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Analytical study of the effect of nitrogen oxides, volatile organic compounds, and ambient temperature on ozone in Tehran

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ABSTRACT: The aim of this study is to evaluate the effect of nitrogen oxides (NOx), volatile organic compounds (VOCs), and ambient temperature on ozone (O3) concentration in the city of Tehran. In this regard, the hourly concentration for ozone and nitrogen oxides for the first half of 1396-98 were used. Moreover, the 2-weeks averaged data for BTEX monitored by passive sampling method and 30-minutes averaged temperature data monitored at Mehrabad airport were used. First, daily variations of ozone and nitrogen oxides with their corresponding indexes were analyzed. Then, the role of nitrogen oxide (NO) and nitrogen dioxide (NO2) on ozone concentration were investigated by statistical analysis. The results show a meaningful relationship between ozone and both nitrogen oxide and nitrogen dioxide with the coefficient of determinations of 0.83 and 0.8, respectively. Although an apparent increasing trend in ozone concentrations has been observed in recent years, however, no similar trends are detected for nitrogen oxide and nitrogen dioxide. The limited available data for BTEX, shows a 17.3% increase from 1394 to 1398. The daytime temperature analysis for the 30 days with the highest ozone concentrations showed an increasing trend from 1396 to 1398. Therefore, it can be concluded that the increasing trends of BTEX concentrations and ambient temperature were probably responsible for the increasing trend of ozone concentration in the study period.

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1- Introduction

The city of Tehran, with a population of more than 8.5 million people per night and more than 11 million people per day [1], faces a number of environmental challenges, including air pollution. Tehran has had an air pollution problem for more than forty years, which has been intensified by the uncontrolled growth of automobiles and an increase in fossil fuel consumption. The increase in the emission of pollutants as well as increases in the temperature and sunlight radiation in Tehran, has resulted in an increase in O₃ concentration. Consequently, O3 has become one of the city's major pollutants, especially during the warm months of the year. Ozone is one of the criteria pollutants that has many adverse effects on human health, especially the respiratory system. A number of studies have been conducted in Tehran to investigate the O, trend and its relationship with NO, the most important of which were undertaken by Shariapour [2], Motesadi Zarandi, et al. [3], and Rafipour et al. [4]. These studies examined O₃ and NO₄ trends and found a good correlation between the two. The role of NO in the production of O₃ has also been researched, and reducing nitrogen oxide emissions has been suggested as the most efficient way to reduce O3. While O3 concentration and its statistical relationship with NO_x and temperature have

been evaluated in previous studies, the role of VOCs as an influential factor in O_3 concentration has not been discussed. For the first time, the effect of VOCs on the O_3 concentration has been examined in this study. On the other hand, due to the significant increase in the O_3 concentrations in recent years and the increase in the number of unhealthy days (based on O_3 concentration) from 7 days in 1396 to 25 days in 1398, the role of NO_x , VOCs, and ambient temperature is examined. As a result, this study aims to analyze the effect of NO_3 , NO_2 , NO_3 , and ambient temperature on O_3 in Tehran from 1396 to 1398.

2- Methodology

The study area covers the 22 urban regions of Tehran designated by the Tehran Municipality. This study analyzes hourly data of O₃ and NO_x acquired from the 21 air quality monitoring stations operated by Air Quality Control Company (a subsidiary of Tehran Municipality) in the period from 1396 to 1398. Additionally, relevant data is extracted from the annual air quality reports for the years 96 [5] and 97 [6] published by the Air Quality Control Company. Furthermore, VOCs data was measured by passive method with a mean of two weeks. Also, the ambient temperature with a time interval of 30 minutes measured at Mehrabad meteorological station has been used.

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MATLAB and SPSS were used to analyze the trends and statistics. The calculations of daily and annual trends and correlations between NO and O₃ concentration data were conducted using MATLAB. In addition, statistical analysis was performed using SPSS.

3- Results and Discussion

The concentration of O_3 in the atmosphere depends on several factors, the most important of which are: environmental conditions (such as temperature, sunlight, and humidity), the concentration of precursors (NO_x , VOCs, carbon monoxide, etc.), and chemical reactions [7-9]. Chemical reactions are very complex. However, these processes can be simplified quite well. In general, the reactions between O_3 , NO_3 , and NO_3 , can be expressed as follows: [7-9]

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{1}$$

$$NO_2 + hv(+O_2) \rightarrow NO + O_3 \tag{2}$$

Thus, O_3 is produced directly from NO_2 in the presence of sunlight, then the products of Reaction (2) participate in Reaction (1) as reactants, consuming the O_3 produced and re-producing NO_2 . Therefore, these two reactions are a closed (null) cycle with no pure chemical output and form an equilibrium between the species involved in the reaction. The equilibrium and the concentration of each species also depend on other factors such as environmental variables and the concentration of VOCs.

Figure 1 shows the cumulative average of NO, NO_2 , and O_3 in the first half of 1396-98. As shown in the graph, the concentration of NO_x decreases during the day and with increasing sunlight. In addition, photochemical reactions increase the O_3 concentration.

The VOCs in August 1398 compared to August 1394 increased by 17.3%. The leading cause of significant changes in the average concentration of VOCs in the study period is toluene and xylene. However, the Mann-Whitney U test showed that the concentrations of all five BTEX pollutants measured in 1394 and 1398 were significantly different from each other (p> 0.05).

Considering the concentration of NO_x and VOCs in Tehran, it can be concluded that the equilibrium state of these species for ozone production is in the NOx-saturated state. Therefore, O₃ concentration is expected to increase with decreasing concentration of NO_x and increasing concentration of VOCs. Also, increasing the concentration of NO_x and reducing the concentration of VOCs reduce O₃ concentration. With the analysis performed during the study period, the concentration of NO_x did not show significant changes, while

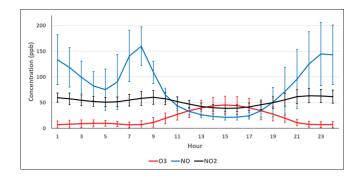


Fig. 1. cumulative average of NO, NO2, and O3

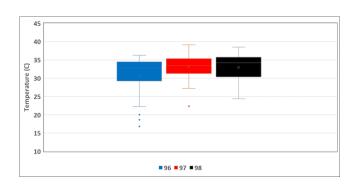


Fig. 2. Daytime temperature for 30 days with the highest average ozone concentration

the concentration of VOCs increased, which could be the reason for the increase in O₃ concentration in this period.

Figure 2 shows the daytime temperature for 30 days with the highest average ozone concentration. According to the figure, the average temperature from 1396 to 1398 had an upward trend. Furthermore, given the average increase from 1396 to 1398, it can be concluded that 15 days with the highest daily ozone concentration experienced higher temperatures in 1398 than in 1397 and 1397 compared to 1396. Therefore, the increase in temperature can be considered one of the factors that increased the ozone concentration from 96 to 98.

4- Conclusions

This study aimed to analyze the effect of NOx, VOCs, and temperature on O_3 in Tehran during the first half of 1396-98. Based on the studies performed, the results are as follows:

- NO and NO₂ have two peaks in the morning and evening, consistent with the traffic pattern.
- Contrary to the increasing trend observed for O_3 , no specific changes are observed for NO_x . Therefore, it can be concluded that the changes in O_3 during this period were not due to an increase or decrease in NO_x .
- The average VOCs in the study period increased by 17.3%. Therefore, assuming a gradual increase in the period 94 to 98, this can also be considered as one of the reasons for the increase in O_3 concentration.

- With no noticeable changes in the concentration of NO_x and an increase in the average temperature and VOCs concentrations during the study period, temperature and VOCs can be considered the leading cause of the O_x increase.

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