

AMBIENT AIR CONCENTRATIONS OF VOLATILE ORGANIC COMPOUNDS AROUND THE HEAVY INDUSTRIAL AREA (ALIAGA) IN IZMIR

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ABSTRACT

The concentrations of volatile organic compounds (VOCs) have been studied in Aliaga region in Izmir, Turkey. Aliaga is surrounded by several major industries, mainly petrochemical industry, refinery and iron-steel smelters. These industries significantly contribute to the air pollution in this region.

The sampling was conducted for 10 sequential days in late March, and 7 sequential days in July, 2005 at two sampling stations concurrently. One of the stations is located at the city center of Aliaga, and the other at Horozgedigi industrial area. The results were evaluated in terms of meteorological conditions such as wind speed, wind direction and temperature.

Keywords: Volatile organic compounds, industrial area, petroleum refineries, petrochemical industry.

1. INTRODUCTION

Izmir metropolitan city, with the 2.7 million of population is the center of a highly industrialized area by the Aegean Sea shoreline of Turkey. Particularly, Aliaga region is surrounded by several major industries, mainly petrochemical industry, refinery and iron-steel smelters. Thus, this region is the source of many anthropogenic pollutants. Particulate matter and gaseous pollutants such as SO₂, NO_x and volatile organic compounds (VOCs) are some of these major pollutants.

Volatile organic compounds (VOCs) are a major group of pollutants which significantly affect the chemistry of atmosphere and human health. They play an important role in the stratospheric ozone depletion and formation of highly toxic secondary pollutants, such as tropospheric ozone and peroxyacetylnitrate (PAN), and they enhance the global greenhouse effect. Their toxic and carcinogenic human health effects are also recognized (Dewulf and Langenhove, 1999; Guo et al., 2004; Srivastava et al., 2005). VOCs can be emitted from combustion processes utilizing

fossil fuels, petroleum storage and distribution, solvent usage and other industrial processes.

The objective of this work was to determine the ambient concentrations of VOCs at heavy industrialized site, Aliaga, in Izmir, Turkey. The results were evaluated in terms of meteorological conditions such as wind speed and wind direction.

2. MATERIALS AND METHODS

2.1 Sampling Site

Aliaga is located at north of Izmir, approximately 50 km far from the city center in Turkey. Aliaga has many industrial plants very close to the town such as petrochemical complex, refinery, liquid petroleum gas storage plants etc. Horozgedigi Industrial Area is approximately 5 km far from the town and located at south of the town. There are many iron-steel manufacturers, a natural gas burning power plant (1500 MW), a fertilizer factory, and some small plants in this industrial area.

The sampling stations were located in Aliaga town and Horozgedigi village. Horozgedigi village is the nearest residential to the industrial area. The sampling point was the monitoring station of the power plant and equipped with a weather station. The meteorological data were taken from this station. The sampling site is demonstrated in Figure 1.

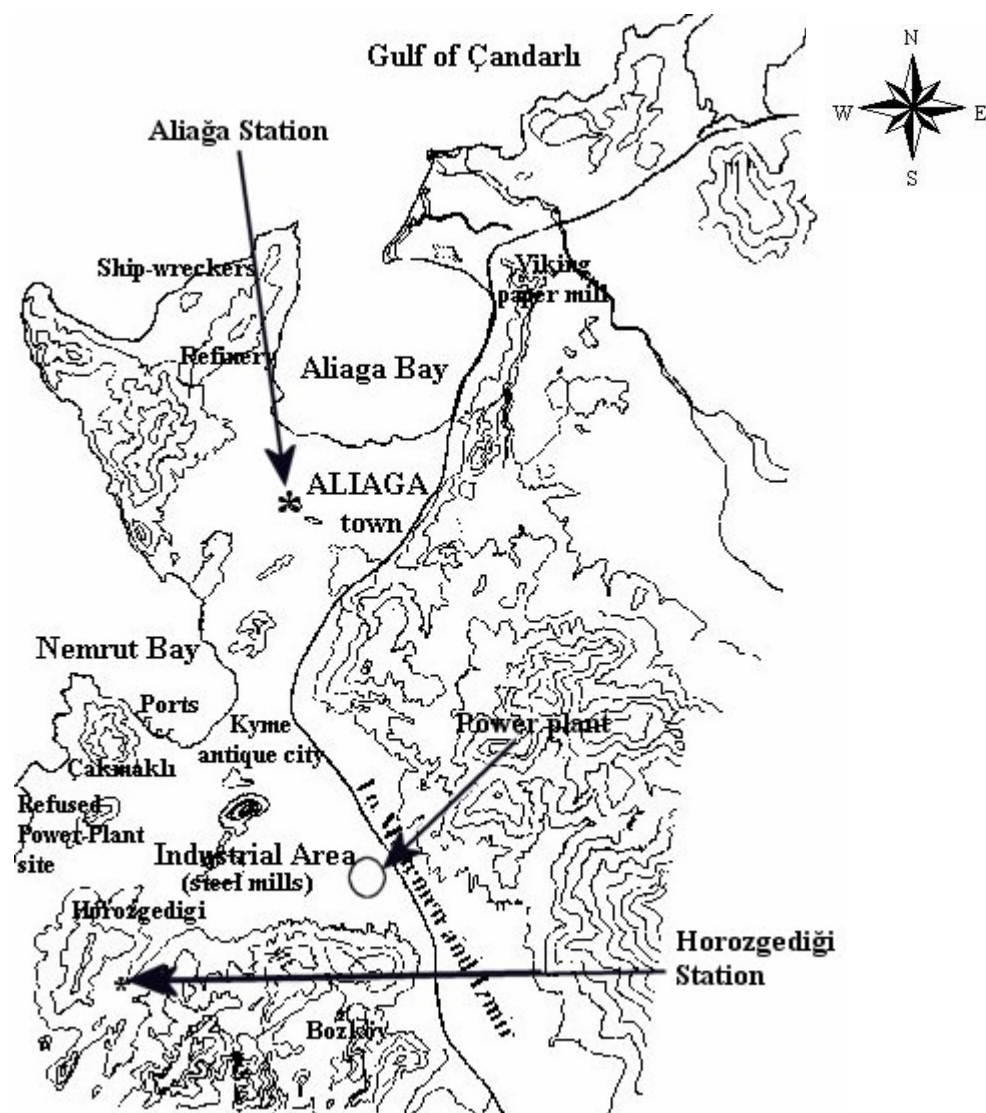


Figure 1. The sampling area.

2.2 Sampling and analysis

The sampling was conducted for 10 sequential days in winter and 7 sequential days in summer periods at two stations, concurrently. The winter period was between 28 March-07 April 2005 and the summer one was 13-19 June 2005.

Ambient VOCs were collected using a sampling train consisted of a moisture trap (calcium chloride), an activated carbon tube, a rotameter, a dry gas meter, and a vacuum pump. Charcoal tubes (Dräger-NIOSH) containing 150 mg of activated carbon in two successive sections were used for sampling (ASTM, 1988a). The average sampling flow rate was 0.5 l min^{-1} .

Adsorption tubes were labeled and closed with special caps to avoid contamination and desorption. The samples were placed into tightly closed special plastic bags and kept in a freezer until they were processed. Before analysis, contents of both sections

of the adsorber tubes were placed into two different vials in which they were weighed, 1.0 ml carbon disulfide (CS₂) was added as the extraction solvent and they were reweighed (ASTM, 1988b). Samples were extracted in an ultrasonic bath for 15 min. Then they were centrifuged for another 15 min to obtain a clear phase at the top. The extracted samples were stored in a freezer until they were analyzed.

The VOC samples were analyzed with a gas chromatograph (GC) (Agilent 6890N) equipped with a mass selective detector (Agilent 5973 inert MSD). The chromatographic column was HP5-ms (30 m, 0.25 mm, 0.25 μ m) and the carrier gas was helium at 1 ml min⁻¹ and 36 cm s⁻¹ linear velocity with a split ratio of 1:20. The inlet temperature was 240°C. Temperature program was: initial oven temperature 40°C, hold for 3 min, 40°C to 120°C at 5°C/min, hold 1 min. Ionization mode of the MS was electron impact (EI). Ion source, quadropole, and GC/MSD interface temperatures were 230, 150, and 280°C, respectively. The MSD was run in selected ion monitoring. Compounds were identified based on their retention times (within ± 0.05 minutes of the retention time of calibration standard), target and qualifier ions. Identified compounds were quantified using the external standard calibration procedure. The calibration for liquid samples was performed injecting (1 μ l) five levels (0.02, 0.1, 1.0, 3.0, and 5.0 μ g ml⁻¹) of standard solutions in CS₂.

Quality control

Blank activated carbon tubes were extracted and analyzed as process blanks to determine if there was any contamination in the activated carbon tubes. Extraction solvent (CS₂) was also analyzed. None of the compounds included in this study were detected in CS₂ and in process blanks. Back-up sections of adsorbent tubes were also extracted and analyzed. VOC amounts in the back-up sections were below the detection limits indicating that breakthrough was not a problem.

3. RESULTS AND DISCUSSION

Total VOCs refer to sum of the concentrations of 36 compounds analyzed in this study. Total VOC concentrations in summer ranged between 3.31-8.25 (average $\pm$ SD, 4.61 $\pm$ 1.61) and 5.11-109.30 (average $\pm$ SD, 35.24 $\pm$ 36.92) μ g m⁻³ in Horozgedigi and in Aliaga regions, respectively. However, in winter the total VOC concentrations were between 3.80-70.97 (average $\pm$ SD, 20.17 $\pm$ 24.99) and 3.18-18.81 (average $\pm$ SD, 8.93 $\pm$ 5.83) μ g m⁻³ in Horozgedigi and Aliaga, respectively (Fig 2 and 3). Total VOC concentrations in Aliaga were higher than those measured in Horozgedigi in summer period. However, this trend is vice versa in winter period. In Figure 2 and 3, wind speed values were also illustrated and it was clearly seen that as expected, total VOC concentrations were inversely proportional with wind speed. There were three peak days of VOC concentration in Horozgedigi in winter period when the wind speed is very low. Also, in summer there were two days with very high VOC concentrations. As can be seen in the figure, these days, the wind speed was also lower than the other days.

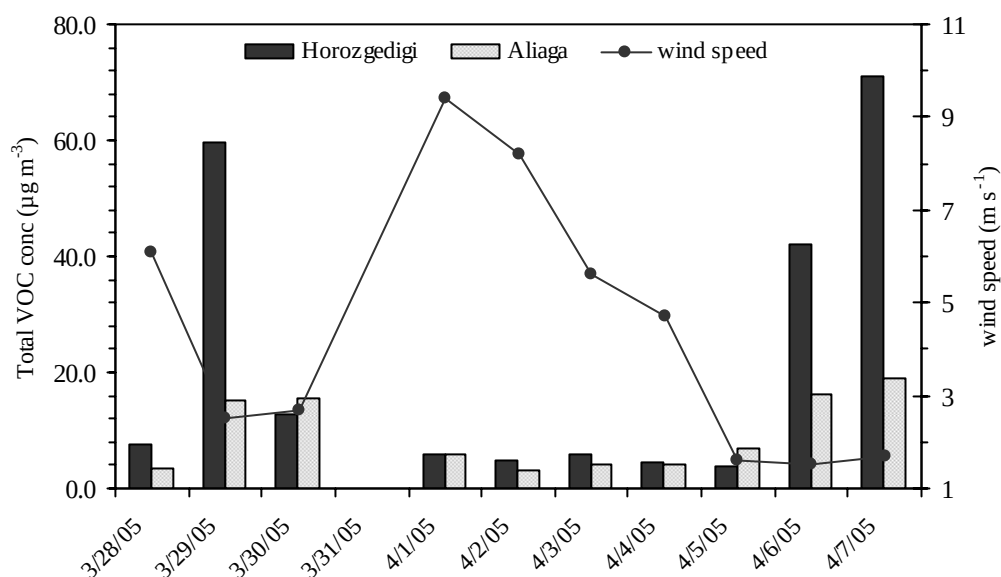


Figure 2. Variation of total VOCs in winter sampling period.

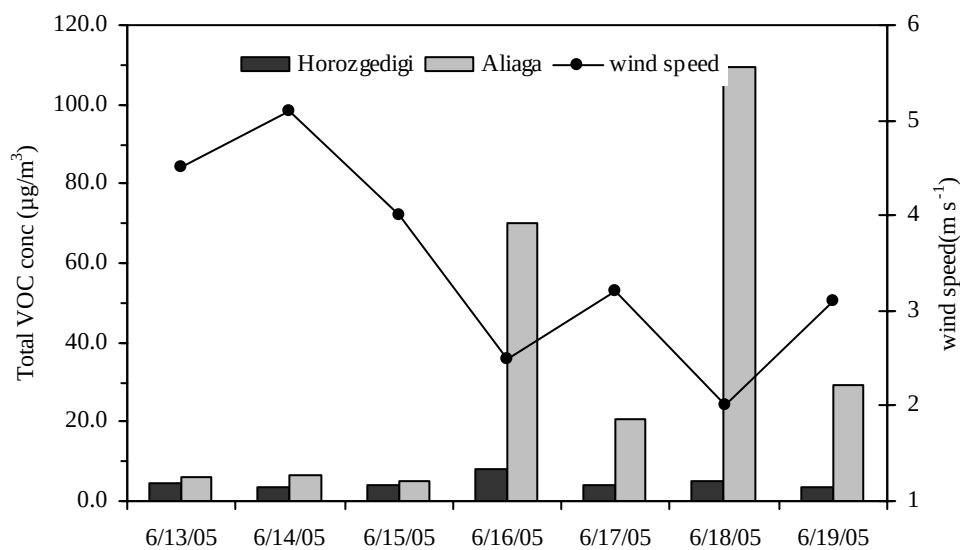


Figure 3. Variation of total VOCs in summer sampling period.

These high concentrations of total VOC concentrations were due to 1,2-Dichloroethane, also called ethylene dichloride, followed by toluene and benzene in Aliaga and Horozgedigi. 1,2 Dichloroethane accounted for %57.0 of total VOCs measured in Horozgedigi and % 21.4 in Aliaga in winter and 16.6 % and 32.4 % of total VOCs measured in Horozgedigi and Aliaga in summer, respectively. A summary of VOC concentrations measured in this study is presented in Table 1.

Table 1. Summary of VOC concentrations ($\mu\text{g m}^{-3}$, average $\pm$ SD) measured in this study

	Horozgedigi ($\mu\text{g m}^{-3}$)		Aliaga ($\mu\text{g m}^{-3}$)	
	Winter (n=10)	Summer (n=7)	Winter (n=10)	Summer (n=7)
1,1-Dichloroethene	0.06 $\pm$ 0.10	0.01 $\pm$ 0.01	0.01 $\pm$ 0.02	0.07 $\pm$ 0.08
Acrylonitrile	0.50 $\pm$ 0.97	0.03 $\pm$ 0.04	0.11 $\pm$ 0.20	0.21 $\pm$ 0.37
1,1-Dichloroethane	0.09 $\pm$ 0.14		0.03 $\pm$ 0.05	0.08 $\pm$ 0.11
Vinyl Acetate	1.46 $\pm$ 3.53	0.45 $\pm$ 0.22	0.37 $\pm$ 0.21	0.68 $\pm$ 0.30
Butanal		0.04 $\pm$ 0.05	0.02 $\pm$ 0.04	0.28 $\pm$ 0.20
Chloroform	0.20 $\pm$ 0.23	0.07 $\pm$ 0.06	0.14 $\pm$ 0.09	0.31 $\pm$ 0.21
2- Butanone	0.13 $\pm$ 0.42			0.13 $\pm$ 0.34
1,1,1-trichloroethane	0.09 $\pm$ 0.01	0.04 $\pm$ 0.00	0.07 $\pm$ 0.01	0.06 $\pm$ 0.01
1,2-Dichloroethane	11.60 $\pm$ 19.14	0.74 $\pm$ 1.06	1.92 $\pm$ 3.25	11.58 $\pm$ 17.16
Crotonaldehyde	0.01 $\pm$ 0.02			0.07 $\pm$ 0.10
Benzene	1.40 $\pm$ 0.95	0.52 $\pm$ 0.37	1.42 $\pm$ 0.68	9.93 $\pm$ 12.95
Carbon tetrachloride	0.61 $\pm$ 0.19	0.30 $\pm$ 0.09	0.37 $\pm$ 0.07	0.44 $\pm$ 0.21
Pentanal			0.04 $\pm$ 0.12	0.85 $\pm$ 0.43
Trichloroethene	0.21 $\pm$ 0.09	0.06 $\pm$ 0.06	0.18 $\pm$ 0.25	0.06 $\pm$ 0.03
Bromodichloromethane		0.01 $\pm$ 0.01	0.03 $\pm$ 0.03	0.03 $\pm$ 0.01
Buthyl formate	0.13 $\pm$ 0.07	0.01 $\pm$ 0.01	0.05 $\pm$ 0.06	0.05 $\pm$ 0.03
4-Methyl - 2 - pentanone		0.06 $\pm$ 0.03	0.05 $\pm$ 0.06	0.12 $\pm$ 0.06
Toluene	1.81 $\pm$ 0.71	0.99 $\pm$ 0.31	1.92 $\pm$ 1.11	6.11 $\pm$ 6.53
1,1,2-Trichloroethane	0.02 $\pm$ 0.04		0.01 $\pm$ 0.02	0.03 $\pm$ 0.04
2-Hexanone	0.02 $\pm$ 0.03	0.07 $\pm$ 0.02	0.64 $\pm$ 0.45	0.34 $\pm$ 0.24
Dibromochloromethane			0.03 $\pm$ 0.04	0.03 $\pm$ 0.02
Hexanal	0.14 $\pm$ 0.18	0.47 $\pm$ 0.18	0.11 $\pm$ 0.17	0.91 $\pm$ 0.52
Tetrachloroethene	0.10 $\pm$ 0.05	0.07 $\pm$ 0.03	0.10 $\pm$ 0.10	0.07 $\pm$ 0.02
Butyl acetate	0.07 $\pm$ 0.06	0.07 $\pm$ 0.04	0.14 $\pm$ 0.19	0.15 $\pm$ 0.14
Chlorobenzene		0.02 $\pm$ 0.03	0.02 $\pm$ 0.01	0.02 $\pm$ 0.01
Ethyl benzene	0.11 $\pm$ 0.05	0.07 $\pm$ 0.02	0.18 $\pm$ 0.12	0.29 $\pm$ 0.21
p-Xylene	0.44 $\pm$ 0.42	0.17 $\pm$ 0.16	0.44 $\pm$ 0.38	1.37 $\pm$ 1.97
Bromoform			0.02 $\pm$ 0.03	0.02 $\pm$ 0.01
Styrene	0.01 $\pm$ 0.01		0.01 $\pm$ 0.01	
O,m-Xylene	0.26 $\pm$ 0.16	0.10 $\pm$ 0.03	0.38 $\pm$ 0.24	0.90 $\pm$ 0.99
Heptanal	0.03 $\pm$ 0.11		0.06 $\pm$ 0.11	
1,4-Dichlorobenzene			0.03 $\pm$ 0.03	0.03 $\pm$ 0.01
1,2-Dichlorobenzene		0.01 $\pm$ 0.02		0.01 $\pm$ 0.02
Nonanal	0.30 $\pm$ 0.48		0.04 $\pm$ 0.09	
Decanal	0.15 $\pm$ 0.23			

1.2 Dichloroethane is produced in vinyl chloride process of the petrochemical complex located in Aliaga area as an intermediate compound using ethylene and Cl_2 . The strong dependency of 1.2 Dichloroethane concentrations on wind direction indicated the association of this compound with the petrochemical complex and the petroleum refinery (Cetin, 2002).

1.2 Dichloroethane is a gasoline additive used as a lead scavenger (Barletta et al., 2002). High concentrations of 1.2 Dichloroethane observed in this study can be also due to the common use of leaded gasoline in this area but probably of minor importance because of significant impact of the petroleum industries.

Benzene is mainly emitted from vehicles. Therefore, benzene is significantly high in Aliaga sampling area, which is in city center (nearly 20 times higher than the samples collected from Horozgedigi in summer period). However, in winter benzene concentrations are nearly the same in both regions.

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