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Role of chemical reaction on concentrations of NO_2, NO, CO and O_3 in warm seasons - case study: Tehran city

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ABSTRACT

The chemical reaction between urban air pollutants is one of the important causes that influence the levels of pollutants in the urban air. The main goal of this research is studying the relation between NO, NO_2, CO and O_3 use of chemical reaction between them. Data that used in this research is the24-h average level of nitrogen oxides (NOx), monoxide carbon (CO) and ozone (O3) in 17 air quality monitoring station in Tehran city in 2012. Methods that used in research are descriptive analyses of 24-h temporal variation pattern of the air pollutant (NO_2, NO, CO and O_3), the correlation coefficient between air pollutants (NO_2, NO, CO and O_3) and regression analyses of ozone (O_3). 24-h Temporal Variation pattern of pollutants divided into four periods. Spring periods different with summer periods partially. Correlation coefficients between pollutants are strong particularly between NO_2 and CO. Regression analyses of O3 indicating linear model used in this study can describe 73.1 percent of spring and 87.2 percent of summer O_3 diurnal

variation. The result from this study on the influence of chemical reactions on the quantity of NO, NO_2, CO and O_3 level in warm seasons in Tehran show these reactions have a distinct role on the concentration of these pollutants.

Key words: Air pollution, chemical reactions, CO, NOx, O_3, Tehran city

1. INTRODUCTION

Pollutants are concentration in the atmosphere of large cities influence by several factors. The most important factor that affects concentrating urban pollutants is the reaction between the pollutants and other atmosphere agents such as radicals and meteorological elements. Nitrogen oxides (NOx = NO + NO_2), ozone (O_3) and carbon monoxide (CO) have bad effects on urban residents health and sustainability. Concentration and distribution of these pollutants in urban environments, besides emission sources and meteorological factors is a function of chemical reactions. Nitrogen oxides (NOx), including nitrogen dioxide (NO_2) and nitrogen monoxide (NO) release from various sources, the most important of which is vehicles. The NO_2 created mainly through a chemical reaction between nitrogen monoxide (NO) and ozone (O_3).

$NO+O_3= NO_2+O_2$ (1)

Other chemical reactions that lead to produce of NO_2 are:

1. NO interactions with organic radicals (RO_2), R is alkyl radical (Seinfeld, 1989 & Grundström, 2015)

$NO+RO_2 =NO_2+RO$ (2)

Alkyl radicals are shown by R, the R represents the alkyl group chemical formula. The chemical formula of alkanes is $CnH_2n + 2$, once the hydrogen atoms separated from alkanes, the remainder consists of a carbon atom with unpaired electrons, and thus convert to free radical molecules with high reactive power. Examples of radical’s alkyl are: methyl (CH_3), ethyl (CH_3-CH_2), n-propyl (CH_3-CH_2-CH_2), isopropyl (CH_3-CH-CH_3) and n-butyl (CH_3-CH_2-CH_2-CH_2)

2. Oxidation of hydrocarbons (HC): This reaction is very important due to affect the production of NO_2 and O_3 concentration. Methane (CH_4) is the most abundant hydrocarbons in the troposphere during the day, the presence of hydroxyl radicals (OH) led to the conversion of methane to methyl radicals (CH_3), then these radicals combines rapidly with O_2 and form the radical proxy methyl (CH_3O_2), M as an intermediary III (which can include molecules of NO or O_2) absorb extra energy and stop reaction process.

$CH_4+OH =CH_3 +H_2O$ (3)
$CH_3 +O_2+M=CH_3O_2 + M$ (4)

As noted, produced methyl radicals react with NO and produced NO_2. Finally remaining radicals (RO; CH_3O) reacts with oxygen and converts to hydroperoxy (HO_2) and formaldehyde (HCHO). HO_2 with high reaction power has important role in the conversion of remaining NO to NO_2. (Derwent and Hertel, 1998)

$NO+CH_3O_2 =NO_2+CH_3O$ (5)
$CH_3O +O_2=HO_2 + HCHO$ (6)
$NO+HO_2 =NO_2+OH$ (7)

Finally, NO_2 breakdown with ultraviolet light during the day and rebuilding the NO and ground-state oxygen atoms, O (3P). Oxygen atoms created in the photolysis process reacts with oxygen and produce O_3. The range of UV wavelengths in photolysis process identified between 200 and 400 nm (Derwent,Hertel 1998), or 280 to 430 nanometers (Seinfeld, 1989 & Mazzeo, Venegas, Choren, 2005).

$NO_2+HV=NO+O$ (3P) (8)

Reaction with OH and producing nitric acid (HNO3) is other chemical process of NO_2 removal. Produced HNO_3 reacts with ammonia to produce particulate nitrate (NO_3). This reaction results in the removal of NO2 from the environment.

$NO_2+OH+M=HNO_3+M$ (9)

Carbon monoxide (CO) is also one of the air pollutants in urban environments, produced due to the consumption of fossil fuels in sectors of urban economy. Carbon monoxide, unlike other molecules containing carbon not react with oxygen, but react with hydroxyl radical easily and produced hydrogen atom. This atom combine with oxygen and form hydroxyl radical (HO_2), (Sillman, 1999; Udhaya Sankar, 2017).

$CO+OH=CO_2+H$ (10)
$H+O_2=HO_2+M$ (11)
$CO+OH=CO_2+HO_2$ (12)

As discussed in the production of NO_2, HO_2 radical reactions play an important role in converting NO to NO_2 and then NO_2 photolysis under the influence of ultraviolet radiation (with a wavelength of less than 424 nm). This process is the primary source for the tropospheric ozone (Seinfeld and Pandis, 1998). Therefore essential condition for the creation of ozone is the simultaneous presence of CO and OH. Since CO is frequent in the urban environment, existence of OH is key for understanding of CO oxidation.

CO and NOx chain reaction through the OH:

Reaction between the atomic and molecular oxygen is the only reaction that produces ozone in the atmosphere. Because photolysis of O_2 need wavelength less than 290 nanometer of sun light and light with this wavelength cannotreachto ground, NO_2 photolysis is only reaction that produces atomic oxygen in the troposphere (Seinfeld and pandis, 1998; Seinfeld and pandis, 1998).

$NO_2+hv=NO+O\ (3P)$ (13)

As mentioned above, ozone reacted with NO to produced NO2. Without O2 in this reaction, final reaction will appear as follows:

$$NO2 \overset{hv}{\Leftrightarrow} NO + O3$$ (14)

When there's CO, OH radical reacts with the CO and produced hydroxyl radicals then radicals react with NO and produced NO_2. (Aneja, Das, 1994 & Seinfeld and pandis, 1998)

$$CO + OH. \overset{O2}{\rightarrow} CO2 + HO2.$$ (15)

$NO+HO_2 = NO2+OH$ (16)

In the presence of co equation of $NO2 \overset{hv}{\Leftrightarrow} NO + O3$ is formed by two cycles.

Chain reaction of CO and OH with NO is a reasonable explanation for decrease of CO concentration in during the day.

$$OH + CO \rightarrow H + CO_2$$ (17)
$$H + O_2 + M \rightarrow HO_2 + M$$ (18)
$$HO_2 + O_3 \rightarrow OH + 2O_2$$ (19)

Tropospheric Ozone (O_3) is one of the secondary gases produced by the chemical reactions that prerequisites are: Particulate matter, nitrogen oxides and carbon monoxide (Saini, Satsangi, Taneja, 2008). The formation of ozone in the troposphere depends on the basic state of oxygen atoms O (3P). Ozone in the troposphere is produced through a combination of O (3P) with O_2 (Hagenbjörk et al, 2017),

$$NO_2 + hv \longrightarrow NO + O(3P) \quad (20)$$
$$O(3P) + O_2 + M \longrightarrow O_3 + M \quad (21)$$

When ozone formation ends, the reproduction of NO_2 by the reaction of NO with O_3 ozone occurs is known as titration (Yarwood, Grant, Koo and Dunker, 2008)

In addition, other reactions affect ozone concentration is oxidation of VOCs and CO. In the process of oxidation of VOCs and CO, organic proxy radicals (RO_2) and hydroperoxy radicals (HO_2) is produced. O_3 formation is a nonlinear and complex process that influenced by many factors (concentration, mixing ratio and the reaction precursor, the meteorological factors such as sunlight- WIND - temperature- humidity) (Thornton et al, 2002). Uncertainty about the VOCs will also have to be another problem of estimating the O_3 in urban areas due to the simultaneous presence of anthropogenic and biogenic VOCs.

2. MATERIALS AND METHODS

The data used in this study include the level of oxides of nitrogen (NOx), carbon monoxide (CO) and ozone (O_3) registered in 17 monitoring stations in Tehran. Figure 1 shows the location of these stations.

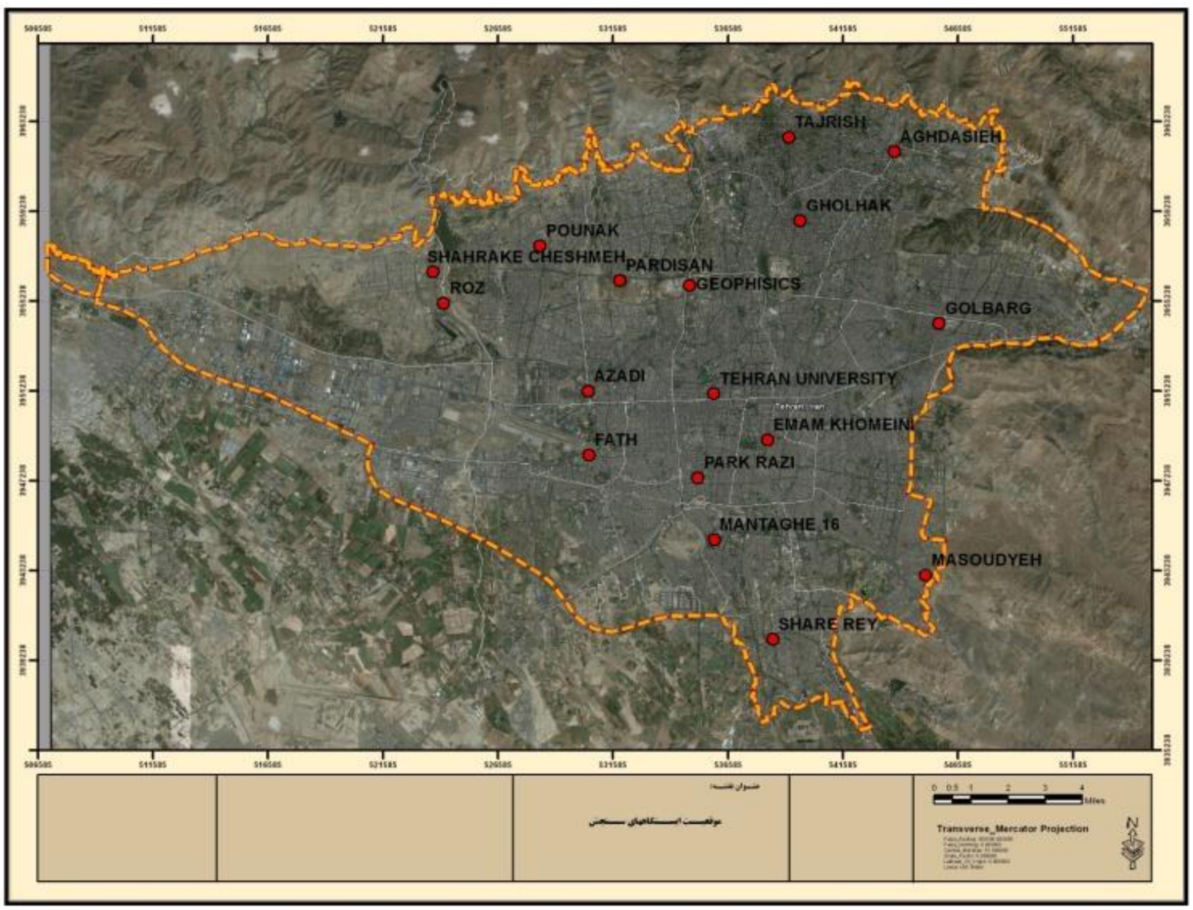

Figure 1 The location of Tehran pollution monitoring stations

To study the relationship between air pollutants concentration, first, the hourly average of pollutants (CO, Nox, O_3)in total stations has been calculated for spring and summer in 2013, then using correlation and regression tests, analyzes the relationship between these emissions .For the statistical analysis SPSS 21 software was used.

3. RESULTS

Temporal pattern (hourly and seasonal) of these air pollutants are very variable according to changes of Effective factors. In the following the patterns and trends of these changes are discussed. Daily average of air pollutants levels in spring 2013 for nitrogen dioxide (NO_2) is 34.76PPB, nitrogen monoxide (NO) is 36.59PPB, (b) carbon monoxide (CO) is 2.98PPM and ozone (O_3) of is 32.03PPB. Figure 2 shows the time pattern of air pollutants in the spring.

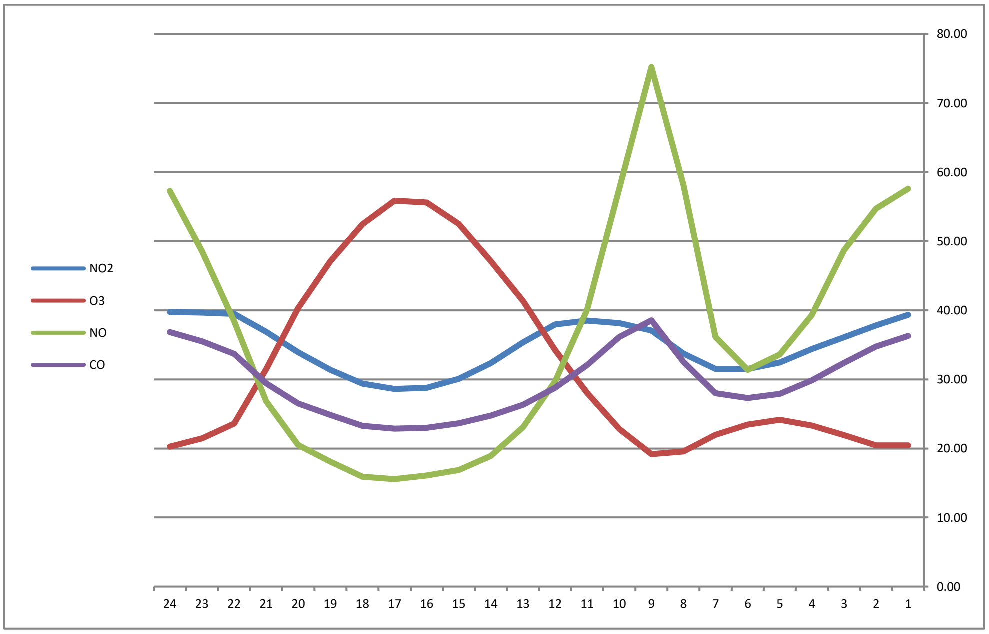

Figure 2 hourly patterns of air pollutants in spring 2013

According to the chart, the hourly patterns of NO, NO_2 and CO are similar, but the hourly patterns of O_3 are unlike other pollutants. The hourly change of these pollutants can be studied in four periods: The first period is 5 AM to 9 AM: In this period level of NO_2, NO and CO increase suddenly and level of O_3 reduce significantly. This phenomenon is related to emissions from urban traffic (home-work and home-school trips) and start of industrial activities. In this period because of increasing level of NO Emitted from vehicles and other activities, O_3 titration starts, thus level of NO_2 increase and level of O_3 decrease. In this period level of CO have increased due to the emissions from vehicles and other activities.

The second period is 9 AM to 4 PM: In this period level of NO, NO_2 and CO decrease significantly that reduction of NO more visible. The O_3, unlike other pollutants increase in this period. So that the concentration from 22.79PPB in 9 AM increased 55.86 PPB in 16 PM. Cause of changes in this period are increasing solar activity and the reactions between pollutants. In this period, NO_2 photolysis process has intensified due to increasing activity of the sun in the sky, which will result in an increase level of O_3.

$$CO+OH.=CO2+H.$$

$$H.+O2=HO2.+M$$

$$CO+OH.=CO2+HO2.$$

$$NO+HO2.=NO2+OH.$$

$$NO2+hv \rightarrow NO+O(3P)$$

$$O(3P)+O2+M \rightarrow O3+M$$

Of course, other chemical reactions have big role in the concentration of O_3, such as the conversion of NO to NO_2 by the hydroxyl radical (OH) and proxy radicals (HO2, RO_2) that is largely dependent on the activity of the sun in the sky. As mentioned in theoretical section, radicals have great effect on CO oxidation process and converting of NO to NO2. The most important chemical reactions between free radicals and pollutants are mentioned in the above figure.

During the reactions decreases level of CO, NO and NO_2 concentration and increases O_3 concentration. Another reason for O_3 increasing in this period is slowing down of titration due to the reaction of NO with proxy radicals.

Third period from 16 AM to 12PM; in this period NO level increase sharply and NO_2, CO level increase gradually and O_3 level decrease rapidly. Cause of increasing level of NO, NO_2 and CO during this period is urban terrific due to urban trips (work-home and recreational-home) as well as the reduction and elimination of some chemical reactions such as NO_2 photolysis process, CO oxidation and reaction of NO with radical proxies. In addition removal of NO_2 photolysis process that occurs after sunset, decrease O3 concentration. The fourth period from 12PM to 5AM; in this period the concentration levels of pollutants decrease and are stable due to the reduction of emissions from major sources (traffic street network and industrial activities) as well as reduction of chemical processes. Daily average of air pollutants levels in the summer 2013 for nitrogen dioxide (NO_2) is 39.59PPB, nitrogen monoxide (NO) is 42.29PPB, (b) carbon monoxide (CO) is 3.28 PPM and ozone (O_3) is 41.97PPB. In summer, Daily average concentration of pollutants decrease Compared with spring because of different meteorological conditions. In Tehran city, the season of spring is unstable in Meteorological aspects and atmospheric conditions that not allows the concentration of pollutants. Also in the summer due to the impact of solar radiation, O_3 concentration is higher than other seasons. Figure 3 show hourly pattern of pollutants in summer.

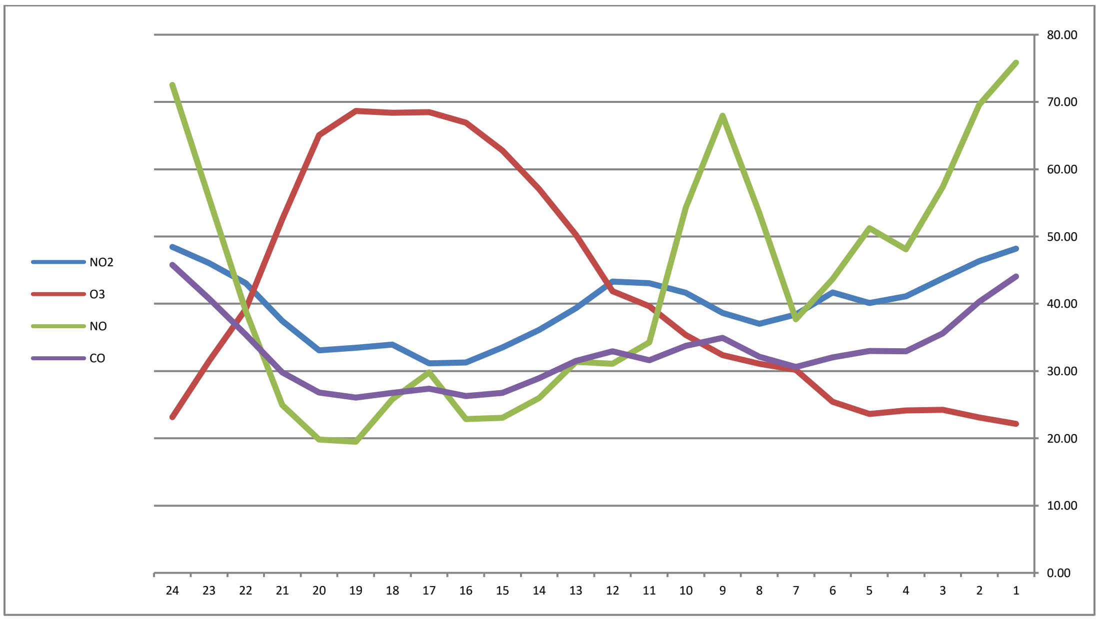

Figure 3 hourly patterns of air pollutants in summer 2013

Hourly changes of 4 pollutants (NO, NO_2 and CO) in this season are similar, but the pattern of O_3 hourly changes differs with them like spring. Temporal pattern of air pollutants changes is like spring but with slight difference. The difference are 1- levels of pollutants concentration that is high compared to the spring 2- difference in periods start and end times due to day length change in summer compared to the spring.

4. DISCUSSION

Pearson correlation coefficient used to study the relationship between pollutants. This coefficient is show in Table 1. According to Table 1, NO_2 in the spring and summer have the highest correlation with CO (R = 0.870 and R = 0.992). This means that increasing the CO level as well as increase NO_2 levels. In the theoretical section was said that reaction between the hydroxyl radical (OH) and carbon monoxide (CO) is known as oxidation produced proxy radical (HO_2), that react with NO and Produce NO_2.

The correlation coefficient between NO2 and NO are positive and between NO_2 and O_3 is negative over two seasons. These means that with increasing levels of NO, concentration of NO_2 increase and with increasing levels of O_3, concentration of NO_2 is reduce. Base on theoretical framework NO_2 produce due to increasing levels of NO and the reaction with O_3 (ozone titration) and proxy radicals (HO_2. RO_2.) Which indicates a positive relationship between NO and NO_2. NO_2 is converted to O_3 by photolysis process so the impact of NO_2 to O_3 concentration should be positive (Pandey et al, 2008). Cause of the negative relationship between NO_2 and O_3 is due to influence of organic hydrocarbons (VOC) and their role in the production of O_3. OH radicals' play a key role in the oxidation of VOC and CO, which leads to the formation of O_3. Furthermore OH reacts with NO_2 and form nitric acid (HNO_3) and lead to the removal of OH and NOx from the system. Thus increasing the reaction between OH and NO_2 limit recovery of HO_2 and OH and reduce the formation of O_3.

Table 1 Pearson correlation between the pollutants in the spring and summer

	CO		NO		O3		NO2		
	summer	spring	summer	spring	summer	spring	summer	spring	
NO2	.922**	.870**	.779**	.701**	-.844**	-.716**	1	1	NO2
O3	-.792**	-.862**	-.854**	-.861**	1	1	-.844**	-.716**	O3
NO	.895**	.952**	1	1	-.854**	-.861**	.779**	.701**	NO
CO	1	1	.895**	.952**	-.792**	-.862**	.922**	.870**	CO

The correlation coefficient is significant at 0.01 level.

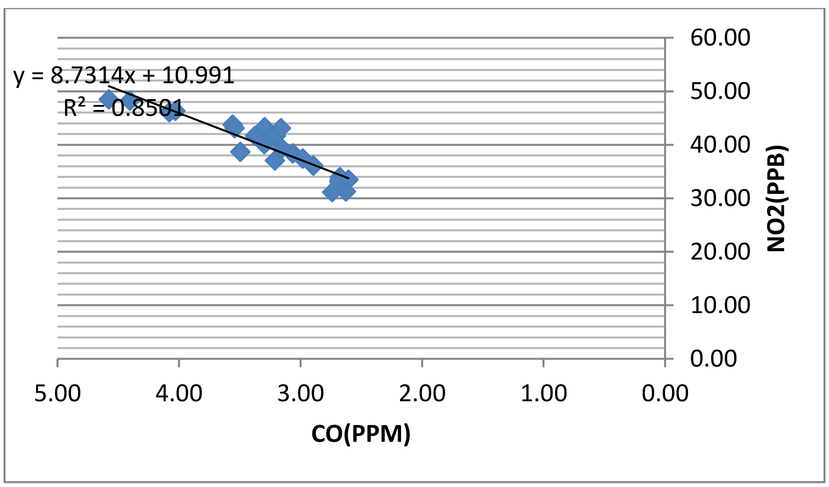

Figure 4 The correlation between CO and NO_2 in summer

$HNO_3+M \longrightarrow NO_2+OH+M$ (22)

In normal atmospheric conditions of the city, VOC + OH and NO + OH reaction constant rate are $3.1 * 10^3$ and $1.7 * 10^4$PPM-1MIN-1 respectively. Since the ratio (NO_2 + OH) to (VOC + OH) is 5.5 if the ratio of VOC to NO_2 reach to 5.5, rate of two reactions are equal. If the ratio of VOC is less than 5.5, NO2 + OH reaction dominant in the system and therefore slowed the process of O_3 forming. Vice versa when the ratio of VOC exceeds from 5.5, reaction between VOC, OH radicals create intermediate products such as NO_2, retrieved proxy radicals and OH radicals that speed up the process of O_3 formation.

There is an optimum ratio between NO and VOC, which led to plenty O_3 formation (Derwent and Hertel, 1998; Seinfeld and Pandis, 2006). Production of O_3 in Tehran city is sensitive to VOC's changes and therefore the relationship between hourly NO_2 and

O_3 is negative. The relationship between (O_3) and other pollutants are negative in the spring and summer, the highest rate with CO (R = -0.862) in the spring and with NO (R = - 0.854) in the summer.

The relationship between NO with O_3 is negative and with NO_2 and CO are positive. Highest correlation coefficient in the spring and summer is with CO (respectively R = 0.952 and R = 0.895. The only chemical reaction between CO and NO is:

CO+OH.=CO2+H.

H.+O2=HO2.+M

CO+OH.=CO2+HO2.

NO+HO2.=NO2+OH.

In this reaction CO has a negative impact on NO, but then produced NO_2 by photolysis process converted to NO and O_3 that cause of positive correlation between these pollutants. Furthermore the source of NO and CO emissions in urban environments are from motor vehicles that is another reason for positive relationship between these two pollutants.

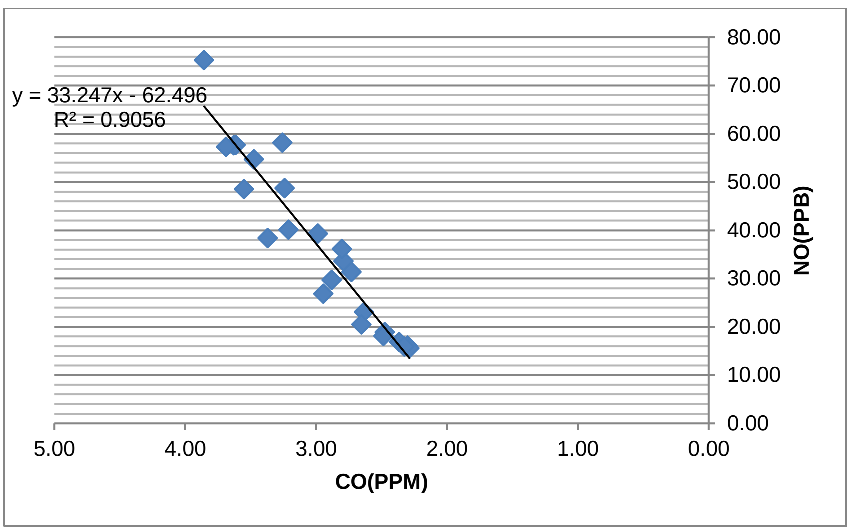

Figure 5 The correlation between CO and NO in spring

Because ozone is a secondary pollutant that produced during chemical reactions in this part make linear equations for O_3 using linear regression during spring and summer.

Table 2 Regression analysis for O3 in spring and summer

	significant factor F	The standard error of estimate	Adjusted coefficient of determination	Independent variables	The dependent variable	Input variable method
Spring	0.01	6.842	0.731	NO_2, NO, CO	O_3	Enter
Summer	0.01	6.236	0.872	NO_2, NO, CO	O_3	Enter

According to the table 2, 73.1% of the O_3 changes determined by NO_2, NO and CO in the spring and 87.2% of the O_3 variation is determined by these pollutants in summer. Based on the significant factor test F independent variables explain dependent variable changes on the 0.01 level.

Table 3 Regression analysis for O_3 in spring and summer

	Standardized regression coefficient (CO)	Standardized regression coefficient (NO)	Standardized regression coefficient (NO_2)	Intercept
spring	0.172	-0.820	-0.291	77.024
summer	1.050	-0.971	-1.056	112.915
Significance level T test (spring)	0.857	0.221	0.481	0.001
Significance level T test (summer)	0.001	0.000	0.000	0.000

Table 3 show intercept, standardized regression coefficients and significant levels of T test. According to data from the O_3 summer model, this model has the potential to predicts level of O_3. Notable cases in regression analysis results are positive impact of CO on the O_3 concentration. It seems due to the chain reaction of CO through hydroxyl radicals (OH) (Oxidation of CO) and proxy (HO_2) And the production of NO_2, followed by the production of O_3.

5. CONCLUSIONS

The main purpose of this study is the highlighting role of chemical reactions in the concentration and accumulation of ozone (O_3), nitrogen monoxide (NO), nitrogen dioxide (NO_2) and carbon monoxide (CO). Analysis conducted in three parts: descriptive, correlational and regression. The results are: The hourly pattern of changes in level of pollutants showed four different periods that Analysis of these periods is possible using traffic flow and meteorological variables (especially sunlight). Correlation coefficient among the pollutants indicates a strong relationship between them. Some of these pollutants such as NO_2 and CO relationship is stronger because of the chain chemical reactions between them. O_3 relationship with other pollutants, especially NO_2 is negative due to the impact of VOC and O_3 production reactions in spring and summer in Tehran. O_3 regression analysis indicates a high potential O_3 regression model to explain variations compared other pollutants.

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