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# Photochemical smog introduction and episode selection for the ground-level ozone in Hanoi, Vietnam

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**Abstract.** Ozone ($O_3$) is a secondary pollutant formed in the atmosphere throughout a complex non-linear chemical reaction involving two classes of precursors: the reactive volatile organic compounds (VOCs) and the oxides of nitrogen (NOx) in the presence of sunlight.

The rapid urbanization and industrialization in Vietnam have brought about high air pollutant emissions including the $O_3$ precursors. Ground level $O_3$ may already be high in large cities like Hanoi and Ho Chi Minh City. The $O_3$ episode is very important for scene of view of photochemical smog in Hanoi. Ozone episodes are selected on the days which have a high concentration that lasts for at least two days time. During the episode selection, ozone concentrations larger than 46ppb were observed at two stations (the Lang and Lac Long Quan stations) in March. The maximum value of 74ppb was measured at the Lang station at 14:00 on March 3. This episode was observed in a common meteorological condition for this time of the year.

*Keywords:* Photochemical smog; Ozone; Volatile organic compounds; Secondary pollutant.

## 1. Introduction

Photochemical smog occurs in the troposphere, the lower portion of our atmosphere. Ground-level ozone, the primary component of photochemical smog, is the most prevalent pollutant that has been known to cause a serious air pollution problem in many developed countries over the past few decades. In this paper, only ground-level ozone is considered as a pollutant.

Ozone ($O_3$) is a secondary pollutant formed in the atmosphere through a complex non-linear chemical reaction involving two classes of precursors: reactive volatile organic compounds (VOCs) and oxides of nitrogen (NOx) in the presence of sunlight. Ozone formation can be described as either VOC- or NOx- sensitive, depending on VOC/NOx ratios, VOC reactivity, and other factors [10].

A stagnant air mass, normally resulting from high atmospheric pressure and light winds, limits the pollution dispersion leading to accumulation of the formed $O_3$ to high levels. It should be noted that VOCs, NOx and ozone do occur naturally in the lower atmosphere, too. However, human activities - fossil fuel use, in particular - have greatly increased the amounts of ozone in urban areas.

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VOCs (also called hydrocarbons) are the most important constituents of oil and natural gas. The major man-made sources of VOC emissions are motor vehicles, evaporation of gasoline, solvents, oil-based paints, and petrochemical industry. NOx are mainly produced by burning coal, oil and gas. The exhaust from fossil fuel combustion in motor vehicles is the primary source, followed by fuel burning in homes, businesses, factories and power plants.

The temperature also affects ozone formation through the change in reaction rates. In particular, a high temperature causes an increase in VOC evaporative emissions. The warming temperature is associated with increased natural emissions of VOCs. Higher outdoor temperature could also enhance energy consumptions produced by fossil fuel combustion, which lead to emissions of NOx - the major pollutant from fuel combustion.

Ground-level ozone built up over the cities that produce large amounts of VOCs and NOx. But it can also migrate up to several hundred kilometers downwind. Topography and meteorological conditions may enhance ozone build-up. Modeling approach is a powerful tool to study the complex processes leading to $O_3$ formation and build up.

## 2. Photochemical smog pollution

Smog is a synchrony of two words - smoke and fog. Smog can be of two types - industrial or winter smog (e.g. London smog) and photochemical or summer smog (e.g. Los Angeles smog).

The industrial revolution has been the main cause for the increase of pollutants in the atmosphere over the last three centuries. Before 1950, the majority of this pollution was created from the burning of coal for energy generation, space heating, cooking, and transportation. Under certain meteorological conditions, the smoke and sulfur dioxide produced from the burning of coal can combine with fog to create industrial smog. In high concentrations, industrial smog can be extremely toxic to humans and other living organisms.

Today, the use of cleaner (than coal) fuels has greatly reduced the occurrence of industrial smog in the industrialized areas. However, the massive burning of fuels in mobile devices in urban areas can create another atmospheric pollution problem known as photochemical smog. Photochemical smog is a condition that is developed when the primary pollutants, i.e. nitrogen oxides and volatile organic compounds, interact under sunlight to produce a mixture of hundreds of different hazardous chemicals known as secondary pollutants. Some of the characteristics of the two smog types are listed in Table 1.

Table 1. Characteristics of industrial and photochemical smog (source: [4, 5])

| Characteristics | Industrial/Winter | Photochemical/Summer |
|---|---|---|
| First occurrence noted | London | Los Angeles |
| Principal pollutants | Sulfur oxides, particulate matter | Ozone, nitrogen oxides, hydrocarbons, carbon monoxide, free radicals |
| Principal sources | Industrial and household fuel combustion (coal, petroleum) | Transportation fuel Combustion (petroleum) |
| Effects on human | Lung and throat irritation | Eye and throat irritation |
| Effects on compounds | Reducing | Oxidizing |
| Time of occurrence of worst episodes | Winter months especially in the early morning | Around midday of summer months |

Photochemical smog is a widespread phenomenon in many population centers of the World. The components of photochemical smog that are the most damaging to plants and detrimental to human health are the photochemical oxidants. These oxidants include ozone ($O_3$), peroxyacetyl nitrate (PAN), peroxybenzoyl nitrate (PBN), hydrogen peroxide ($H_2O_2$), formic acid (HCOOH), and other trace substances. They are collectively termed photochemical oxidants with ozone and PAN, and are present in the highest concentrations. In addition, the aerosols formed during the chemical reactions cause a marked reduction in visibility with a brownish cast in the atmosphere [13]. PAN in photochemical smog can irritate the eyes, causing them to water and sting.

### *2.1. Condition for development of photochemical smog*

Certain conditions are required for the formation of photochemical smog. These conditions include:

(1) Emission rates of the sources of nitrogen oxides (NOx) and volatile organic compounds (VOC). High concentrations of these two substances are associated with industrialization and transportation, which create these pollutants through fossil fuel combustion.

(2) The time of day is a very important factor influencing on the amount of photochemical smog. Fig. 1 illustrates the typical daily variation in the key chemical factors in photochemical smog formation.

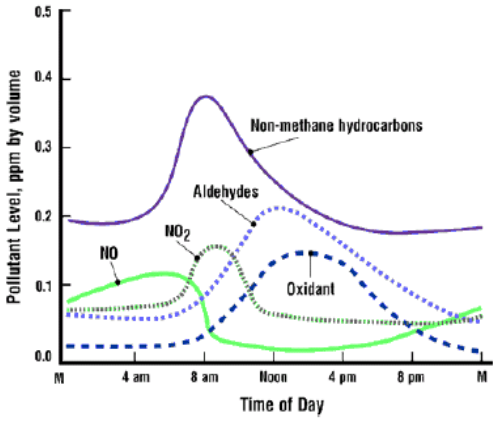


Fig. 1. Generalized reaction scheme for photochemical smog formation. (source: [3])

Based on the graphs in Fig. 1, some suggestions are made as follows:

• Early morning traffic increases the emissions of both nitrogen oxides and non-methane hydrocarbons (NMHC) - a type of VOCs - as people drive to work.

• Later in the morning, traffic reduces and the nitrogen oxides and volatile organic compounds begin to react to form nitrogen dioxide and increase its concentration.

• As the sunlight becomes more intense later in the day, nitrogen dioxide is broken down and its by-products form increasing concentrations of ozone.

• At the same time, some of nitrogen dioxide can react with the volatile organic compounds to produce toxic chemicals such as PAN.

• As the sun goes down, the production of ozone is stopped. The ozone that remains in the atmosphere is then consumed by several different reactions.

(3) Meteorological factors are important in the formation of photochemical smog. These conditions include:

• Precipitation can reduce photochemical smog as the pollutants are washed out of the atmosphere with the rainfall.

• Winds can transfer photochemical smog away, replacing it with fresh air. However, the problem may arise in distant areas that receive the pollution.

• Temperature inversions can enhance the severity of a photochemical smog episode. If a temperature inversion is developed, the pollutants can be trapped near the Earth's surface. Inversions can last from a few days to several weeks. The atmosphere temperature directly affects the reaction rates and some emission rates.

(4) Topography is another important factor influencing on how severe a smog event can become. Communities situated in valleys are more susceptible to photochemical smog because the hills and mountains surrounding them tend to reduce the air flow, allowing for pollutant concentrations to rise. In addition, valleys are sensitive to photochemical smog because relatively strong temperature inversions can frequently develop in these areas.

### *2.2. Effects of photochemical smog*

a. Effects on human health

Low concentrations of ground-level ozone can irritate the eyes, nose and throat. As smog increases, it can trigger more serious health problems, including:

• Asthma, bronchitis, coughing and chest pain;

• Increased susceptibility to respiratory infections;

• Decreased lung function and physical performance.

b. Effects on vegetation and materials

Sensitive crops, trees and other vegetation are harmed at lower ozone concentrations than is human health. Ground-level ozone can damage leaves, and reduce growth, productivity and reproduction. It can cause vulnerability to insects and disease, and even plant death. When ozone levels are fairly high over a long period, agricultural crops can suffer significant harm. Smog can also accelerate the deterioration of rubber, plastics, paints and dyes,...

c. The enhanced greenhouse effect and acid rain

The pollutants emitted into atmosphere are implicated in numerous environmental problems. Ozone, for example, is not only a major component of smog; it also contributes to the enhanced greenhouse effect, which is predicted to lead to global climate change. Similarly, NOx - one of the building blocks of ground-level ozone - plays a major role in formation of acid rains.

## 3. Ozone episode in Hanoi City

The rapid urbanization and industrialization in Vietnam have brought about high air pollutant emissions including the $O_3$ precursors. Ground-level $O_3$ may already be high in large cities like Hanoi and Ho Chi Minh City.

The $O_3$ episode is very important for scene of view of photochemical smog in Hanoi.

### *3.1. Selection of episode*

The simulation target is the Hanoi Metropolitan Region (HMR). Through analyses of ozone concentrations and meteorological parameters measured at three monitoring stations of Hanoi City, past photochemical episode was identified based on the following criteria:

• Ozone concentrations are relatively high at least at two stations in HMR.

• Time period of high ozone concentration: high ozone concentrations at the station last at least two hours.

• Meteorological condition: meteorological conditions of episodes are representative for the frequently occurring ones and representative for high $O_3$. In general for Hanoi, the episode days were characterized with light winds, clear skies.

### *3.2. Data collection and processing*

According to the size of the simulation domain and the distribution of the ambient air quality monitoring network set up by the Vietnam Environment Protection Agency (VEPA), three continuous ambient air monitoring stations were selected. Air quality and meteorological data from these stations where $O_3$ data were available were collected on an hourly basis for two years (2002 and 2003). The stations are located at 150 m from the main roads and are general ambient air monitoring stations. Air pollutants that were collected include CO, NOx, $SO_2$, $O_3$, $CH_4$, and NMHC (Non-Methane Hydrocarbons). The station names and types, air pollutants and meteorological parameters observed in these surface monitoring stations are listed in Table 2.

Table 2. Station types, names and observed parameters in HMR

| Station type | Station name | Parameter |
|---|---|---|
| Surface weather and ambient air quality monitoring station | Lac Long Quan<br>Lang<br>Xay Dung | CO, NO, $NO_2$, $SO_2$, $O_3$, $CH_4$, NMHC, WS, WD,T,RH,P,R |
| Upper air weather stations | Noi Bai | $O_3$, S,WD,T,RH and P |

However, the Xay Dung station had a problem with data quality and equipment. Therefore, the data created by this station can not be used for study.

### *3.3. Ozone episode selection*

According to the collected data at two monitoring stations in Hanoi, the graphs of monthly averaged ozone concentration were drawn for 2003 year (Fig. 2). On these graphs, the $O_3$ concentration was highest in three months: January, February, and March. Therefore, these months were used to find the ozone episodes for simulation.

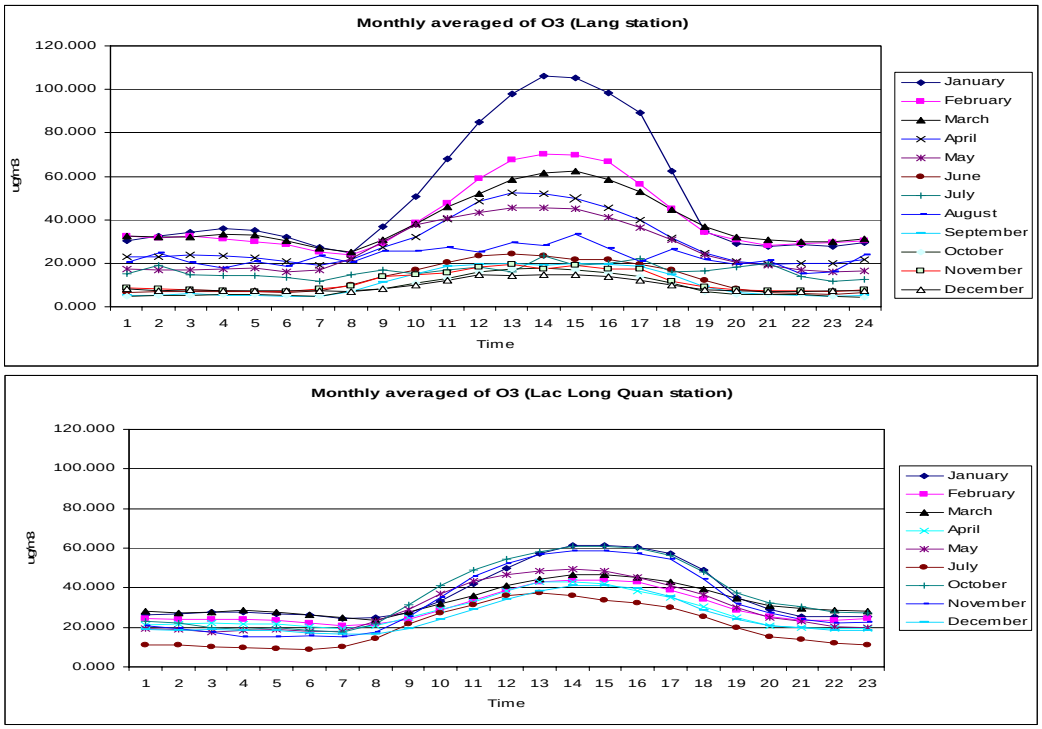


Fig. 2. Monthly averages of ozone concentration at two monitoring stations in 2003.

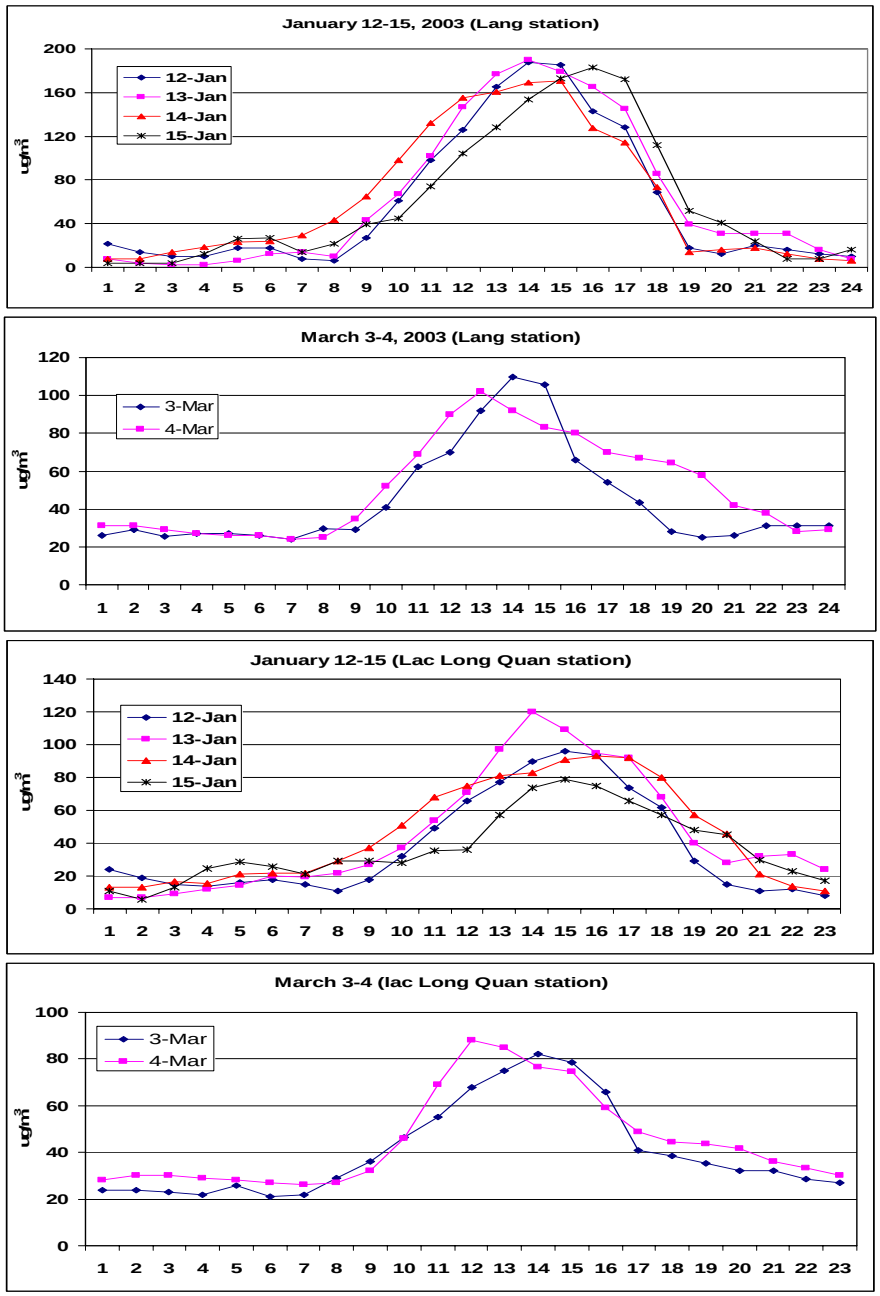


Fig. 3. The days with high ozone concentrations at 2 monitoring stations in 2003.

Fig. 2 shows that the $O_3$ concentration in Hanoi was not so high and the max average $O_3$ did not exceeded Vietnam ambient air quality standard of 102.08ppb (1-hour standard). The daily maximum $O_3$ concentration reached highest value in the January - March period, but it is still below the standard.

Ozone episodes are selected on the days which have high concentration lasting for at least 2 days time. From Fig. 3 the days with the

highest $O_3$ come at both stations have been selected. Based on the variation of ozone of maximum concentration (Fig. 3), two periods of high $O_3$ were selected, including: January 12-14, 2003 and March 2-4, 2003.

## 4. Conclusions

The photochemical smog potential in Hanoi seems to be still low. The available data collected in 2003 shows that all of the peaks of ozone concentration at two monitoring stations were lower than the Vietnam ambient air quality standards (VN AAQS).

During the episode, ozone concentrations larger than 46ppb were observed at two stations (Lang and Lac Long Quan station) in March. The maximum value of 74ppb was measured at Lang station at 14:00 on March 3. This episode was observed in a common meteorological condition for this time of the year.

There is a severe shortage of monitoring station data and also many errors in observed data. Therefore, equipments at monitoring stations in Hanoi should be checked and maintained and improved so that more parameters could be measured and more accurate results to be obtained at 3 monitoring stations, especially Xay Dung station. More monitoring stations, especially at the downwind locations of Hanoi should be made available to capture the max $O_3$ in the domain.

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