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Research Article

Contribution of VOCs to Ozone Formation in Bursa Atmosphere

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Abstract

Weekly passive sampling campaigns were carried out over two sample periods to measure SO_2, NO_2,O_3 in Bursa, one of the most heavily industrialized cities in Turkey. The measurements were conducted at 40 points in October 2005 and 49 points in April 2006. Ozone formation potential related to VOCs measured in same sampling points is calculated by Maximum Incremental Reeactivity (MIR) technique. M&p xylene is the most dominant contributor to ozone formation among all sectors. Toluene is the second largest contributor. On average, these two compounds account for 70% and 75% of the total for October 2005 and April 2006 sampling campaigns, respectively. According to factor analysis results conducted in the previous study, these two compounds came mainly from the use of solvents and gasoline evaporation

Keywords: Spatial distribution, **T**he Maximum Incremental Reactivity (MIR), Volatile organic compounds (VOCs), Ozone, Nitrogen dioxide

1. Introduction

Volatile organic compounds (VOCs) emitted into atmosphere have received muct attention in recent years due to their direct and indirect effects. The direct effect is their possibilities of causing adverse health effects. Many VOCs are toxic, and some are known or are suspected to be carcinogenic (Ling et al. 2011, WHO 1989). Indirect effect of VOCs is associated with their reactions in the troposphere. VOCs play a significant role in the formation and fate of airborne toxic chemicals and, in the presence of NO_x, they react with OH^- radicals to form ozone (Krol et al. 2010, Carter 1994). Different VOCs species (aromatic, olefin, parafin, etc.) have different contribution the formation of tropospheric ozone (Cai et al. 2010).

Ozone is a major concern due to its adverse impact on human health and vegetation. Elevated ozone has been observed many cities since 1970s (Guicherit and Dop 1977 and MARI 1994). Since ozone formation is enhances with the temperature, plenty of sunlight and presence of organic compounds and NO_x, Turkey, like other countries in the Mediterranean region, experiences high ozone levels, particularly on the Mediterranean coast. Therefore the relationship between ozone and its two main precursors, nitrogen oxide (NO_X) and VOCs, represents one of the most important issues to be handled about the urban air quality in Turkey.

It is well known that the formation of ozone is controlled with some conditions. Ozone can be produced either through VOCs-limited chemistry or by NO_x-limited chemistry, but it is difficult to determine which one of these chemical processes operates at a particular location. Furthermore, sensitivity of ozone formation on NO_x or VOCs can change from one location in the city to another (Sillman 1999). The NO limited regions are generally areas that downwind from urban and suburban areas; whereas VOCs-limitation is generally observed at highly polluted urban areas. (USEPA 1998). Previous studies have indicated that the increasing trend of ground-level ozone (O_3) in urban areas was related to high anthropogenic VOC emissions (Chang et al. 2005, Shiu et al. 2007, Zhang et al. 2008, Wang et al. 2009, Cheng et al. 2010). Since ozone formation depends on atmospheric conditions

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*Corresponding author: mihriban.civan@kocaeli.edu.tr and levels of VOCs and NO_x, it can be controlled by formation of either VOCs or NO_x. Consequently, to develop an effective strategy for controlling photochemical air pollution in urban location the relationships between O_3 production and VOCs could be formulated (Ling et al. 2010).

The evaluation of ozone-VOCs-NO_x sensitivity is based on predictions from Eulerian model, which includes emission rates, atmospheric dynamics and photochemistry. However, the model predictions of ozone-NO_x-VOCs sensitivity should be accepted as scientifically valid only when there is extensive measurement-based evidence to show that the specific model prediction is true (Silman 1999).

In the currents study, the VOCs and inorganic pollutants (SO_2, NO_2 and O_3) concentrations were measured at varying sampling locations with different features – urban, urban heavily affected by industry, traffic or densely populated areas – to evaluate ozone formation due to wide range of VOCs including aromatics, olefins, paraffin and halogenated compounds. The Maximum Incremental Reactivity (MIR) method proposed by Carter (1994) were used to calculate VOCs reactivity.

2. Material and Methods

2.1 Study Site

Bursa with a population of over 1,617,487 in the city center is one of the most densely populated areas in Turkey (SSI 2008). Bursa occupies the 6th place in terms of bank investment per person in Turkey, and in terms of the number of vehicles in traffic, it is the 4th in Turkey. The city has quite an important place in automotive sector, which is the most developed industrial sector in the country and also in machinery, textile, and food industries. Bursa comes in the 3th order after Kocaeli and Istanbul considering the proportion of general budget expenses to income. In addition to these features, another significant point is the geographic location of the city. It is served by both minor and major roads since the city stands at the crossroads of Ankara-Istanbul and Izmir routes. It has a high traffic level as a result of its geographic importance. Today, these transit roads pass through residential areas and cause severe air pollution within the city.

The climate in Bursa displays a transition between Mediterranean and Black Sea. Winters are not much harsh and similarly severe droughts do not happen in summer. The highest precipitation is in winter and spring months. The amount of mean annual precipitation is 70.6 cm. The average relative humidity is around 69%. The average annual temperature of the central district is 14.4 ^{0}C.

The city center of Bursa consists of three districts, namely, Osmangazi, Yıldırım, and Nilüfer. Air samples were collected at 50 sites of these districts in Bursa. The study includes locations with high settlement densities, areas strongly impacted by traffic and industries and areas which are e not under direct influence of any pollution sources.

2.2 Sampling Campaigns

VOC and inorganic pollutants were collected in two weekly sampling campaigns carried at October 2005 and April 2005 at 40 and 49 points selected within a sampling grid composed of 450 km^2, which covers the whole territory. Number of samples collected in each station group is given in Table1.

Table 1. Number of samples collected at different sectors for all campaigns.

Sectors	October 2005	April 2006
Residential	20	25
Background	4	4
Roads	8	11
Industry	8	10
Field blank	2	2
Lab blank	2	2
Total	**44**	**54**

Meteorological information was obtained from the General Directorate of Meteorology, which is presented in Table 2. Since meteorological data were hourly, whereas sampling was for one week, we averaged hourly values of meteorological parameters for the whole week corresponding to passive sampling period.

Table 2. Meteorological parameters for October and April sampling campaigns.

Sampling Campaign	Relative Humidity (%)	Wind Speed (m/sec)	Temp. (C^0)	Total Precp. (mm)	Mixing Height (m)
October 2005	71.04	1.7	14.8 (-3.8-31.8)	9.5	966
April 2006	66.56	2.1	13.7(-3.4-30)	No prec.	797

2.3 Sampling Methodology

Stainles steel passive tubes were used to anayze VOCs. Measurements of VOCs were performed using GC-FID (Agilent 6990) dual column coupled with Markes Unity Thermal Desorption System. GC oven was programmed for 40 °C hold for 5 min and ramped to 195 °C at a rate of 5 °C/min with 10 min hold at 195 °C. Nitrogen was used as carrier gas with flow rate of 2.8 mL/min and 5.2 ml/min. The external calibration standard mixture supplied by Environment Technology Center, Environment Canada (Ottawa, Canada) was used for the calibration during first and second sampling campaigns. Extensive validation was conducted for sampling and analytical methodology for quality assurance and quality control (QA/QC) procedure. Further details of the validation procedure are described in Civan et al. (2011).

NO_2 and O_3 passive sampling tubes consist of screen covered with different chemicals and a polyethylene body to protect the gauze. Though various designs can be found in different companies for these sampling tubes, since Gradko is a well-known and accepted firm in the world, the tubes were obtained from this company (England). The exposed tubes were sent back to the same company for analysis at the end of sampling. The findings of the analyses were taken from gradko via e-mail. Inorganic samplers were kept in plastic tubes.

The Gradko passive tubes consist of a 7.1 cm length acrylic tube with 1.1 cm internal diameter which have stainless steel screen impregnated with TEA (triethanolemine). Nitrogen dioxide and sulfur dioxide are chemiadsorbed onto TEA respectively as nitrite and sulphite or suphate ions. Nitrite is quantified by visible spectrophotometry while sulphite and sulphate are analysed by ion chromatography. For ozone measurement, the stainless steel screen coated with sodium nitrite. Nitrate ions formed as a result of oxidation of nitrite with ozone were analyzed with ion chromatography.

3. Result and Discussion

3.1 VOC and Inorganic Pollutants Correlations

Benzene, Toluene, Ethylbenzene, m&p and o- Xylene (BTEX) levels measured in Bursa were detailed evaluated in Civan et al. (2011). Coefficient and p values denote probability of chance correlation. The results of correlation analysis between BTEX and inorganic pollutants are presented in Table 3. Strong correlations were found among BTEX. The very good correlation (R>0.9) between ethylbenzene, o-xylene and m&p xylene were observed when compared with benzene and toluene. It could be interpreted that all of these compounds originated from the same source, vehicle emissions (Hoque et al. 2008, Baldasano et al. 1998, Wang et al. 1996).

SO_2 only strongly correlated with benzene among BTEX groups. This correlation between SO_2 and benzene shows that the vehicle emission as the main source of these compounds in the studied area.

Table 3. Correlation between BTEX and inorganic compounds.

		SO_2	NO_2	O_3	Benzene	Toluene	Ethyl benzene	m&p Xylene	o-Xylene
SO_2	R	1	-.296*	.662**	.538**	.226	.331*	.317*	.363*
	p		.039	.000	.000	.119	.020	.026	.010
NO_2	R	-.296*	1	-.456**	-.199	-.246	-.113	-.093	-.111
	p	.039		.001	.171	.088	.440	.525	.448
O_3	R	.662**	-.456**	1	.392**	.293*	.350*	.354*	.375**
	p	.000	.001		.005	.041	.014	.013	.008
Benzene	R	.538**	-.199	.392**	1	.558**	.446**	.509**	.593**
	p	.000	.171	.005		.000	.001	.000	.000
Toluene	R	.226	-.246	.293*	.558**	1	.661**	.637**	.641**
	p	.119	.088	.041	.000		.000	.000	.000
Ethyl benzene	R	.331*	-.113	.350*	.446**	.661**	1	.959**	.911**
	p	.020	.440	.014	.001	.000		.000	.000
m&p Xylene	R	.317*	-.093	.354*	.509**	.637**	.959**	1	.948**
	p	.026	.525	.013	.000	.000	.000		.000
o-Xylene	R	.363*	-.111	.375**	.593**	.641**	.911**	.948**	1
	p	.010	.448	.008	.000	.000	.000	.000	

* Correlation is significant at the 0.05 level and **. Correlation is significant at the 0.1 level

Ozone correlated with SO_2 and BTEX while negatively correlated with NO_2. Ozone is secondary pollutant that is affected VOCs and NO_x and meteorological conditions (Hung-Lung et al. 2007). The positive correlation between BTEX and ozone were observed in the data set. Since NO_2 concentration is commonly associated with secondary formation from reactions between primary emissions of NO and O_3 (Mukerjee et al. 2004, Seinfeld and Pantis 1998), the concentration of ozone increase with decreasing that of NO_2.

3.2 Ozone Formation Potential

To evaluate the ozone-forming potential of VOCs concentrations measured in this study, the maximum incremental reactivity (MIR. g O_3/g VOCs) obtained from Carter (1994) was used. The unit of MIR is grams ozone formed per measured gram VOCs. Ozone forming potential was estimated by summing up the products of individual VOC amounts and their corresponding MIR factors. The MIR factor reported is represented in Table 4.

Table 4. Tabulation of incremental reactivities in the MIR scale.

VOC	MIR*	VOC	MIR*
Benzene	0.42	2-Methylhexane	1.08
Toluene	2.7	3-M-Hexane	1.40
Ethylbenzene	2.7	2,2,4-Trimethylpentane	0.93
m& p Xylene	14.8	2-Methylheptane	0.96
o-Xylene	6.5	Styrene	2.2
1,3-Butadiene	10.9	Isopropylbenzene	2.2
1,3,5-Trimethylbenzene	10.1	n-Propylbenzene	2.1
Isopropylbenzene	2.2	n-Pentane	1.04
n-Hexane	0.98	1,2,4-Trimethylbenzene	8.9
Octane	0.60	Napthalene	1.17
Nonane	0.54	Methylcyclohexane	1.8
n-Decane	0.46	2,2-Dimethylbutane	0.82
3-Methyl pentane	1.5	2,3-Dimethylbutane	1.07
2,2,3-Trimetylbutane +2,3-Dimethylpentane	2.63	2-Methyl pentane	1.5
Cyclohexane +Cyclohexene	6.98	Methylcyclopentane +2,4-Dimethylpentane	4.3

*Incremental reactivities in units of grams ozone formed per gram VOC emitted for the ozone yield reactivity scale for the MIR scale (grO_3/grVOC).

Data sets generated in October 2005 and April 2005 were used in order to investigate the contribution of VOCs on ozone formation. Table 5 depicts the total ozone formation production as ng calculated at each sector. Figure 1 also shows produced ozone mass (ng) from individual VOC at different sectors. In the figure, the mass of ozone formation for each individual compound was summed and the contribution of each compound to that total was calculated by dividing the total mass of ozone formation. It is concluded from the figure that m&p xylene is the most dominant contributor to ozone formation among all sectors. Toluene is the second largest contributor. On average, these two compounds account for 70% and 75% of the total for October 2005 and April 2006 sampling campaigns respectively. According to factor analysis profile (Civan et al. 2011), these two compounds came mainly from the use of solvents and gasoline evaporation. The contribution of benzene to ozone formation potential was the lowest even though it is the most hazardous species in VOCs. It is also clearly seen in the figure and the table that hydrocarbons known to be emitted by vehicular and industrial emissions are a larger contributor to ozone formation for both sampling campaigns. According to the factor analysis profile, the urban atmosphere was mainly affected by both vehicular exhaust and industrial emissions. High ozone production was expected due to high level of m&p xylene and toluene concentrations in these sites. At the

Table 5. Total ozone formation potential (ng) at each sector.

	Total ozone formation potential (ng)			
	Background	**Industry**	**Road**	**Residential**
October 2005	157.26	542.64	566.87	480.78
April 2006	244.51	748.17	691.36	549.78

background site, the ozone formation of VOCs was at a low level. The background ozone concentrations had a fairly high value when compared to other sites of the city since it takes several hours to produce ozone via photochemical reactions in an urban atmosphere. Hence, the production of ozone in the urban atmosphere is detected in rural areas.

4. Conclusions

Ozone formation potential related to VOCs measured in same sampling points is calculated by maximum incremental reactivity technique (MIR. G O_3/g VOCs) obtained from Carter (1994). According the results large spatial variations of ozone formation potentials were detected between the sampling points. The data calculated showed that ozone formation potential at road level were up to 4 times higher than those found in background site. M&p xylene is the most dominant contributor to ozone formation among all sectors. Toluene is the second largest contributor. On average, these two compounds account for 70% and 75% of the total for October 2005 and April 2006 sampling campaigns respectively. According to factor analysis profile (Civan et al. 2011) these two compounds came mainly from the use of solvents and gasoline

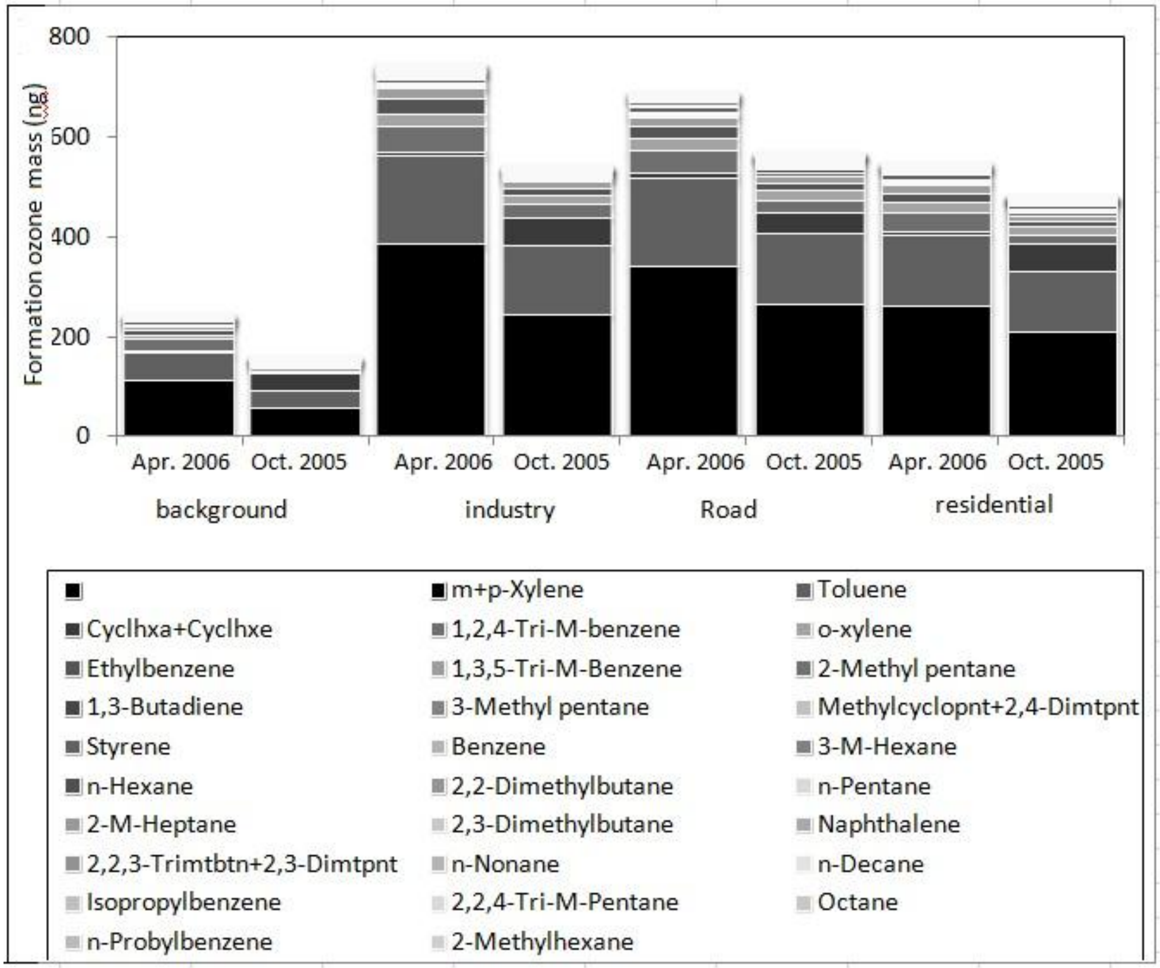

Figure 1. The ozone production potential (ng) of selected VOC conducted at a) October 2005 and b) April 2006.

evaporation. These results suggest that these sources play important roles in controlling ozone chemical formation in Bursa. The results gained from this study may provide useful information to local government agencies in the development of ozone pollution control strategies.

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