

## **DETERMINATION OF TRANSPORT PROCESSES OF NOCTURNAL OZONE IN ISTANBUL ATMOSPHERE**

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### **ABSTRACT**

Ozone, usually has a minimum value at nights, often increases its concentration level, depending on atmospheric movements especially in urban areas. This increased level of ozone at night is known as nocturnal or secondary ozone maximum. Theories about formation of this nocturnal ozone concentration in the studies can be grouped into two major categories which are vertical and horizontal transport processes. In this study, the magnitude, frequency and timing of nocturnal ozone maxima were determined and the reason of nocturnal ozone maxima was examined in May-September 2001-2004 years at Kadikoy and Aksaray stations, in Istanbul. The magnitude and frequency of late and early peaks for peak ozone nights were examined based on stations and years. A total of 40 days which were likely to have secondary ozone maxima due to horizontal transport processes, were selected. HYSPLIT model with back trajectory analysis were conducted for these days in order to determine where air parcel comes from in 24 hours at different ground levels.

**Key Words:** Secondary Ozone Maximum, Horizontal Transport, Vertical Mixing, Back Trajectory Analysis, HYSPLIT.

### **1. INTRODUCTION**

The tropospheric ozone is a volatile secondary photochemical pollutant. It is formed in the atmosphere as a result of the photodissociation of nitrogen dioxide (NO<sub>2</sub>). This reaction occurs only in the presence of ultra-violet light. The typical diurnal cycle of ozone under clear air conditions indicates a maximum during early afternoon, a sharp decrease during the late afternoon, while at night a minimum value is measured. The reason of this minimum value at night is deposition and chemical transformation. Homogeneous and heterogeneous chemical processes in the lower atmosphere at night have long been recognized to have uncertainties stem from several considerations. The reasons of these uncertainties lack detailed kinetic information about reaction of nitrogen compounds and due to the paucity of observations, model description of aerosols and reactive trace gases at night are highly uncertain.

The typical diurnal cycle cannot always be observed, especially at night. Most of the studies about ozone, report an ozone peak in the late night between midnight and

sunrise. Theories about forming of this nocturnal ozone concentration in the studies which are about nocturnal ozone, can be grouped into two major categories. As known, in the absence of any known sources of O<sub>3</sub> in the nocturnal boundary layer (NBL), any increase in concentration is likely to result from transport processes; where horizontal transport processes are of importance secondary maxima can occur. As often no significant change in wind direction is correlated with the secondary ozone maxima, horizontal advection of air pollutants near the surface is not likely and vertical mixing of ozone from the reservoir layer to the ground is a proper explanation. But this needs specific conditions like enhanced turbulence. Turbulence typically results from shear associated with changes in wind velocity with height (Salmond, 2002, Lee, 2002).

Ozone, usually has a minimum value at nights, often increases its concentration level, depending on atmospheric movements especially in urban areas. This increased level of ozone at night, known as nocturnal or secondary ozone maximum, has been observed and reported by several authors, around the world. For example; Chung (1977), Samson (1978), Steinberg and Ganor (1980), Zurita and Castro,(1983), Liu et al. (1990), Corsmeier et al. (1997), Eliasson (2003). Most of these studies report an ozone peak in the late night, between midnight and sunrise, and the nocturnal ozone maximum concentrations can be high .

In this study, we examine summer nocturnal ozone maxima and meteorological data from Istanbul, which is located on the both Asia and Europe continents. The city is located at 40<sup>0</sup> 58<sup>1</sup> N, 29<sup>0</sup> 05<sup>1</sup> E. Istanbul is an urban district, with its coastal location in combination with industry and heavy traffic, represents one of the most polluted areas in Turkey. Local authorities have monitored ozone (O<sub>3</sub>) and other pollutants during the last years. The aim of this study is to examine the magnitude, frequency and timing of nocturnal ozone maxima in Istanbul, to determine the reasons of the increase the ozone concentration in the night and to determine horizontal transport processes.

## **2. METHODS**

Summer nocturnal ozone pollution episodes have been analysed in Istanbul. Istanbul is the most populated city of Turkey, and it is located on the both Asia and Europe continents. In this city there are two ozone measurement stations. Ozone measurements were performed with Environmental S.A. O3 41M model ozone measurement equipment. Meteorological data which were used in this study, had taken from two meteorological stations which were the nearest to the ozone measurement stations.

The study was conducted during 2001-2004 years. During this period, nocturnal ozone formation time were determined as May-September months. It was concluded that total 101 and 74 days have been determined as a nocturnal ozone periods for Kadikoy and Aksaray sampling stations respectively for this season. In the selection it was determined that; where the reduction of ozone was broken and with an ozone increase of 10 µg/m<sup>3</sup> or higher, compared to the breaking point, were classified as

nights with nocturnal ozone maximum. The threshold value was chosen based on the accuracy of the instrument in accordance with above (Eliasson, 2003). In these days the concentration of ozone rose on the order of ½ to 2 of the days maximum. In some days or periods, sample collection in ozone measurement stations could not be done because of technical or meteorological problems. In table 1, total number of ozone maxima days and number of late and early peaks, in two stations and different years are given. Late peak is the days which has an ozone increase 3 hours after sunset and early peak is the days which has an ozone increase within the first 3 hours after sunset. It can be seen from table 1, nocturnal ozone maksimum had late peaks of 59% and 32% , respectively in Kadikoy and Aksaray stations.

### 2.1 Selection Criteria:

Nocturnal ozone maxima can be explained by vertical mixing of high ozone concentrations from higher levels or horizontal transportation from other areas, or countries. Previous studies have shown that nocturnal ozone maxima occurred during stable atmospheric conditions (Corsmeier, 1997, Eliasson, 2003). In order to select nights, that have such conditions, criteria given in table 2, were conducted during these 175 nights. In order to conclude that the observed nocturnal ozone maximum is caused by horizontal transportation, all of the three criterias shown in Table 2 must be fulfilled with the exception of the basic criterion, the reversed case, i. e. Criteria 2 and 3 are not fulfilled indicates that vertical mixing caused the nocturnal ozone maximum. In this criterisation, Richardson number, which is the one of the best indicators for stability of atmosphere, cannot be used, because in none of the meteorological measurement stations temperature in two stages is measured. Because of the horizontal advection alternative is examined in this study, the selected days are decreased total 40 days depending atmospheric stability of nights, wind speed and changing in wind direction for two stations which are given in Table 2. By this separation it is determined that the reason of the nocturnal ozone maxima is horizontal advection, the reselected days have been analyzed in detail, together with meteorological conditions in the measurement period.

Table 1. Frequency and typical nocturnal ozone maksima.

Year		O <sub>1</sub> (Kadikoy station)				O <sub>2</sub> (Aksaray Station)			
		Late peak	Early peak	Late+early peak	total	Late peak	Early peak	Late+early peak	Total
2001	Number	5	-	2	7	9	-	18	27
	Percent	71	-	29	-	33	-	67	-
2002	Number	17	-	21	38	2	1	-	3
	Percent	45	-	55	-	67	33	-	-
2003	Number	19	-	4	23	6	1	3	10
	Percent	83	-	17	-	60	10	30	-
2004	Number	18	12	3	33	15	14	5	34
	Percent	55	36	9	-	44	41	15	-
<b>Total</b>		59	12	30	101	32	16	26	74

Table 2. Criteria for analysis of nocturnal ozone transpotation process

Criteria	
1	Wind speed $\leq 2 \text{ m s}^{-1}$ 3 h before sunset until sunrise and stable stratification
2	Total cloud cover $\leq 2,5$ decas 3 h before sunset until sunrise and stable stratification
3	Change in wind direction (W-NW to E-SE) at meteorological stations

### 3. RESULTS

In this study, nocturnal ozone maxima which has been formed in Istanbul were observed in summer and spring days. In these days early peak is an dominant fenomenan for Istanbul. When seen in yearly conjuncture, seeming frequency of night ozone has a decreasing trend from 2001 to 2004. Generally it can be said that, vertical mixing is a dominant reason for night ozone when comparing to horizontal transport process.

#### 3.1 Hysplit Projectory analysis

The HYSPLIT (Hybrid Single-Particulate Lanrangian Integrated Trajectory) map shows an aerial view of the path(s) an air parcel(s) took, and a vertical view of its movement at different altitudes (NOAA, 2005).

In this study HYSPLIT back trajectory analysis were conducted to determine where air parcel came from in a 24 hour period at different ground levels for the selected 40 days. From this analysis, when main 16 directions are decreased to 4 directon, it is observed that back trajectory has a northly direction 82 and 64% of the period respectively for Kadikoy and Aksaray measurement station. In table 3, results of hysplit backtrajectory analysis are showed at different heights for Kadikoy and Aksaray stations. In this division, 16 directions are decreased to 8 directions clockwise. It can be easily seen that the NNE-NE direction (Russian-The Crimea-Black Sea) is dominant for 100-500-1000 and 1500 m for both stations. Generally, as height is increased, direction of trajectory goes to North West direction, but as height is decreased direction didn't change.

In the next sections, hysplit projection analysis are investigated by giving representative examples for 2001, 2002, 2003 and 2004 years.

**Table 3.** Result of HYSPLIT analysis

Direction	Kadikoy (%)						Aksaray (%)					
	100	500	1000	1500	2000	3000	100	500	1000	1500	2000	3000
<b>I-Scandinavia-Balkans (NNW- N)</b>	3,0	9,1	18,2	30,3	<b>51,5</b>	<b>54,5</b>	15,4	-	23,1	23,1	23,1	<b>30,8</b>
<b>II- Russian-The Crimea-Black Sea (NNE-NE)</b>	<b>69,7</b>	<b>66,7</b>	<b>69,7</b>	<b>51,5</b>	30,3	9,1	<b>38,5</b>	<b>30,8</b>	<b>46,2</b>	<b>38,5</b>	23,1	15,4
<b>III- Russian-The Caucasia-Black sea (ENE-E)</b>	21,2	18,2	6,1	9,1	3,0	3,0	-	<b>30,8</b>	-	7,7	-	-
<b>IV- Middle Anatolia (ESE-SE)</b>	6,1	3,0	-	-	-	-	23,1	7,7	-	-	-	-
<b>V- Akdeniz-Taurus Mountains (SSE-S)</b>	-	3,0	6,1	-	-	-	7,7	7,7	-	-	-	-
<b>VI-Africa-Mediterranean Sea (SSW-SW)</b>	-	-	-	6,1	6,1	9,1	7,7	7,7	7,7	7,7	7,7	7,7
<b>VII Sicily-South Greece-Aegean (WSW-W)</b>	-	-	-	-	-	3,0	-	-	7,7	7,7	15,4	23,1
<b>VIII Middle East-North Greece (WNW-NW)</b>	-	-	-	3,0	9,1	21,2	7,7	15,4	15,4	15,4	<b>30,8</b>	23,1

**Year 2001:** In 2001, average numbers are given in Table 4 according to years and stations. In figure 1, ozone concentration and wind velocity graphic related to 19-20-21 July 2001 for Kadikoy station is given as an example. As can be seen from this figure ozone concentration is high and wind velocity is low at ozone peak hours. In the morning of 20 July, there was a peak at 04:00 at  $136 \mu\text{g}/\text{m}^3$ . At this hour wind velocity was about 1,2 m/sec. After this peak, there was a decrease until 10:00 am. And it continued by increasing and decreasing during the day. At 23:00, there was an increase from 51 to  $81 \mu\text{g}/\text{m}^3$ . This increase decreased until 01:00 and at 02:00 there is a second peak until  $93 \mu\text{g}/\text{m}^3$ .

In Figure 2a, HYSPLIT projection of 20 July is given. It can be seen from this figure air parcel came from NNE (Russian-The Crimea-B.Sea) direction in 24 hours (beginning from 05:00 am) for 100, 500 and 1000 m heights for this day.

**Table 4.** Properties of ozone maxima days

<b>Year</b>	<b>Station</b>	<b>Aver.</b>	<b>Ozone maxima day</b>	<b>Ozone maxima night</b>	<b>Ozone minima day</b>	<b>Ozone minima night</b>
<b>2001</b>	<b>Aksaray</b>	65	142 (18.05.01, 16:00)	136 (20.07.01, 04:00)	2 (18.05.01, 08:00)	18 (23.07.01, 22:00)
	<b>Kadikoy</b>	75	125 (20.07.01, 16:00)	91 (22.07.01, 03:00)	6 (17.07.01, 01:00)	36 (17.07.01, 04:00)
<b>2002</b>	<b>Aksaray</b>	25	72 (01.08.02, 13:00)	54 (01.08.02, 21:00)	7 (02.08.02, 08:00)	0 (01.08.02, 03:00)
	<b>Kadikoy</b>	49	140 (15.07.02, 16:00)	116 (27.08.02, 06:00)	3 (15.07.02, 08:00)	2 (14.05.02, 00:00)
<b>2003</b>	<b>Aksaray</b>	42	128 (04.07.03, 14:00)	103 (15.08.03, 04:00)	0 (03.06.03, 06:00)	4 (09.08.03, 00:00)
	<b>Kadikoy</b>	43	85 (16.06.03, 14:00)	83 (27.06.03, 04:00)	0 (11.09.03, 06:00)	0 (30.09.03, 23:00)
<b>2004</b>	<b>Aksaray</b>	27	70 (29.07.04, 13:00)	61 (29.07.04, 04:00)	2 (23.06.04, 12:00)	3 (11.06.04, 22:00)
	<b>Kadikoy</b>	26	87 (29.07.04, 14:00)	72 (29.07.04, 03:00)	0 (05.06.04, 09:00)	0 (05.05.04, 02:00)

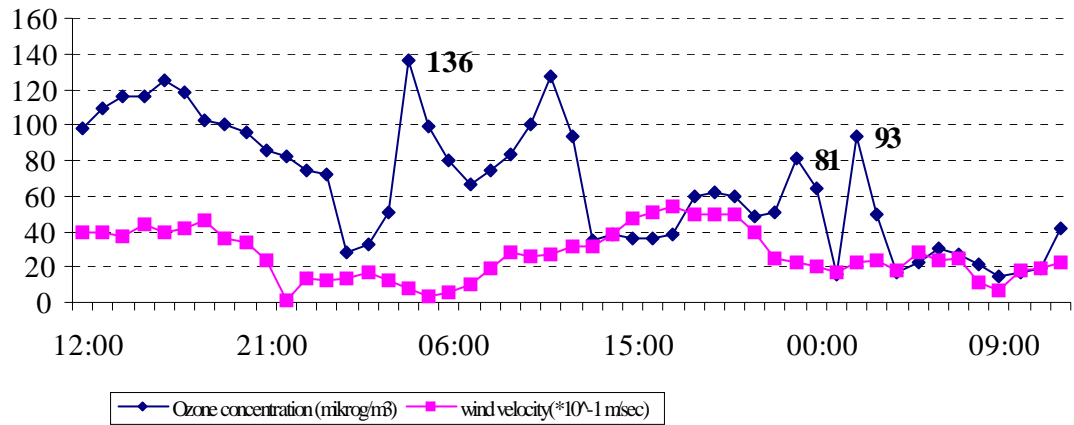


Figure 1. Ozone concentration and wind velocity at 19-20-21 July 2001

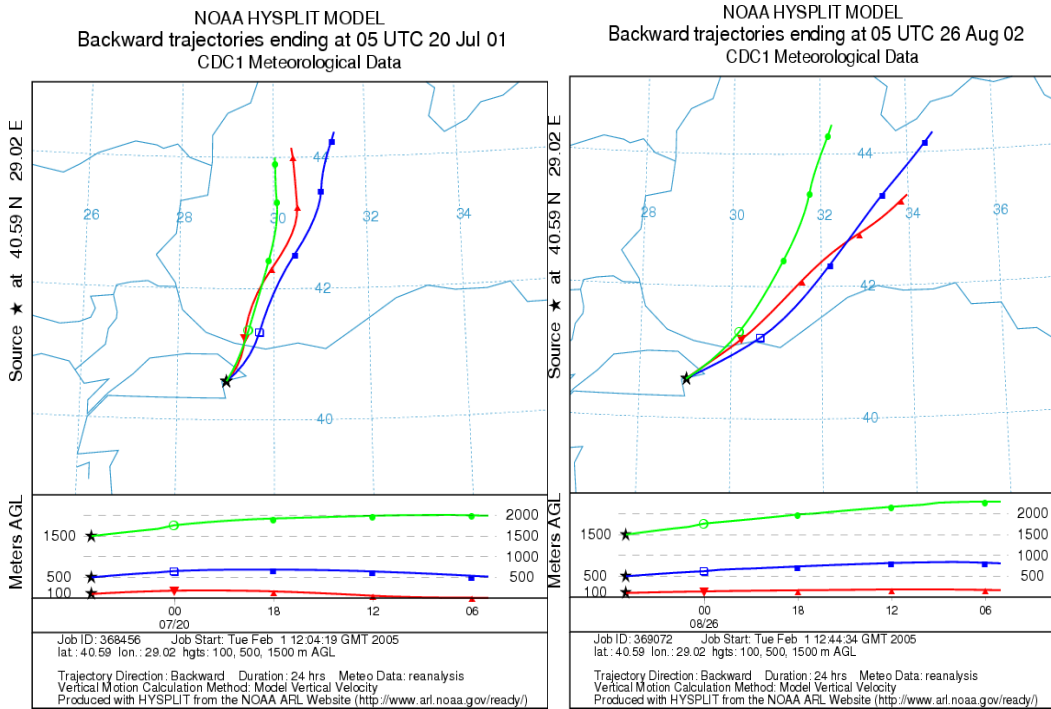


Figure 2.a

Figure 2.b

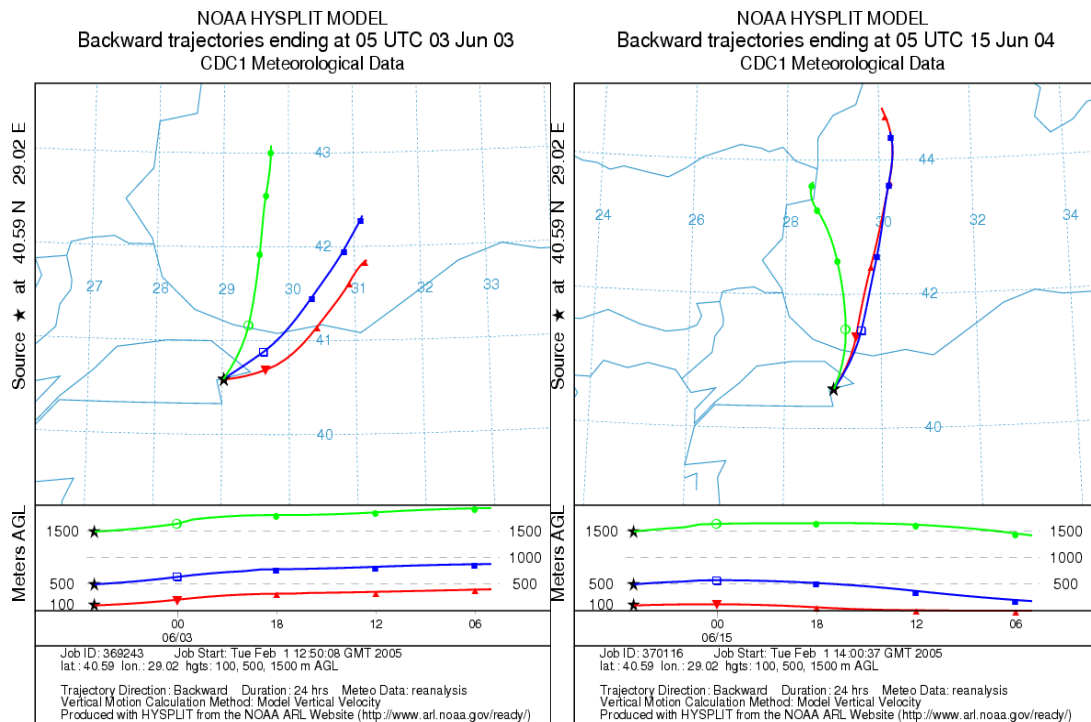


Figure 2.c

Figure 2.d

Figure 2. HYSPLIT Projection of example days

**Year 2002:** For 2002, average numbers are given in Table 4 according to years and stations. In figure 3, ozone concentration and wind velocity graphic related to 25-26-27 August 2002 for Kadikoy station is given as an example. On 25 August 2002, ozone concentration during the day was generally above  $60 \mu\text{g}/\text{m}^3$ . In night there were two peaks at 01:00 and 04:00. After 05:00 a.m., ozone concentration continued decreasing. On 26 August there were three peaks at 22:00 ( $73 \mu\text{g}/\text{m}^3$ ), 23:00 ( $91 \mu\text{g}/\text{m}^3$ ) and 05:00 ( $112 \mu\text{g}/\text{m}^3$ ) a.m. In figure 2b, HYSPLIT projection for 26 August is given. It can be seen from this figure that the air parcel came from NE (Russian-The Crimea-Black Sea) direction in 24 hours (beginning from 05:00 a.m.) for 100, 500 and 1000 m heights for this day.



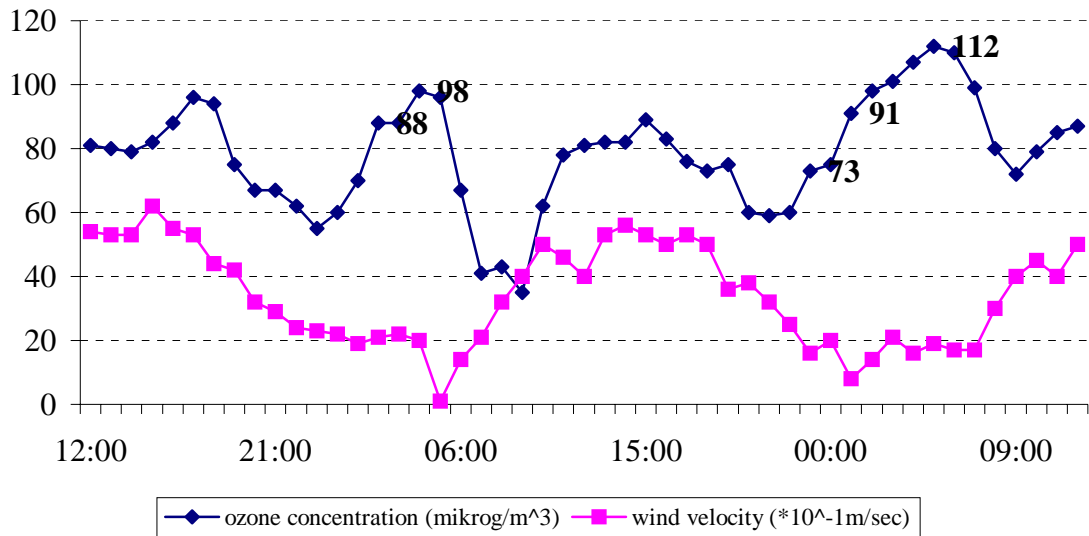


Figure 3. Ozone concentration and wind velocity at 25-26-27 August 2002

**Year 2003:** Average numbers are given in Table 4 for 2003 according to years and stations. In figure 4, ozone concentration and wind velocity graphic is relating to 02-03-04 June 2003 for Kadikoy station is given as an example. On 02 June 2003, ozone concentration in day generally changed from 42 to 81  $\mu\text{g}/\text{m}^3$  until 20:00. On 03 June, two peaks formed at 01:00 and 03:00. It continued decreasing during the next day and there were two peaks at 04:00 and 05:00 a.m. subsequently.

In figure 2, HYSPLIT projection of 03 June is given. It can be seen from this figure that the air parcel came from ENE (Russian-The Caucasia-Black sea) direction for 100 m heights and NE and NNE direction (Russian-The Crimea-Black Sea) direction for 500 and 1500 m in 24 hours respectively for this day.

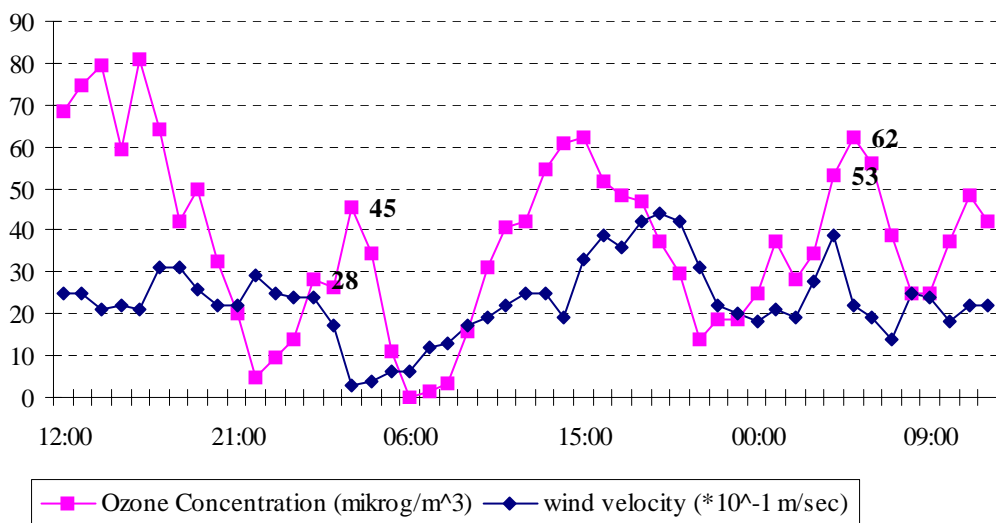


Figure 4. Ozone concentration and wind velocity at 02-03-04 June 2003

**Year 2004:** Average numbers are given in Table 4 for 2004 according to years and stations. In figure 5, ozone concentration and wind velocity graphic is relating to 13-14-15 June 2004 for Kadikoy station is given as an example. On 13 June 2004, ozone concentration was changing 13-54  $\mu\text{g}/\text{m}^3$  and on 14 June there was a peak at 03:00 a.m., daily ozone concentration increased until 60 and on 15 June at 02:00, there was a peak at 44  $\mu\text{g}/\text{m}^3$ . In figure 2, HYSPLIT projection of 15 June is given. It can be seen from this figure that the air parcel came from NNE (Russian-The Crimea-Black Sea) direction for 100 and 500 m heights and N direction (Scandinavia-Balkans) direction for 1500 m in 24 hours for this day.

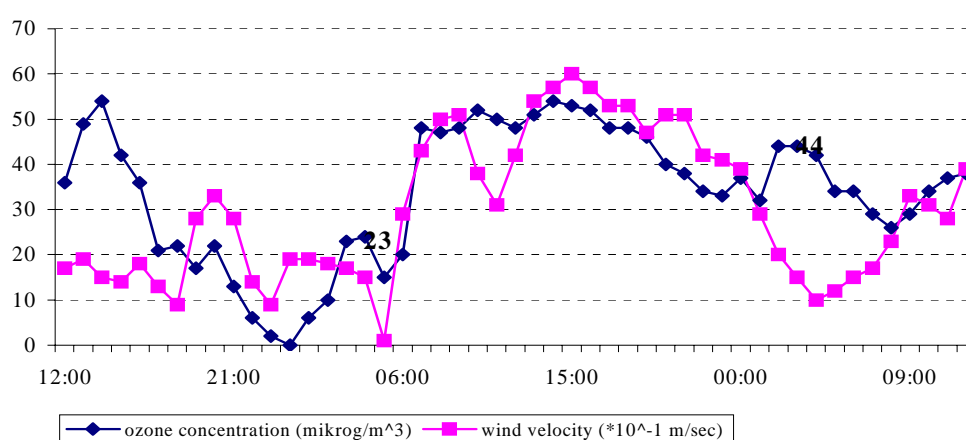


Figure 5. Ozone concentration and wind velocity at 13-14-15 June 2004

As can be seen from this discussion, night ozone concentration could be high in Istanbul at summer months. Sources and contributors of this phenomenon must be investigated by removing meteorological absences (such as Richardson number).

## REFERENCES

- Chung, Y.-S., 1977. Ground-level ozone and regional transport of air pollutants. *Journal of Applied Meteorology*, 16 (11), 1127–1136.
- Corsmeier, U., Kalthoff, N., Kollé, O., Kotzian, M., Fiedler, F., 1997. Ozone concentration jump in the stable nocturnal boundary layer during a LLJ event. *Atmospheric Environment* 31,1977-1989.
- Eliasson, I., Thorsson, S., Andersson-Sköld, Y., 2003. Summer nocturnal ozone maxima in Goteborg, Sweden. *Atmospheric Environment* 37, 2615–2627.
- Lee, Y.C., Calori, G., Hills, P., Carmichael, G. R., 2002. Ozone Episodes in Urban Hong Kong 1994-1999. *Atmospheric Environment* 36, 1957-1968.
- Liu, C-M., Liu, S., Shen, S.-H., 1990. A study of Taipei ozone problem. *Atmospheric Environment* 24A, 1461–1472
- NOAA ARL Quality Forecasting internet site, [www.arl.noaa.gov](http://www.arl.noaa.gov)
- Salmond, J.A., McKendry, I.G., 2002. Secondary ozone maxima in a very stable nocturnal boundary layer: Observations from the Lower Fraser Valley, BC. *Atmospheric Environment* 36, 5771-5782.

- Samson, P.J., 1978. Nocturnal ozone maxima. *Atmospheric Environment* 12, 951–955.
- Steinberger, E.H., Ganor, E., 1980. High ozone concentrations at night in Jerusalem and Tel-Aviv. *Atmospheric Environment*, 14, 221–225.
- Zurita, E., Castro, M., 1983. A statistical analysis of mean hourly concentrations of surface ozone at Madrid (Spain). *Atmospheric Environment* 17 (11), 2213–2220.