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Source Identification of Volatile Organic Compounds and Particulate Matters in an Urban and Industrial Areas of Turkey

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Abstract
Elevated levels of volatile organic compounds (VOCs) and particulate matters have been observed in recent years in Kocaeli, Turkey, despite improvements in pollution prevention technology that have led to a reduction in gas and particulate emissions. Local authorities should devise alternative strategies to reduce the possible health effects of a variety of pollutants that affect air quality. The objective of this study was to identify potential sources of VOCs, fine particulate matter ($PM_{2.5}$) and coarse particulate matter (PM_{10}) concentrations in atmospheric aerosols that were collected in the highly industrialised area of Kocaeli, Turkey, during the winter and summer months by using wind directions. Samples were collected from May 2006 to January 2007, and concentrations of eight elements (As, Cr, Cu, Mn, Ni, Pb, V and Zn) were measured using energy dispersive X-ray fluorescence (EDXRF) and wavelength dispersive X-ray fluorescence (WDXRF) spectrometer. Samples were analysed for thirteen VOCs, including benzene, toluene, m/p-xylene, o-xylene, ethylbenzene, styrene, cyclohexane, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, hexane, nonane and dodecane using thermal desorption (TD) and a gas chromatography/flame ionisation detector (GC/FID). The results show that vehicular emissions, oil and coal combustions, petroleum refinery and hazardous and medical waste incinerator are the significant sources of VOCs, $PM_{2.5}$ and PM_{10} concentrations in Kocaeli.
Keywords: $PM_{2.5}$, PM_{10}, trace elements, volatile organic compounds, wind directions.

Türkiye'de Endüstriyel ve Şehirleşmiş bir Alanda Uçucu Organik Bileşik ve Partikül Madde Kaynaklarının Tanımlaması

Özet
Son yıllarda gaz ve partikül madde emisyonlarını azaltan kirlilik önleme teknolojilerindeki gelişmelere rağmen Kocaeli'de yüksek seviyelerde uçucu organik bileşik (UOB'ler) ve partikül madde konsantrasyonu gözlemlenmektedir. Bu nedenle, yerel yetkililer, hava kalitesini etkileyen çeşitli kirleticilerin olası sağlık etkilerini azaltmak için alternatif stratejiler geliştirmelidir. Bu çalışmanın amacı, endüstrileşmiş bir bölge olan Kocaeli'de atmosferik UOB, ince partikül madde ($PM_{2.5}$) ve kaba partikül madde (PM_{10}) konsantrasyonlarının potansiyel kaynaklarının yaz ve kış aylarında rüzgar yönlerine göre değerlendirilmesidir. Örnekler Mayıs 2006 ile Ocak 2007 tarihleri aralığında toplanmış ve As, Cr, Cu, Mn, Ni, Pb, V ve Zn elementleri, enerji dağılımlı X-ışını floresan (EDXRF) ve dalga boyu dağılımlı X-ışını floresan (WDXRF) spektrometresi kullanılarak ölçülmüştür. Benzen, toluen, m/p-ksilen, o-ksilen, etilbenzen, stiren, siklohekzan, 1,2,3-trimetilbenzen, 1,2,4-trimetilbenzen, hekzan, nonan ve dodekan dahil olmak üzere on üç UOB, ısısal desorpsiyon (TD) ve gaz kromatografisi/alev iyonizasyon dedektörü (GC/FID) kullanılarak ölçülmüştür. Sonuçlar Kocaeli'de UOB, $PM_{2.5}$ ve PM_{10} konsantrasyonlarının önemli kaynaklarının, araç emisyonları, petrol ve kömür yanması, petrol rafinerisi ve tehlikeli ve tıbbi atık yakma tesisi olduğunu göstermiştir.
Anahtar Kelimeler: Eser elementler, $PM_{2.5}$, PM_{10}, rüzgar yönleri, uçucu organik bileşikler.

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INTRODUCTION

With the industrial developments in the last 30 years, Kocaeli has become a province that attracts attention, due to not only the increasing population and fast paced urbanization, but also the resultant air pollution. Although Kocaeli is one of the smallest provinces by area in Turkey (eighth out of 81 provinces; 3.626 km2), it has a high population density (333 persons per km2, second in Turkey) and population growth rate (2.7%, 10th in Turkey). At present, more than 1000 industrial institutions in various sectors are located in Kocaeli, including a huge refinery meeting >30% of the fuel usage in Turkey, a petrochemical complex, a hazardous and medical waste incinerator, LPG filling plants, and many industrial processes in various sectors such as textile, tire, machine, mine, metal, food, automotive, paper, chemistry, wood, petroleum, tanning, coal, etc (Pekey et al. 2010).

Volatile Organic Compounds (VOCs) are a large group of carbon-based chemicals that easily evaporate at normal room temperature. When VOCs are released to the environment, they quickly disintegrate in the atmosphere or evaporate. For this reason, the photodegradation and atmospheric photochemistry of volatile organics are important. VOCs originate from traffic, transportation and use of organic chemicals (such as solvents) and crude oil, use and distribution of natural gas, and though in small amounts, waste disposal areas and wastewater treatment plants (Bardana and Montanaro 1996, Baek et al. 1997).

Particles with diameters <10 μm (PM_{10}) or 2.5 μm ($PM_{2.5}$) are important because of their ability to penetrate into the alveoli of lungs (Brunekreef and Holgate 2002, Anıl et al. 2009) Moreover, some trace metals (As, Cd, Cr, Ni, Pb) that may be detected in the elemental composition of these particles are human carcinogens. Most of these elements are related to emission sources such as oil and coal combustion, waste incineration, motor vehicles, and metal processes. Other sources of heavy metals in suspended particles are earth crust materials from road dust, building activities, wheel/brake attrition, and the cement industry (Shareef et al. 1988, Chow and Watson 1994, Watson et al. 2001, Anonymous 2003, Özdemir et al. 2010, Onat and Sahin 2012).

This study aimed to identify the contributing sources of outdoor VOCs (benzene, toluene, m/p-xylene, o-xylene, ethylbenzene, styrene, cyclohexane, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, hexane, nonane and dodecane) and heavy metals (As, Cr, Cu, Mn, Ni, Pb, V and Zn) in particulate matters (both $PM_{2.5}$ and PM_{10}) measured simultaneously in 28 sampling points located in Kocaeli (Turkey) during winter and summer.

MATERIALS AND METHODS

Sampling

Sampling points were randomly selected for the determination of outdoor Heavy Metal concentrations on Particulate Matters ($PM_{2.5}$ and PM_{10} fractions) and VOC exposure in the city of Kocaeli. Samples were taken from 28 sampling points during the summer and winter months in Kocaeli (Figure 1). Each of the sampling points was sampled only once in each season. The sampling equipments were protected from rain and direct sunlight and placed away with a minimum distance of 1 m to trees or bushes (if present) and a minimum distance of 5 m to traffic roads and ventilation exits.

VOCs were collected from outdoor environment for 24 hours using Radiello (Fondazione Salvatore Maugeri, Padova, Italy) passive samplers containing 350 mg of graphitized charcoal (Carbograph 4) with 35–50 mesh particle size (Pekey and Arslanbaş 2008). Airborne atmospheric particles in two different fractions ($PM_{2.5}$ and PM_{10}) were collected daily by using a low volume air sampler (Gent type PM_{10} stack filter unit, SFU) consisting two 47-mm diameter filter cartridges, placed in series. The first cartridge intercepts particles larger than 10 μm. The flow rate through the SFU was 16.7 L/min. It collects particulates <10 μm in separate coarse (2.5-10 μm) and fine (<2.5 μm) size fractions on two sequential 47-mm diameter nuclepore polycarbonate filters (Pekey et al. 2010). The first filter cartridge is equipped with an 8-μm pore size nuclepore polycarbonate filter, and the second cartridge contains a 0.4-μm pore size nuclepore polycar-bonate filter (Hopke et al. 1997).

Extraction and Analysis

Prior to sampling, each passive sampler was conditioned by passage of an ultra-pure stream of nitrogen gas at 350°C for 6 hour. A Unity™ thermal desorber (Markes International Limited, UK) unit coupled to an Agilent gas chromatograph (Model 6890) and two independent flame ionization detectors (FID; Agilent Technologies, Inc. Santa

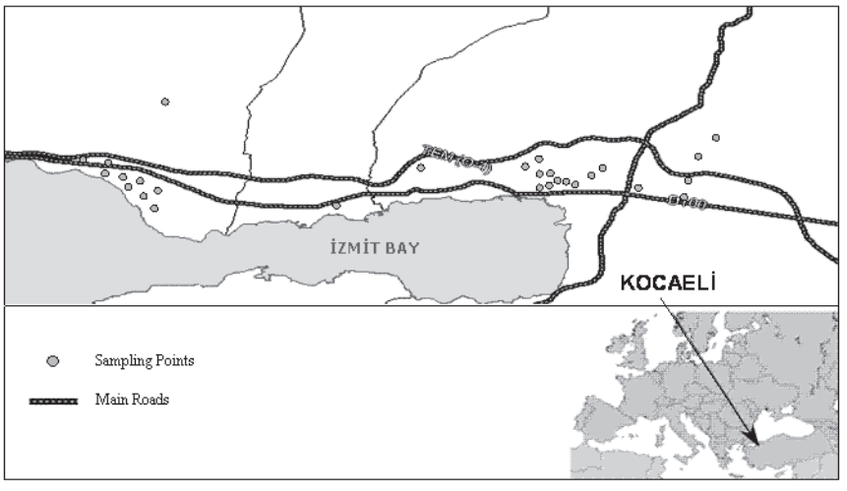

Fig. 1. Location of Kocaeli province in Turkey.

Clara, CA, USA), one to measure total hydrocarbons and the other to measure methane and non-methane components, were used to determine the target compounds. The analytical columns used for separating targets comprised a DB-1 capillary column (60 m, 0.25 mm i.d., 1 μm film thickness) and an HP-PLOT Al203 "S" deactivated capillary column (50 m, 0.32 mm i.d., 8 μm film thickness). The oven temperature program was initially set to 40°C for 5 min., which then increased at a rate of 5°C min^{-1} up to 195°C, and was then finally maintained for 10 min at 195°C. The FID temperature was set to 300°C. The ultra-pure nitrogen carrier gas flow rate was kept at 2 mL min^{-1}. Thirteen target VOCs including benzene, toluene, m/p-xylene, o-xylene, ethylbenzene, styrene, cyclohexane, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, hexane, nonane and dodecane were investigated. Details of the overall methodology and quality control procedures can be found in Pekey and Arslanbaş (2008). Filter samples were analyzed for Cr, Cu, Mn, Ni, Pb, and Zn by energy dispersive X-ray fluorescence (EDXRF). For As and V a PANalytical Axios-Advanced wavelength dispersive X-ray fluorescence (WDXRF) spectrometer were used. Analyses of blank samples, determination of detection limits, and recovery tests were also performed for the quality control of analytical procedures used in the PM sampling and analysis studies. The precision of the method was assessed for both repeatability and reproducibility of measurements. The repeatability of spectrometers was determined by measuring a single filter sample (NIST SRM 2783) 10 consecutive times in a single day. The reproducibility was determined by measuring the same sample once a day over a 7-day period. Repeatability and reproducibility data for a selected element are excellent. The results of the selected elements show good agreement (recovery ratios varied between 91.2% [Ni] and 108.1% [Cr]) with the certified values. Details of the overall methodology and quality control procedures can be found in Pekey et al. (2010).

RESULTS AND DISCUSSION

Samples were obtained from 28 sampling locations in Kocaeli during the summer from May 31, 2006 to June 29, 2006 and during the winter from December 16, 2006 to January 20, 2007. Meteorological data, such as wind speed and wind direction, were obtained from the Kocaeli meteorological station. Table 1 includes the mean concentrations of the elements and VOCs targeted in this study. The prevailing wind directions and most abundant compounds within the total mass of PM2.5, PM10 and VOCs in the summer and winter samples are presented in Tables 2 and 3, respectively.

Results Obtained from Summer Samples

An assessment of the meteorological station's data indicated the wind directions in the summer were 24% from the southeast (SE), 19% from the north (N), 11% from the west-northwest and south-southeast (WNW and SSE), 7% from the northwest (NW), 6% from the east-southeast and 0-4% from other directions.

Daily average wind directions were used in this study to obtain information about important local sources that may have contributed to the concentrations of VOCs and particulate matter

samples obtained from each outdoor sampling point. For this purpose, hourly wind data were converted to daily data, and wind roses were drawn for each day on which samples were taken. Information about potential pollution sources was obtained by comparing the percentage of each compound within the total mass sampled to the sectors downwind from the specific sampling site.

To evaluate wind sectors for the types of pollution sources contributing to the concentrations of the compounds in the samples, the sampling field was examined in three main parts: 1) city centres, where there is heavy traffic, 2) industrially congested areas, and 3) areas outside of zones 1 and 2, which have relatively low traffic and industrial activity. In city centres with heavy traffic and high population density, pollution cannot diffuse because of emissions from intense vehicle traffic, the dense built environment and the city's dish-shaped topographical structure. Instead, pollution tends to settle in a small area. In this study, the most important pollution source in city centres was vehicle traffic.

The effect of distant sources on centrally located measurement points could not be distinguished from the contribution from heavy vehicle traffic, even when the prevailing wind direction changed. Furthermore, the effect of industrial facilities on the particulate matter composition was indistinguishable from the influence of other sources at all measurement points except for those points downwind from the facilities. Particulate matter samples collected from sampling points 12, 13 and 14, which are located approximately 4 km southwest of a hazardous and medical waste incinerator, contained high levels of Cr, Cu, Mn, Ni, Pb and Zn. The incinerator had a substantial influence on $PM_{2.5}$ samples taken from sampling point 12 on a day in which the wind blew from the north (Table 2). In a study conducted by Bakoglu et al. (2003), the concentrations of Cr, Pb, Cu, Mn, Ni, Sn, Co and Zn in sub ash, fly ash, filter press cake and flue gas emitted from this incinerator changed significantly depending on the type of waste and burning conditions. In the same study, pollutants that stick to the fine particles could not be fully captured with the existing waste gas control systems, and thus, additional facilities for metal removal were needed. The results from Ragosta et al. (2008) supported our characterisation of the $PM_{2.5}$ species Pb and Zn as elements resulting from motorised road vehicles and the species Ni, Cr and Cu as elements resulting from industrial operations.

Two stations, sampling points 18 and 21, are located in the city's centre where the population is dense and the traffic is heavy. These points were exposed to mainly north and west-northwest winds and had the highest detected toluene percentages (Table 2). High levels of m-p-xylene, o-xylene and benzene compounds were also present in the samples from points 18 and 21, thus indicating that these compounds were resultant from motor vehicle traffic. Samples from other areas of heavy traffic, including sampling points 7, 8, 9, 10, 11, 12, 13, 15, 16, 17, 25 and 26, also had high levels of benzene, toluene, ethylbenzene and xylenes (BTEX). Additionally, especially when the prevailing wind direction was from the north and east, hexane, nonane, dodecane and cyclohexane were the most frequently observed compounds (Table 2) after BTEX. Emissions from three, large automobile tire manufacturing facilities and allied industries, the automotive industry, the chemical industry and solid waste burning and storage facilities located in the region are the primary sources of these compounds.

In areas with dense industrialisation, such as sampling points 1, 2, 3, 4, 5, 19, 20, 22, 23 and 27, the most significant sources of VOCs were an oil refinery and black carbon and LPG filling facilities located to the east and southeast. Other than heavy traffic, a significant source of VOCs in west-northwest direction was the engine and industrial oils mixing and storage facility located approximately 2 km from the sampling points. The VOCs detected in the industrial region, apart from BTEX, were styrene, hexane, cyclohexane, 1,2,4-trimethylbenzene and nonane.

West-northwest and southeast winds often corresponded with the sampling times in the industrial region. PM10 and PM2.5 samples taken at times with west-northwest and southeast winds had similar compositions. Zinc and Pb concentration in the samples increased on days when the wind direction was predominantly from the west-northwest. Samples with high relative concentrations of Cu and Pb were collected on days when the prevailing winds were from the southeast. The Dilovası and Gebze region is located west-northwest of the industrial area and has numerous

Table 1. Mean outdoor elemental ($PM_{2.5}$ and PM_{10} fractions) and VOCs concentrations ($\mu g/m^3$) in Kocaeli

	SUMMER						WINTER					
	Elemental ($PM_{2.5}$ and PM_{10} fractions) Concentrations											
	$PM_{2.5}$			PM_{10}			$PM_{2.5}$			PM_{10}		
	Conc.±SD	Min.	Max.	Conc.±SD	Min.	Max.	Conc.±SD	Min.	Max.	Conc.±SD	Min.	Max.
Mass	22.0 ± 7.70	4.67	50.5	70.8 ± 32.0	27.2	156.0	22.2 ± 11.6	4.12	57.0	90.9 ± 45.6	22.9	196.8
As	0.0018 ± 0.0025	0.0001	0.0120	0.0020 ± 0.0032	0.0001	0.0160	0.0042 ±0.0054	0.0007	0.0260	0.0071±0.0083	0.0010	0.0385
Cr	0.0036 ± 0.0026	0.0007	0.0135	0.0111 ± 0.0061	0.0031	0.0290	0.0089 ±0.0045	0.0033	0.0215	0.0255±0.0215	0.0078	0.1230
Cu	0.0185 ± 0.0100	0.0009	0.0495	0.0480 ± 0.0224	0.0185	0.1030	0.0446 ±0.0238	0.0320	0.1630	0.0846±0.0434	0.0535	0.2035
Mn	0.0408 ± 0.0377	0.0005	0.1840	0.1658 ± 0.1545	0.0105	0.7820	0.0472 ±0.0767	0.0027	0.3670	0.1861±0.1663	0.0115	0.5710
Ni	0.0016 ± 0.0022	0.0005	0.0065	0.0010 ± 0.0009	0.0005	0.0030	0.0033 ±0.0004	0.0028	0.0040	0.0046±0.0005	0.0039	0.0055
Pb	0.0346 ± 0.0372	0.0010	0.1640	0.0834 ± 0.0968	0.0080	0.4810	0.0708 ±0.0519	0.0010	0.2685	0.1457±0.1124	0.0253	0.5270
V	0.0057 ± 0.0027	0.0028	0.0130	0.0032 ± 0.0020	0.0003	0.0090	0.0095 ±0.0077	0.0028	0.0290	0.0129±0.0094	0.0031	0.0385
Zn	0.0546 ± 0.1085	0.0010	0.4940	0.1543 ± 0.3564	0.0010	1.7855	0.1083 ±0.2251	0.0010	1.1960	0.3414±0.4359	0.0363	1.8355

	VOCs Concentrations					
	Conc.±SD	Min.	Max.	Conc.±SD	Min.	Max.
Benzene	8.68±6.04	1.92	23.5	9.25±5.74	2.27	30.2
Toluene	30.5±35.6	4.85	160.0	24.1±15.7	3.56	69.9
m/p-xylene	10.9±9.68	2.11	46.2	15.6±8.55	2.49	35.0
o-xylene	6.75±6.06	0.86	24.2	8.65±4.40	1.24	17.9
Ethylbenzene	5.05±3.00	0.72	10.3	5.82±4.52	1.48	23.4
Styrene	4.25±1.84	1.65	8.74	5.49±4.03	0.69	20.7
Cyclohexane	4.46±2.43	0.65	8.31	5.89±3.93	1.51	17.2
1,2,3-TMB	2.53±2.02	0.42	7.52	1.08±0.84	0.13	3.36
1,2,4-TMB	4.97±7.53	0.13	25.9	1.66±1.88	0.13	7.39
Hexane	8.45±7.67	0.34	29.7	7.5±6.23	1.73	34.9
Nonane	5.19±3.38	1.52	12.8	4.03±2.12	0.74	8.52
Dodecane	6.57±6.08	0.18	26.5	2.54±2.57	0.14	11.8

Table 2. The prevailing wind directions and the most abundant compounds within the total mass of $PM_{2.5}$, PM_{10} and VOCs in the summer samples.

Sampling Point		Most Abundant Compounds within the Total Mass (%)	Prevailing Wind Directions (%)
5	PM_{10}	Zn (41), Mn (29), Pb (18), Cu (8)	WNW (48), SE (13), NW (13)
	$PM_{2.5}$	Zn (47), Mn (23), Pb (20), Cu (5)	
	VOCs	Toluene (17), hexane (14), benzene (14), cyclohexane (11)	
6	PM_{10}	Zn (50), Mn (26), Pb (19), Cu (4)	WNW (46), NW (38), W (17)
	$PM_{2.5}$	Zn (55), Mn (21), Pb (18), Cu (2)	
	VOCs	Toluene (15), benzene (10), m/p-xylene (10), hexane (9)	
12	PM_{10}	Mn (34), Cu (29), Pb (14), Zn (14)	N (50), NNE (25), SE (20)
	$PM_{2.5}$	Ni (22), Pb (22), Cr (16), Mn (16)	
	VOCs	Hexane (41), benzene (18), toluene (7), dodecane (6)	
18	PM_{10}	Zn (56), Mn (24), Pb (15), Cu (3)	WNW (48), SE (17), NW (17)
	$PM_{2.5}$	Cu (31), Zn (24), Mn (18), Pb (16)	
	VOCs	Toluene (44), benzene (13), m/p-xylene (7), o-xylene (6)	
21	PM_{10}	Mn (77), Cu (12), Cr (4), Pb (4)	N (39), SE (33), SSE (11)
	$PM_{2.5}$	Mn (48), Cu (30), Ni (8), V (6)	
	VOCs	Toluene (45), m/p-xylene (10), o-xylene (9), ethylbenzene (6)	
23	PM_{10}	Mn (59), Pb (20), Cu (14), Cr (5)	SE (38), SSE (38), N (13), NNE (8)
	$PM_{2.5}$	Cu (36), Mn (34), Pb (10), Cr (7)	
	VOCs	Toluene (17), dodecane (11), cyclohexane (9), m/p-xylene (9)	

iron, steel, paint, metal, cement and chemical facilities that emit metal containing particles that contribute to the concentrations at the sampling sites. Furthermore, D-100 and TEM highways also pass through the Dilovası and Gebze region. Zinc and Pb are the most prevalent pollutants emitted from the iron and steel industry and from vehicle traffic (Ragosta et al. 2008, Yatkın and Bayram 2008).

Table 3. The prevailing wind directions and the most abundant compounds within the total mass of $PM_{2.5}$, PM_{10} and VOCs in the winter samples.

Sampling Point		Most Abundant Compounds within the Total Mass (%)	Prevailing Wind Directions (%)
1	PM_{10}	Zn (48), Pb (29), Mn (16), Cu (4)	E (29), SE (25), NNW (17)
	$PM_{2.5}$	Pb (50), Zn (33), Mn (7), Cu (6)	
	VOCs	Toluene (19), m/p-xylene (13), styrene (11), dodecane (9)	
6	PM_{10}	Zn (50), Pb (20), Mn (16), Cu (8)	NW (58), SE (25), WNW (8)
	$PM_{2.5}$	Zn (57), Pb (18), Mn (9), Cu (8)	
	VOCs	Toluene (19), m/p-xylene (15), benzene (12), hexane (9)	
14	PM_{10}	Zn (56), Pb (17), Mn (16), Cu (7)	NW (48), NNW (24), SE (12)
	$PM_{2.5}$	Zn (49), Pb (25), Cu (8), Mn (8)	
	VOCs	Toluene (17), m/p-xylene (13), hexane (11), cyclohexane (10)	
21	PM_{10}	Zn (32), Mn (31), Cr (15), Pb (10)	SE (30), NW (26), SSE (17)
	$PM_{2.5}$	Cu (21), V (18), Pb (17), As (5)	
	VOCs	Toluene (14), benzene (10), m/p-xylene (10), ethylbenzene (9)	

The largest point source to the southeast of the industrial region was the oil refinery, which is located close to the sampling points. At the time of the sampling, the use of leaded compounds in gasoline production had been terminated. Previously, leaded compounds diffused into the environment from oil refineries and lead gasoline fuelled vehicles. However, the re-suspension and wind transport of soils containing lead was thought to be a significant source of lead concentrations in the samples. The shipbuilding yard located approximately 6 km southeast of the industrial area was another important point source of pollution. In addition to lead concentrations, high concentrations of Zn and Cu in the samples indicated that polluted soils were the main source of these heavy metals. Heavy metals are often found together because they are carried with soil from sources of anthropogenic $PM_{2.5}$, such as areas with industry, traffic and burning.

Sampling point 6 was located far from traffic activity and industrialisation, the prevailing wind directions were west-northwest, northwest and west, and the most significant source of particulate concentration was the TEM highway. Traffic associated compounds, such as BTEX and hexane, dominated the composition of VOCs in the samples from this sampling point (Table 2). Industry and traffic related emissions can affect the Kocaeli province, depending on meteorological conditions, although pollutant levels were relatively low compared with other sampled areas. Samples from points 14 and 24, despite being located far from any of sources, had significant levels of BTEX compounds, hexane, nonane, dodecane and 123-trimethylbenzene from the TEM highway, tire factories and chemical facilities located southeast of the points and automotive industry and solid waste burning and storage facilities located east and northeast of the points. The particle samples collected at sampling points 14 and 24 were high in Zn and Pb and had compositions similar to the samples collected in areas with dense industrialisation. Therefore, pollutants from industrial operations and traffic seem to be carried with the wind and greatly affect pollutant concentrations elsewhere.

Results Obtained from Winter Samples

The prevalent wind directions observed during winter sampling period were 25% from the northwest (NW), 20% from the southeast (SE), 13% from the north-northwest, 7% from the north and west-northwest (N and WNW) and 1-4% from other directions.

The northwest and southeast winds predominated in the industrialised region during the winter sampling period. In the samples, styrene was the most abundant compound after toluene and m,p-

xylene; the most significant sources of VOCs were the oil refinery and black carbon production (from the petrochemical facility located at the region) and LPG filling facilities. As with the summer samples, the contents of the $PM_{2.5}$ samples collected during the winter were similar in composition to the PM10 samples. However, a significant percentage of anthropogenic elements were present in the $PM_{2.5}$ samples. The $PM_{2.5}$ samples collected from the industrialised region during the winter season were similar in composition to the summer samples. The most abundant pollutants in the samples from all points were Zn, Cu, Pb and Mn, respectively. The northwest wind direction prevailed at all sampling times in the industrialised region, except for at sampling point 1. During the sampling conducted at point 1, north and southeast winds were also common. In addition, samples from point 1 had high levels of Pb; in some samples, 50% of the $PM_{2.5}$ mass was from Pb (Table 3). Concurrent with results of the summer samplings, the Pb particles collected in winter samples originated from the north-northwest, west-northwest, northwest and south-southeast. The most significant Pb sources from the north-northwest, west-northwest, northwest and south-southeast directions were the D-100 and TEM highways that stretch in these directions and that are located close to the sampling point. However, because lead was banned as a fuel additive in 2003, polluted road dusts are believed to be re-suspended and carried by the wind to the sampling area. Additionally, because the Pb content of the PM_{10} mass is almost half of the Pb content of the $PM_{2.5}$ mass, an industrial source unrelated to road dust must also be contributing to the particulate composition. An important point source to the northwest of the sampling point was the cement factory. The most important disperse area sources were the paint, iron, steel, chemical industry and metal works facilities located in Dilovası and Gebze. An oil refinery and a shipbuilding yard are located to the southeast of the sampling point.

Winds were predominantly from the northwest for samples collected in the industrialised region at other times of the sampling period. Although the percentage of anthropogenic elements in samples varied from one sample to another, Cu, Zn and Pb dominated the samples' compositions. Only one sample contained a higher percentage of Mn compared with other elements. We concluded that Mn was fully contained in the $PM_{2.5}$ because the masses of PM_{10} and $PM_{2.5}$ had the same percentage of Mn. Concentrations of Mn in PM_{10} and $PM_{2.5}$ were similar in many samples collected from several sites, but not in samples collected from sampling point 1. Manganese in these samples is likely from anthropogenic origin because there is less re-suspension due to wet soil at the receptor site during winter compared to summer samples. The most significant Mn particle sources at the northwest side of the industrialised region are the industrial facilities located in Gebze and Dilovası and motor vehicle traffic. In a study conducted by Yatkın and Bayram (2008) in Izmir, Turkey, the primary elements emitted from the iron and steel industries were Zn, Pb and Mn. Furthermore, the results from studies by Manoli et al. (2002) regarding the chemical characterisation and source determination of fine and coarse particles also indicate that traffic is the most significant source of Mn. PM_{10} and $PM_{2.5}$ samples from sampling point 3, located in the industrialised region, had a high Cu percentage relative to the total mass. The sampling point was located among high buildings in an area with dense traffic, thus indicating that the primary source of Cu was vehicle traffic. Copper is emitted from motor vehicles, and previous research indicates that the wearing of brake linings may be responsible for 50-75% of the total Cu emission in Europe (Denier et al. 2007). Sampling point 21 produced samples with unique elemental compositions (Table 3). Although Kocaeli has started to use natural gas, coal and oil are still used as sources of heating in many places. Information obtained from the Kocaeli Provincial Directorate of Environment and Urbanisation indicates that the types of fuel used for domestic heating purposes are 62% coal, 18% natural gas, 17% wood, and 3% fuel-oil. In the winter, high concentrations of V, Cr, Cu and As in the samples indicate that coal and other fuels were burned for domestic heating.

Winds from the north were prevalent at sampling sites located in the city centre. At the centrally located sampling points, the dominant VOCs were BTEX, which are traffic-related trace compounds. As noted earlier, the city's centre is an area of dense population and heavy traffic. Furthermore, during the winter season, in addition to the traffic activity, the burning of fuel-oil for domestic heating purposes adds to the pollutant

concentrations. However, widespread use of natural gas for heating purposes did not prevented the effect of traffic activity from coming into prominence during the winter season. Consequently, concentrations from the sampling points located in the city centre were affected primarily by traffic activity, regardless of the wind direction.

Traffic activity was the primary source affecting pollutant concentrations at sampling points 14 and 24 during the winter season, even though these sampling points are located in rural areas and the wind blows from the industrial area in the summer season. At sampling point 6, a point located outside of the city centre, the wind came from the northwest during both winter and summer sampling periods. Therefore, the wind direction seems to dictate the source areas that have a dominant influence on the composition of the samples collected in the winter and summer. Furthermore, in both seasons, PM_{10} and $PM_{2.5}$samples were composed of predominantly Zn, Pb and Mn (Table 3). A significant difference between the PM_{10} and $PM_{2.5}$ samples was that the PM_{10} sample contained 2% As, but the PM2.5 sample contained 3% As. Arsenic is an important trace compound of coal (Yatkın and Bayram 2008), and coal is burnt, in addition to natural gas, for domestic heating purposes in the winter season. Therefore, in addition to industrial processes and traffic activity, coal burning should be considered as an important pollution source.

In sampling points 14 and 24, located outside of the city centre, the prevailing wind direction was from the northwest. Natural gas is the most common fuel used for heating purposes in this region. Because the Zn and Pb were the most common elements in samples collect from these two sites (Table 3), the most significant sources of pollution from the northwest were traffic and industrial activity. In addition, the TEM highway runs approximately 500 m. to the southeast of sampling points 14 and 24, and large-scale industrial factories, such as tire manufacturing and allied industries, food industry, medicine industry facilities, are located approximately 2–3 km northwest of the sampling locations. Traffic activity and industrial operations influenced pollutant concentrations obtained from sampling points 14 and 24, despite their placement far from the city centre and industrial activity.

CONCLUSIONS

This study was conducted in a complex and highly industrialised area of Turkey. The characterisation of specific pollution sources in this location is particularly challenging because of a large number of industrial and urban sources with roughly identical emissions profiles. However, we identified wind directions and accounted for wind roses to determine pollution sources. In Kocaeli, the most important sources of VOCs and particulate matter are traffic emissions, oil and coal combustion for electric power generation and domestic heating, industrial activities of a petroleum refinery, a petrochemical complex, a hazardous and medical waste incinerator, three major tire factories and LPG filling plants. To reduce the possible hazards to public health, authorities will need to develop extensive policies that consider the complexity of numerous emission sources. The results obtained in this study are valuable for assessing the impact of further industrial development in the study area.

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