There was a linearly significant relationship between the rate constant of O3 and increasing RH. RH had an impact on NOx wall losses' rate constant, but their relationship was not statistically significant.
Uses for photochemical pollution Models to evaluate acid deposition, particulate matter air quality.	2012	Oanh, N.T.K. et al	Integrated Air Quality Management (AQM) strategies must be developed using analysis of air pollutant emissions and deposition.
Assessment of photochemistry in the atmosphere.	2013	Mason, R.S.	Ozone depletion as a result of chlorofluorocarbon photochemistry. Photochemical smog is the result of the interaction between intense sunlight and vehicle emissions. Aerosols are essential for dissolving the oxidized hydrocarbons and soluble reactants that are formed.
To assess the chemical composition, size distribution, and particle number concentration during photochemical smog and haze episodes in Shanghai.	2014	Wang, X. et al	Haze events resulted in an increase in all soluble ions, with NH4+, SO42 -, and NO3 - showing the largest increases.
To forecast the dispersion of pollutants from the elevated stacks and their roles in the formation of photochemical smog in a highly industrialized area.	2015	Aidaoui, L. et al	Throughout the simulation period, there was a significant correlation between photochemical pollutants and the weather. The correlation shows that solar radiation, temperature, wind speed, and topography are the main contributors to the formation of ozone.
Examine China's photochemical smog: scientific issues and consequences for air quality regulations.	2016	Hallquist, M. et al	Many stakeholders in business, government, and society at large may be impacted by a decrease in secondary air pollution.
Estimation of photochemical smog production and ground level ozone using NOx and O3 concentrations in Isfahan	2017	Canaani, F. et al	Ozone concentrations have been produced as a result of photolysis reactions that have increased the concentration of pollutants on the ground. The city of Isfahan's atmosphere has experienced ozone loss due to photochemical reactions.
The purpose of this study is to assess photochemical smog's impact on COPD patients in Nigeria critically.	2018	Ihedike, C. t al	In contrast to the developed world, where there is evidence of a connection between air pollution and respiratory health, the precursors of photochemical smog are much more prevalent.
The causes of photochemical smog and its effects on the environment and the health of living things were briefly explained.	2019	Ibrahim, M.	Ozone modeling is divided into two main stages: the base case and the future case, each of which has a number of smaller steps. The base case checks that processes are being evaluated and that the model is operating as intended.
Estimation of Shanghai's Photochemical Smog Episode's Secondary Organic Aerosol Formation.	2020	Wang, H. et al	For more than seven days in a row, the daily maximum solar radiation reached 800 W/m2, and for more than eleven days in a row, the daily peak temperatures exceeded 35 °C.

Forecast the photochemical smog modeling of PM for the purpose of evaluating the related health effects in Southeast Asia's densely populated urban areas.	2021	Chi, N. N. H. and Oanh, N.T.K.	Achieving the WHO guideline for annual PM2.5 reduction would help prevent 1,415 deaths. Reducing PM2.5 even more to the counterfactual level of 2.4 μg/m³ would assist in preventing 2,990 BMR deaths linked to PM2.5, of which 1,770 occur in Bangkok alone.
Examine the effects of using smog chambers in atmospheric process research.	2022	Chu, B. et al	The formation of HONO was caused by the photo-enhanced reaction between NO2 and water, as the photolytic HONO source increased with the square of RH.
To assess VOC concentrations and photochemical losses.	2023	Wu, Y. et al	The results emphasize the significance of tracking VOC photochemical degradation to accurately identify emission sources.
To investigate how OH radicals in the atmosphere break down polymethyl substituted benzenes and contribute to photochemical smog,	2024	Zhao, H. et al	The atmospheric lifetimes were calculated to be 2.17 and 2.78 hours in the presence of OH radicals.

5. Conclusion

This review contained information related to the chemistry involved in the production of photochemical smog and the variables that affect its formation. Photochemical smog is created by reactions involving sunlight, volatile organic compounds (VOCs), and nitrogen oxides (NOx). Primary pollutants are converted into secondary pollutants reactions when react with each other. Indeed the review emphasizes the importance of understanding the transportation precursor and sources as well as meteorological conditions. It emphasizes how anthropogenic activities, such as motor vehicle emissions, industrial processes, and agricultural practices can release VOCs and NOx. Photochemical smog has severe effects on human health, plants, and the environment. Photochemical smog can cause respiratory issues, cardiovascular problems, and other negative health effects. It can harm crop yield, disrupt ecosystems, and increase greenhouse gas emissions. In short, this review provides useful information about the photochemical smog formation processes and their effects on the environment. Understanding these intricate mechanisms enables policymakers, scientists, and to collaborate on mitigation strategies.

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