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A STUDY OF PHOTOCHEMICAL POLLUTION IN İSTANBUL

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Hourly ozone and nitrogen oxide concentration levels measured between 2001-2004 in Kadıköy and Saraçhane – two urban districts in Anatolian and European sides of İstanbul, respectively – are analyzed. Concentration levels exceeding 100, 150, and 240 μgm^{-3} are selected in order to determine photochemical pollution episodes within the period. The highest ozone concentration was observed in Saraçhane on 10th of August 2001 as 310 μgm^{-3}. On 21st of June 2003, ozone concentration of 163 μgm^{-3} and on 21st of June 2003 in Saraçhane, ozone concentrations up to 225 μgm^{-3} were observed in Kadıköy. In 27th of August 2002 episode, ozone concentrations around 116 μgm^{-3} were detected in Kadıköy. It is found that high concentrations of photochemical smog are associated with relatively high pressure systems having very low wind speeds or calm conditions and sunny days with maximum temperatures above 25°C.

Key Words: Ozone, photochemical pollution, İstanbul, Pearson's correlation

1. INTRODUCTION

İstanbul is a city with a population of over 10 million people and located at 41°N and 29°E coordinates (Figure 1). Bosporus, a sea water strait extending from Black Sea to Marmara Sea, divides the city into European and Anatolian sides. The city has experienced a rapid growth in urbanization and industrialization. Statistics show that the population of the city is over 10 million and there are more than 2 million motor vehicles (Anonymous, 2000) contributing to the environmental problems of the area. Black Sea in the north and Marmara Sea in the south produce a differential heating of surfaces, leading to different meteorological conditions that may play a role in the transport of ozone. The complex terrain of İstanbul also influences the circulation systems over the city. The city experiences a transition climate between Mediterranean and temperate climate types. Strong inversion conditions in the summer period sometimes cause ozone concentrations to reach maximum levels in the late afternoon hours (Topçu *et al.*, 2002).

Ozone levels in Southern Europe and Mediterranean region have been studied by Klemm *et* al., 1998, Gusten *et al.,* 1997, Peleg *et* al., 1997. Kalabokas and Bartzis, 1998 studied the Aegean region. Photochemical pollution in İstanbul has also been studied by Anteplioğlu, 2000, Kocak *et* al., 2000, Topçu and İncecik, 2002, and Topçu *et* al., 2003. In our study, the collected meteorological and air – quality observations by National Weather Service and the İstanbul Greater Municipality, respectively, are analyzed. The diurnal variations of O_3, NO_x and VOCs are

investigated for selected episodes in two stations on both sides of İstanbul. The NO_x and VOC sensitivities to ozone formation during these days are analyzed by examining the correlations between ozone and its precursors.

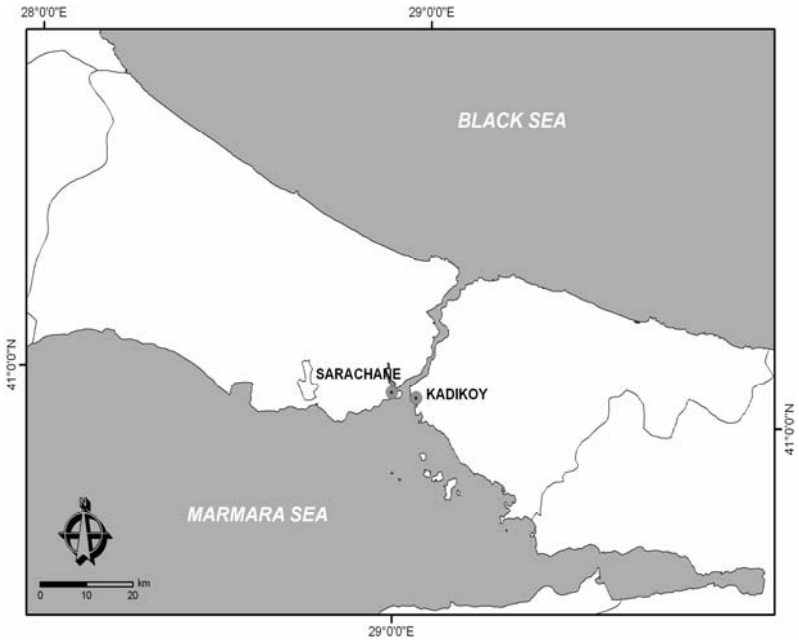


Figure 1. Map of the study region and locations of the air – quality stations

2. MATERIALS AND METHODS

2.1. Data and Statistical Analysis

Air quality data used in the study are obtained from İstanbul Greater Municipality between years 2001 to 2004. The selected stations for air quality data are the Kadıköy station on the Anatolian side and the Saraçhane station on the European side. Pollutants measured at the Kadıköy and Saraçhane stations are CO, NO, NO_2, NO_x, and O_3. Starting from 2002 in Saraçhane and 2003 in Kadıköy, Total Hydrocarbons (THC), Methane (CH_4) and non – Methane Hydrocarbons (nMHC) were added to the analyzed parameters. NO_x species are monitored using the Chemiluminescence method, CO by IR Adsorption method, O_3 by UV Photometry method and HC by Gas Chromatography (FID).

Statistical techniques are used for the quality control of the dataset. Days containing more than 12 hours of missing data and months containing more than 15 days of missing data are discarded from the dataset. Hourly ozone concentration levels exceeding 100,150 and 240 μgm^{-3} are selected in order to determine photochemical pollution episodes within the period. Based on the results of the statistical analyses, 4 episodes are selected for the study. These were 10th of August 2001 , 27th of August 2002 and 21st of June 2003 for the Kadıköy station and 21st of June 2003 for the Saraçhane station. Meteorological conditions during the episodes are presented in Table 1.

Table 1. Meteorological conditions during the episodes

Date	Mean wind speed (ms-1)	Wind direction	Mean Pressure (mb)	Max. Temp. (ºC)
10.08.2001	6.4	NE	1015	33
27.08.2002	4.5	NE	1018	26
21.06.2003	2.8	NE	1010	25

3. RESULTS

The highest ozone concentration recorded within the selected episodes are presented in Table 2. As seen in Figure 2, on 10th of August 2001, almost all concentrations are above 150 μgm^{-3}. The high concentrations are related to the high-pressure system over the region and the low wind speeds. We can see that peak concentrations are observed in the early morning hours pointing to a high accumulation rate of ozone over the region. The wind speed is at its minimum indicating a very restricted transport. The correlation factors of NO_2 and CO with O_3 are calculated as – 0.39 and – 0.23, respectively, meaning that NO_2 was more dominant over ozone formation than CO. These conditions can be explained as the result of high NO_x emissions or a possible advection of NO_x from other regions. As can be seen from Figure 3, NO_2 and CO are highly correlated with O_3 on 27th of August 2002 The destruction of ozone through reacting with NO, forming NO_2 can be clearly seen from Figure 3. The correlation factors are calculated as – 0.94 and – 0.85 for NO_2 and CO, respectively. The correlation coefficients show that both CO and NOx, with a higher NOx – sensitivity, enhance the formation of ozone. Because of the high-pressure system and low wind speeds ozone was trapped over the region and the peak concentration was reached at nighttime. After the sunrise, with the increase in photolysis rate of NO_2 to NO, the ozone levels started to decrease. THC, CH_4 and nMHC datasets were also available for the period. Since nMHCs are the dominant organics in photochemical processes (Skov *et al.*, 1997), the relation between ozone and nMHCs is illustrated in Figure 3. There are positive correlations between all three hydrocarbon species and ozone. The correlation factors for THC, CH_4 and nMHC are calculated as 0.25, 0.19 and 0.25, respectively, agreeing that nMHCs are more important in ozone formation. These positive correlations show that with the increase in VOCs, ozone formation was slightly enhanced, especially by non – methane hydrocarbons.

Table 2. Maximum concentration levels on the selected episodes

Episode date	Station	Maximum Concentration (μgm^{-3})
10.08.2001	Saraçhane	310
27.08.2002	Kadıköy	116
21.06.2003	Kadıköy	163
21.06.2003	Saraçhane	225

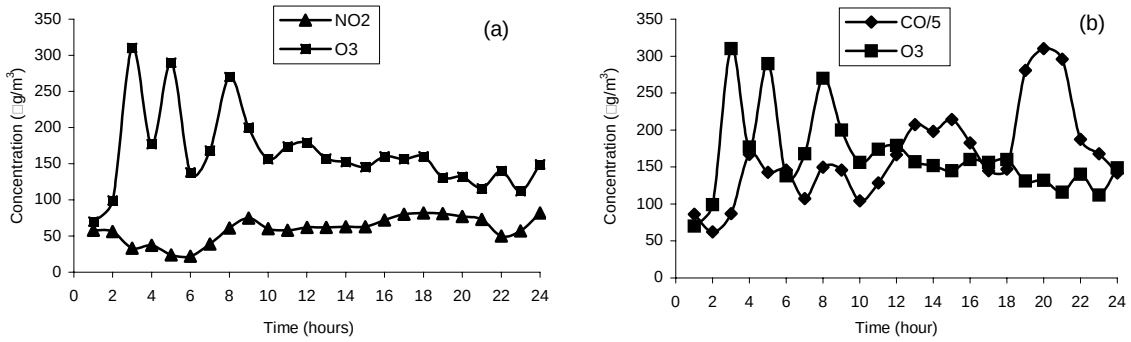


Figure 2. Diurnal variations of (a) O_3 and NO_2, (b) O_3 and CO (original values divided by 5) on 10th of August 2001

Diurnal variations of ozone, NO_2, CO and nMHCs in Kadıköy on 21st of June 2003 are presented in Figure 4. In Figure 5, relations between ozone and NO_2, CO and wind speed in Saraçhane on the same day are presented. As can be seen from the figures, there is a better correlation between the concentrations in Saraçhane. The correlation factors for NO_2 and ozone in Kadıköy and Saraçhane are calculated to be –0.54 and –0.63, respectively, showing that formation of ozone in Saraçhane was more enhanced by NO_x meaning that ozone formation in Saraçhane was more enhanced by CO. On the other hand, ozone formation in Kadıköy was NO_x – sensitive. The relation between VOCs and ozone are also analyzed for the Kadıköy region. The correlation factors are calculated as –0.44, -0.39 and –0.51 for THC, CH_4 and nMHC, respectively. Non – methane hydrocarbons were the dominant ozone formation initiators among the total VOCs. These correlation coefficients also confirm that ozone formation in Kadıköy was more NO_x – sensitive. The Pearson's correlation coefficient of wind speed with ozone in Kadıköy and Saraçhane stations are calculated to be 0.52 and 0.55, respectively.

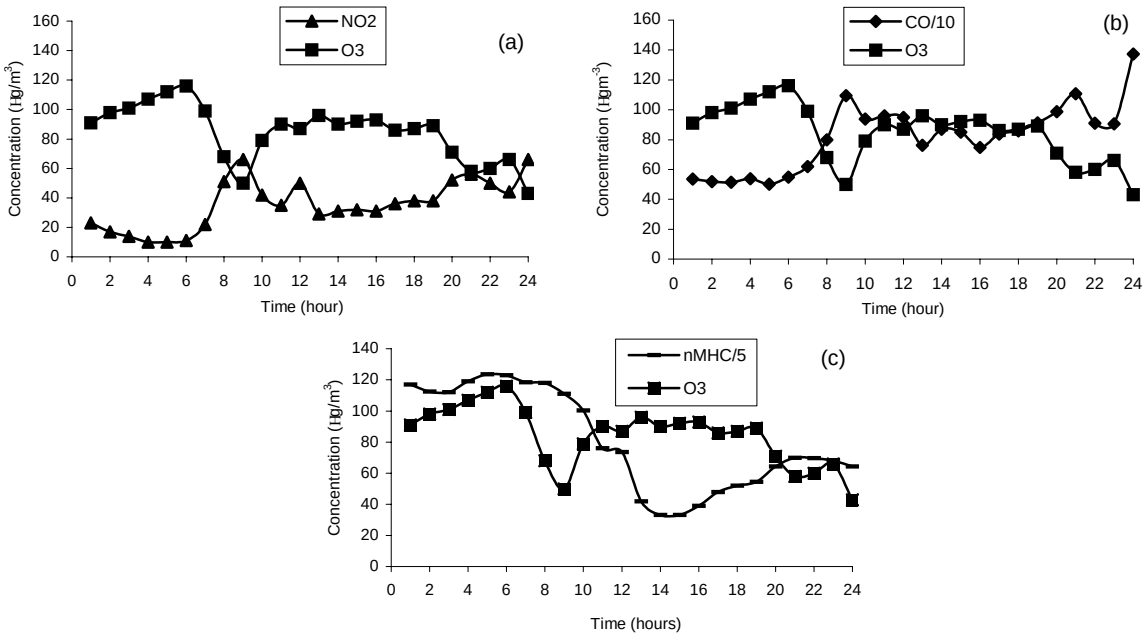


Figure 3. Diurnal variations of (a) O_3 and NO_2, (b) O_3 and CO (original values divided by 10) and (c) O_3 and nMHCs (original values divided by 5) on 27th of August 2002

Pearson's correlation factors for the selected episodes are presented in Table 3. Topçu and İncecik, 2002, reports that correlation coefficients calculated for the ozone months varied from 0.49 to 0.67 in years 1998 and 1999, which implies higher correlation than our calculations for 2001 to 2003. On the other hand, except for August 2001, Saraçhane episode, the selected episodes in this study presents very high correlations. The ozone production mechanism under intense solar radiation is also a key parameter and it is expected that high temperatures will enhance ozone production.

Table 3. Pearson's correlation coefficients between ozone, its precursors and wind speed for the selected days

	Pearson's correlation coefficients of Ozone			
	10.08.01 Sarachane	27.08.02 Kadikoy	21.06.03 Kadikoy	21.06.03 Sarachane
CO	-0.23	-0.85	-0.27	-0.75
NO	-0.16	-0.46	-0.47	-0.77
NO_2	-0.39	-0.94	-0.54	-0.63
NO_x	-0.31	-0.91	-0.56	-0.81
THC	-	0.25	-0.44	-
CH_4	-	0.19	-0.39	-
nMHC	-	0.25	-0.51	-
Wind	-0.39	-0.003	0.55	0.55
Temp.	0.14	0.74	0.74	0.08

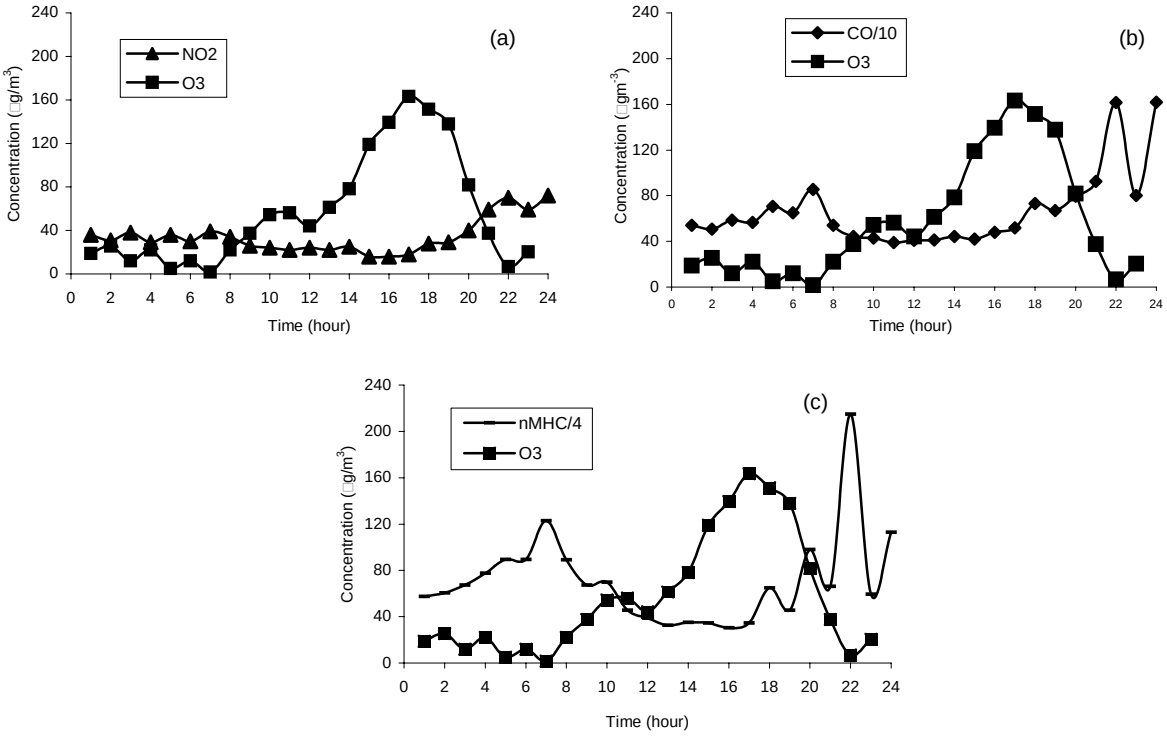


Figure 4. Diurnal variations of Ozone with (a) NO_2, (b) CO and (c) nMHCs in Kadıköy on 21st of June 2003

Figure 6 presents the correlation analysis between NO_x and NO levels from 2001 to 2003 in Kadıköy and Saraçhane, respectively. The results indicate very strong correlations to exist between the two precursors of ozone in both sites. NO plays the key role in formation of NO_x, and the high correlation coefficients between measured NO and NO_x values illustrated in Figure 6 confirms this relation.

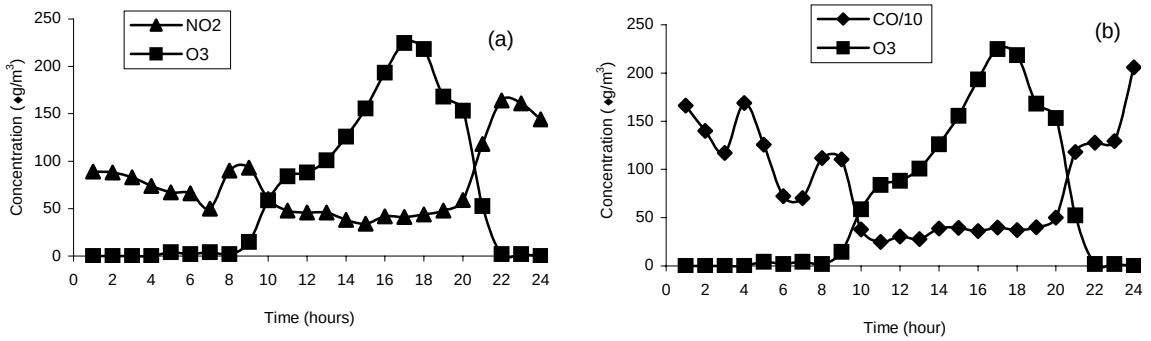


Figure 5. Diurnal variations of Ozone with (a) NO_2 and (b) CO in Saraçhane on 21st of June 2003

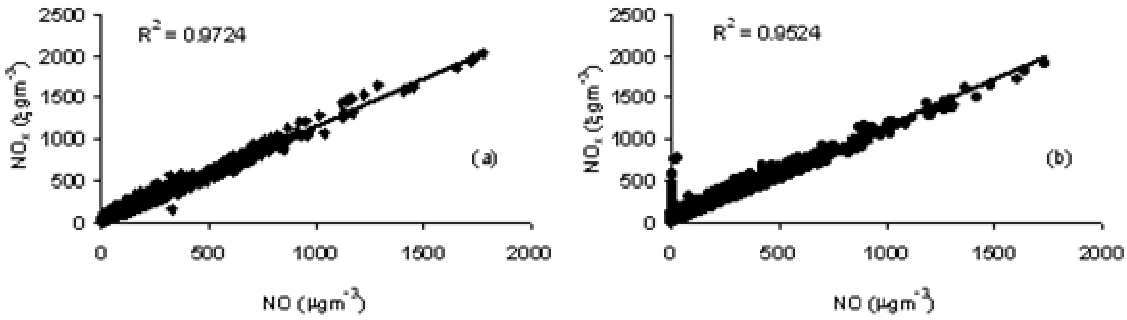


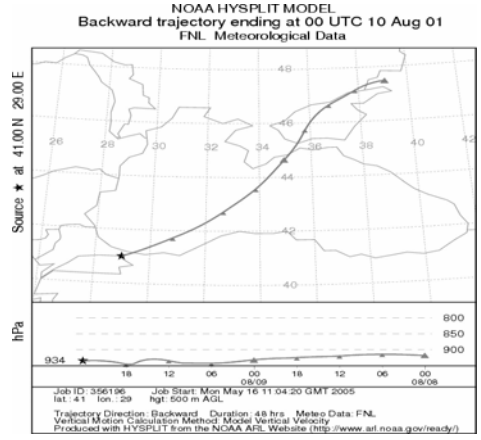
Figure 6. Relations between NO_x and NO levels in (a) Kadıköy and (b) Saraçhane

In order to estimate the transport to İstanbul on the episodic days, Hysplit model was run using the back – trajectory module. The results clearly show the north–easterly transport from the blacksea region to İstanbul city. Model results are presented in Figure 7.

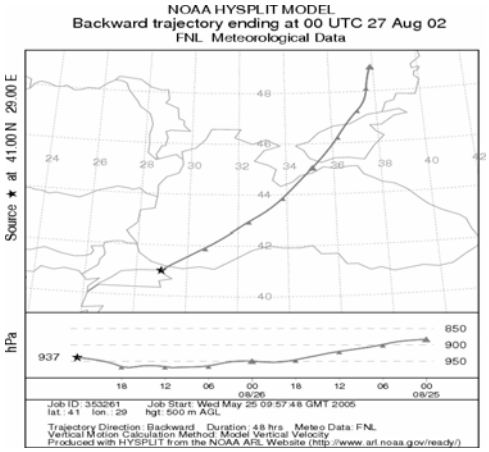
4. CONCLUSIONS

İstanbul is experiencing a rapid and uncontrolled growth in urbanization, industrialization and transportation. Air quality data from the continuous measurements of ozone and its main precursors at two stations on both sides of İstanbul are analyzed in order to understand the relation between the various chemicals that are involved in photochemical processes in the atmosphere. The results show that high levels of ozone are observed mostly under anticyclonic conditions with relatively low wind speeds. It can also be concluded that Kadıköy experienced the higher ozone concentrations for the study periods. The correlations showed us that the ozone formation in İstanbul during these episodic periods was NO_x – sensitive. CO – involved mechanisms were also enhancing the ozone formation and NO_x species were dominant in Kadıköy whereas ozone formation was CO – sensitive in Saraçhane. Correlations between ozone and hydrocarbon species show that ozone formation by hydrocarbons was not as effective as NO_x species, with non – methane hydrocarbons dominating over other hydrocarbon species. The ozone trends on selected days imply that ozone was not local originated, but rather advective at early morning hours, except for 2003 episode. 2003 episode was probably local originated and illustrated a typical diurnal variation.

Ozone concentrations generally increased with increasing temperature, especially in Kadıköy 2002 and 2003 episodes, high correlations were determined between ozone levels and temperature. High ozone levels were also enhanced by light – wind conditions, as expected. Positive correlation between wind speeds and ozone levels were determined on June 2003 episode, meaning that wind speeds were not effective in dispersing the ozone accumulation and the production rate was dominant.



(a)



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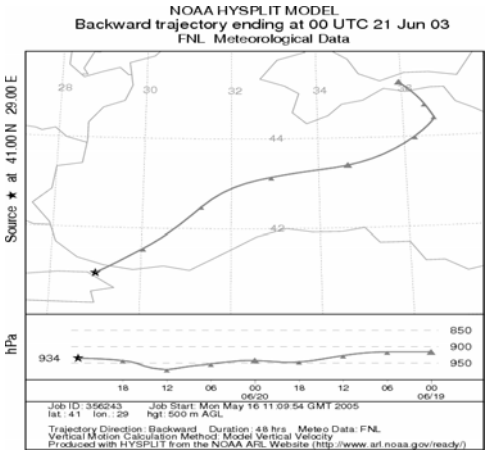

(c)

Figure 7. Hysplit results for (a) 10th of August 2001, (b) 27th of August 2002, and (c) 21st of June 2003

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