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Atmospheric Environment

Spatial and temporal variations in atmospheric VOCs, NO$_2$, SO$_2$, and O$_3$ concentrations at a heavily industrialized region in Western Turkey, and assessment of the carcinogenic risk levels of benzene

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HIGHLIGHTS

- VOCs, NO$_2$, SO$_2$ and O$_3$ were measured around a densely populated industrial zone.
- Five separate weekly passive sampling campaigns were conducted at 55 locations.
- The spatial distribution of pollutants extracted in PMF were used to realize sources.
- Six factors were identified using a large number of chemical species available.
- The cancer risk due to benzene inhalation was calculated using Monte Carlo simulation.

ARTICLE INFO

ABSTRACT

Ambient concentrations of volatile organic compounds (VOCs), nitrogen dioxide (NO$_2$), sulphur dioxide (SO$_2$) and ground-level ozone (O$_3$) were measured at 55 locations around a densely populated industrial zone, hosting a petrochemical complex (Petkim), a petroleum refinery (Tupras), ship-dismantling facilities, several iron and steel plants, and a gas-fired power plant. Five passive sampling campaigns were performed covering summer and winter seasons of 2005 and 2007. Elevated concentrations of VOCs, NO$_2$ and SO$_2$ around the refinery, petrochemical complex and roads indicated that industrial activities and vehicular emissions are the main sources of these pollutants in the region. Ozone concentrations were low at the industrial zone and settlement areas, but high in rural stations downwind from these sources due to NO distillation. The United States Environmental Protection Agency's positive matrix factorization receptor model (EPA PMF) was employed to apportion ambient concentrations of VOCs into six factors, which were associated with emissions sources. Traffic was found to be highest contributor to measured $\sum$VOCs concentrations, followed by the Petkim and Tupras.

Median cancer risk due to benzene inhalation calculated using a Monte Carlo simulation was approximately 4 per-one-million population, which exceeded the U.S. EPA benchmark of 1 per one million. Petkim, Tupras and traffic emissions were the major sources of cancer risk due to benzene inhalation in the Aliaga airshed. Relative contributions of these two source groups changes significantly from one location to another, demonstrating the limitation of determining source contributions and calculating health risk using data from one or two permanent stations in an industrial area.

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1. Introduction

Ambient monitoring of VOCs is a field of increasing interest due to their direct effects on human health and indirect effects on ecosystems through the contribution to formation of ground level ozone. In the presence of NO_x and solar ultraviolet radiation (sunlight), VOCs react with OH radicals to form tropospheric ozone (Atkinson, 2000). They are also involved in aerosol generation (Fuzzi et al., 2006), which can have important visibility and climate implications. Some types at particular concentrations have been linked to various adverse health outcomes such as sore throats and feelings of sickness or dizziness, increase the risk of asthma (ATSDR, 2014), and affect the nervous, immune, and reproductive systems (Ras et al., 2010). Some VOCs such as benzene, 1,3-butadiene, and formaldehyde have also mutagenic or carcinogenic effects after long-term exposure (USEPA IRIS, 2013; Zhang et al., 2012). Vehicular exhaust and industrial emissions, particularly from petroleum industries, are the major sources of anthropogenic VOCs in urban air (Cetin et al., 2003; Watson et al., 2001). Accordingly, determination of VOCs levels together with another ground-level ozone precursor, NOx, and SO_2 in ambient air, especially in heavily industrialized areas, is crucial to understand their influences on human health and urban air quality, and to identify the respective emission sources of these pollutants.

Tools of receptor modeling, such as chemical mass balance (CMB), (Badol et al., 2008), Factor analysis (FA) (Kuntasal et al., 2013) and positive matrix factorization (PMF) (Ling and Guo, 2014) are frequently used to identify VOCs sources and quantify their contributions to atmospheric pollution in urban and industrial areas. In most of these applications receptor models were applied to VOCs data generated in one or two permanent stations. Since source contributions change rapidly with distance from the source in industrial areas with one or more point sources with high VOCs emissions, determining source contributions in one or two locations may not be representative for the whole region. Application of source apportionment techniques to spatially distributed VOCs data is very scarce (Lan et al., 2014; Civan et al., 2011).

Aliaga, a town with population of 70,000, is located approximately 60 km to the north of the metropolitan city of Izmir in Turkey. Aliaga region hosts one of the most important industrial zones in Turkey, consisting of a petroleum refinery and a petrochemicals complex. Approximately 36% of Turkey' crude oil production is processed in Aliaga. Limited number of VOCs including hexane, ethylene dichloride, ethyl alcohol, butyl alcohol, ethyl acetate, butyl acetate, acetone and methyl isobutyl ketone have been previously measured at three locations around petroleum industries at Aliaga by Cetin et al. (2003). Ambient levels of VOCs around petroleum industries were found to be 4–20 fold higher than those around suburban sites in Izmir (Cetin et al., 2003), indicating a strong association between the industrial emissions and VOC levels in the Aliaga airshed. Therefore, it is essential to perform an exhaustive study to better understand the temporal and spatial distribution, sources and health effects of VOCs over an industrial region.

Concentrations of VOCs, SO_2, NO_2, and O_3 were simultaneously measured at 55 different locations in five weekly passive sampling campaigns conducted between December, 2005 and February 2007. The contributions of VOCs, NO_2, and SO_2 sources to local air quality were then assessed using Positive Matrix Factorization (EPA PMF v.3.0) receptor model. Spatial distribution of VOCs and inorganic pollutants (i.e., NO_2, SO_2, O_3) were mapped using a GIS software. Both spatial distribution patterns of VOCs and composition of factors extracted by PMF were used to understand possible sources of VOCs contributing to measured VOCs concentrations in the region. Finally, the cancer risk due to inhalation of benzene by the population living in this area was estimated using the Monte Carlo simulation.

2. Material and methods

2.1. Study area

Passive sampling was performed at 55 sites within the Aliaga region (38.43^0 N and 27.13^0 W) home to an important industrial zone including a petroleum refinery, a petrochemicals complex, iron − and steel plants with scrap iron storage and classification sites, a gas-fired power plant (1100 MW), ship dismantling facilities, transportation of scrap iron from ship dismantling facilities to iron and steel plants, heavy road and rail traffic and several ports. General layout of the study area is shown in Fig. 1.

In order to investigate the spatial distribution of the pollutants in the area, 55 sampling points were selected over a grid system based on their different land-use categories, populations, and traffic and industrial densities. Locations of passive sampling sites, which were classified as rural ($n = 14$), roadway ($n = 16$), industrial ($n = 12$), and residential ($n = 13$), are also illustrated in Fig. 1.

2.2. Meteorology of the region

Meteorological data were obtained from a meteorological station in the Aliaga industrial area. Dominant wind directions in the region are N and NNE (Fig. 1). Approximately 52% of the time winds blow from these directions both summer and winter seasons. Meteorological parameters averaged for each sampling period are in the range of monthly averages (see Table S1 in Supporting Information (SI)).

In this study, both ventilation coefficient and mixing height of the atmospheric boundary layer adjacent to ground were calculated as indicators for the assimilation capacity of the Aliaga airshed (Goyal and Roa, 2007). To calculate hourly mixing height, rawinsonde data measured two times in a day on 00 UTC and 12 UTC by the State Meteorological Service were used as an input to a meteorological processor program (PCRAMMET) developed by the US EPA (USEPA, 1999). Diurnal variations of mixing height and ventilation coefficient in Aliaga atmosphere for the winter and summer periods are depicted in Figure S1 in SI. Mixing height ranged from 920 to 1005 m and from 800 to 1350 m during the days in winter and summer, respectively. Similarly, hourly average ventilation coefficients varied between 3000 and 4800 m^2 s^{-1} in winter and between 4500 and 8600 m^2 s^{-1} in summer. In addition to their diurnal variation, both mixing height and ventilation coefficient showed well-defined seasonal variations. Monthly average mixing height increased from 650 m in November to 1350 m in August, then decreased back to 650 m in November. Monthly variation in ventilation coefficients were similar to those observed in mixing height.

2.3. Sampling, analysis, and quality assurance/qulatiy control (QA/QC)

Ambient VOCs were sampled through stainless steel tubes (6.35 mm O.D. × 88.9 mm; Gradko, England) containing 160 mg Chromosorb 106 adsorbent (Supelco 60−80 mesh). Concurrent VOCs, SO_2, NO_2 and O_3 samples were collected weekly in five sampling campaigns between December 19−27, 2005; March 21−28, 2006; June 19−26, 2006; August 29 -September 5, 2006; and February 9−16, 2007.

Sampling, analytical methods, and QA/QC procedure were discussed in detail by our previous studies (Civan et al., 2012; Yurdakul et al., 2013). The performance characteristics of passive sampling
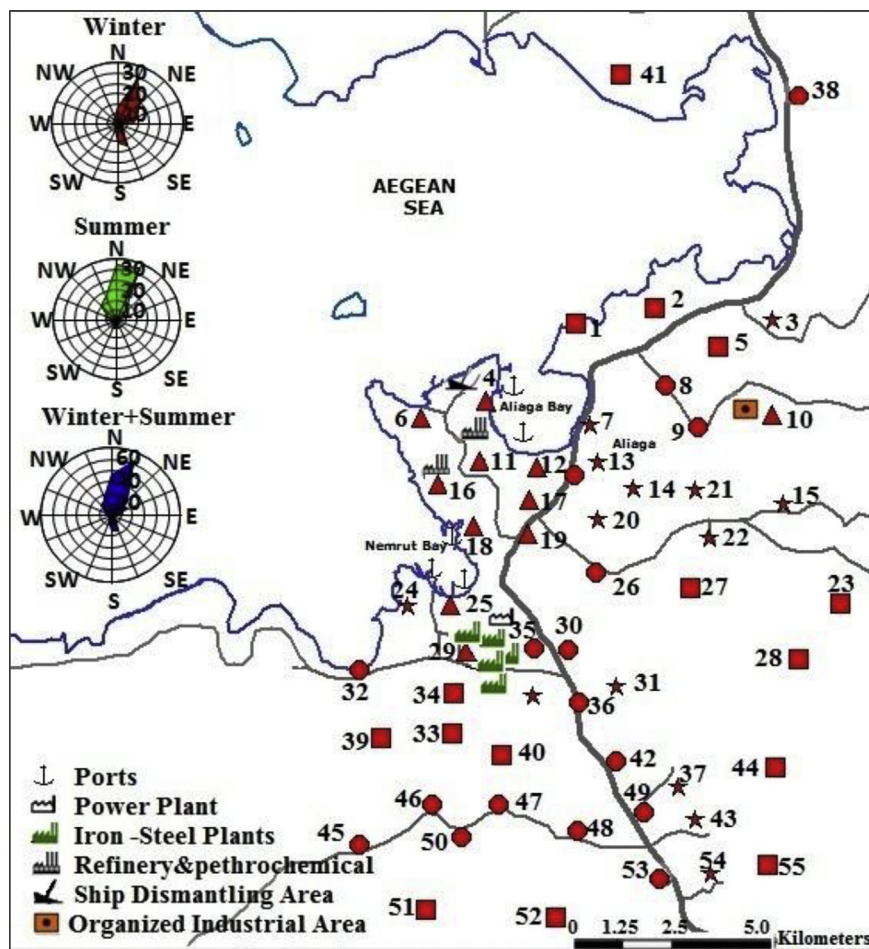
Fig. 1. General layout of the study area demonstrating locations of the sampling points (rural sides: ■, road sides: ●, industrial sites: ▲, residential sites: ★) and possible pollutant sources. Wind roses show the frequency (%) of the prevailing wind directions during the sampling programs.

tube for ambient measurements were evaluated in accordance with EN-13528-&2 protocols (EN-13528-1&2, 2002). The method detection limits (MDLs) of the analytical system ranged from 0.01 (benzene) to 0.17 (1,3,5 trimethylbenzene) µg m^{-3}. The percent relative standard deviation (RSD) values ranged from 1.65 to 9.87 % with an average of 6.92%. Furthermore the masses collected on the blank tubes did not exceed the 6% of average masses collected on sample tubes. A full description of the VOCs sampling and analysis performance evaluations are described in SI.

Thirty-two VOCs including aromatic compounds, olefins, paraffins and halogenated compounds were quantified using a Gas Chromatography equipped with a flame ionization detector (GC-FID, Agilent 6990) coupled to Markes Unity Thermal Desorption (TD) system. The GC oven was programmed to hold at 40 °C for 5 min and ramped to 195 °C at a rate of 5 °C min^{-1}, then again hold at 195 °C for another 10 min. Nitrogen gas, at a flow rate of 5.2 mL min^{-1}, was used as carrier gas.

Diffusion tubes used for SO$_2$, NO$_2$, and O$_3$ sampling were obtained from Gradko Co., UK. Tubes were stored at −4 °C before they were exposed. The labeled tubes and exposure sheets including sampling information (e.g., exposure times, sampling locations) were returned to Gradko for the analysis as soon as possible after sampling.

Concentrations of measured pollutants were calculated using Fick's first law (Gorecki and Namiesnik, 2002). Detailed information on the use of Fick's law to calculate concentrations of VOCs are

given in SI. Experimental uptake rates that were derived for 34 VOCs depending on meteorological conditions (Civan et al., 2012) were used to convert measured analyte mass on adsorbent to atmospheric concentrations of individual compounds.

2.4. Health risk assessment

Among VOCs quantified in the study, benzene was selected as the prominent agent due to its known human carcinogen effect causing leukemia (Rinsky et al., 1987). The health-risk assessment for benzene was conducted using Monte-Carlo (MC) simulation method from slope factors given by the USEPA Integrated Risk Information System (USEPAIRIS, 2013), benzene concentrations from this study, and time-activity data corresponding to different inhalation rates and body weights obtained from the questionnaires, which were applied on the population living in this area. Details on the risk assessment, the statistics methods and the questionnaires are provided in SI.

3. Result and discussion

3.1. Concentrations of VOCs at Aliaga airshed

Ambient levels of the 16 most abundant VOCs, $\sum_{29}$VOCs (sum of the concentrations of 29 individual compounds including 16 most abundant VOCs), and inorganic pollutants measured during each

Table 1
Ambient levels of the most abundant VOCs (n = 16), $\sum_{29}$VOCs, and inorganic pollutants measured at the sampling points (n = 55) for each sampling period (n = 5). The concentrations are given as a range, mean, and median values in μg m⁻³.

Compounds	19–27 December 2005 (1st sampling campaign)			21–28 March 2006 (2nd sampling campaign)			19–26 June 2006 (3rd sampling campaign)			29 August–5 September 2006 (4th sampling campaign)			9–16 February 2007 (5th sampling campaign)		
	Mean	Median	Min–Max	Mean	Median	Min–Max	Mean	Median	Min–Max	Mean	Median	Min–Max	Mean	Median	Min–Max
Hexane	0.74	0.62	0.08–8.8	0.61	0.57	0.11–7.3	0.69	0.69	0.001–0.69	0.19	0.17	0.001–3.47	0.6	0.11	0.008–12.7
Benzene	1.67	0.51	0.13–37.1	1.89	0.82	0.40–45.6	0.31	0.21	0.003–2.20	0.22	0.06	0.002–4.11	1.49	0.5	0.046–33.7
2mhexane	0.63	0.48	0.08–2.49	1.37	0.63	0.12–11.3	0.51	0.36	0.002–0.67	0.83	0.76	0.65–8.7	0.42	0.37	0.001–4.79
3mhexane	1.08	0.89	0.1–9.7	1.15	0.83	0.24–14.2	0.87	0.52	0.04–10.4	0.23	0.12	0.04–4.41	0.29	0.21	0.009–9.06
Toluene	1.46	1.17	0.07–13.56	2.51	1.83	0.02–16.2	1.06	0.6	0.17–9.06	0.51	0.25	0.01–3.97	1.74	0.87	0.14–16.4
n-Octane	0.46	0.28	0.001–5.55	0.62	0.25	0.10–9.4	0.93	0.07	0.005–9.12	0.63	0.09	0.003–7.32	0.47	0.05	0.001–4.13
Ethylbenzene	0.33	0.23	0.02–2.14	0.53	0.37	0.14–4.16	0.16	0.11	0.01–0.83	0.07	0.02	0.001–0.73	0.08	0.02	0.003–0.66
m,p-Xylene	0.6	0.25	0.04–8.97	1.24	0.43	0.05–18.9	0.26	0.1	0.02–1.91	0.17	0.04	0.001–2.31	0.21	0.06	0.003–3.58
Styrene	0.97	0.8	0.004–4.57	1.42	1.22	0.03–6.78	7.33	6.29	0.33–30.6	0.74	0.61	0.02–2.82	0.63	0.29	0.04–2.63
o-Xylene	0.18	0.08	0.006–1.37	0.29	0.1	0.01–4.14	0.21	0.06	0.003–1.65	0.12	0.03	0.001–1.37	0.12	0.02	0.002–1.76
n-Nonane	1.17	0.14	0.001–8.42	0.32	0.13	0.01–5.29	0.56	0.08	0.001–6.68	0.29	0.04	0.001–3.10	0.2	0.03	0.001–1.65
4-Ethyltoluene	0.17	0.1	0.001–0.96	0.18	0.13	0.03–1.31	0.14	0.06	0.003–0.89	0.09	0.06	0.001–0.30	0.07	0.04	0.004–0.20
1,3,5-Tmbenzene	0.17	0.17	0.034–0.46	0.12	0.06	0.02–0.56	0.06	0.02	0.002–0.22	0.03	0.01	0.001–0.11	0.03	0.02	0.004–0.09
2-Ethyltoluene	0.06	0.03	0.006–0.30	0.07	0.04	0.01–0.68	0.08	0.01	0.001–0.67	0.03	0.01	0.001–0.23	0.03	0.01	0.001–0.15
1,2,4-tmbenzene	0.23	0.16	0.005–0.64	0.59	0.54	0.25–1.79	0.29	0.11	0.009–1.78	0.19	0.16	0.02–0.84	0.08	0.02	0.002–0.46
n-decane	0.57	0.33	0.041–3.36	0.39	0.19	0.05–3.80	0.74	0.18	0.002–5.61	0.21	0.07	0.001–1.63	0.27	0.09	0.02–0.88
$\sum$29 VOCs	11.1	9.3	0.87–102.5	23.4	18.5	0.38–132.2	12.7	8.3	0.69–91.6	8.1	6.3	0.14–82.5	5.2	3.7	0.018–80.1
SO2	17.6	11.7	2.18–125	25.8	16.8	2.56–121	20.22	11.61	3.39–152	20.46	13.71	4.53–121	21.7	13.14	3.94–135
NO2	15.8	15	3.84–42.2	23.4	19.2	1.41–166	16.73	14.3	5.28–62.6	15.59	13.94	0.69–47.3	18.12	13.71	4.65–48.1
O3	44.3	48.1	10.2–62.3	56.7	52.1	20.1–97.4	115	119.9	2.31–147	101.6	101.5	59.0–136	61.3	61.8	23.8–82.4

passive sampling period (n = 5) are given in Table 1. Twenty-nine VOCs formed basis for most of the discussions, because they were regularly detected in more than 30% of passive samples (n > 183) collected in this study.

The $\sum_{29}$VOCs concentrations were highly variable, ranging from 0.018 (at rural site no 41, in the 5th sampling period) to 132 μg m⁻³ (at industrial site no 16, which is in the proximity of petrochemical plants, in the 2nd sampling period). In general, toluene, benzene, xylenes, styrene, ethylbenzene, 3-methylhexane, 2-methylhexane, decane, 3-ethyltoluene, and octane were the most abundant compounds among the VOCs studied, accounting for 16%, 15%, 13%, 11%, 10%, 7%, 4%, 4%, 3%, and 2% of the $\sum_{29}$VOCs levels on the average, respectively.

Ambient concentrations of inorganic pollutants also covered a wide range between 0.69 and 166 μg m⁻³ for NO₂, between 2.6 and 152 μg m⁻³ for SO₂, and between 2.3 and 147 μg m⁻³ for O₃. Relatively wide ranges in concentrations of both organic and inorganic pollutants are due to the presence of fairly different environments, extending from industrial areas to unimpacted rural areas. Such high variability in VOCs concentrations between the sampling points also reflected in variations in source contributions, as will be discussed later in the manuscript, and proved to be one of the important advantages of passive sampling in source apportionment studies over permanent stations.

Concentrations of benzene, toluene, ethylbenzene, xylenes (BTEX) compounds measured at the Aliaga industrial zone are comparable to corresponding concentrations reported for industrial areas in Belgium (Yoo et al., 2011), China (Cai et al., 2010), Spain (Ras et al., 2009), Greece (Kalabokas et al., 2001), and France (Badol et al., 2008) (see in Table S6 in SI). However, it should be pointed out that this is only a very crude comparison and values higher than ours can be found in literature. We avoided detailed comparison of data generated in this study with data from literature, because VOCs concentrations found in any study depends, very strongly, on the distance between sampling location and VOCs sources, such as roads or point emissions from industries.

3.2. Spatial distribution of VOCs and inorganic gases

Spatial distribution maps of VOCs and inorganic pollutants were prepared by interpolating their concentrations, measured at 55 sites, using a GIS software (Mapinfo, Professional, version 7.5). Mapping was performed both for individual sampling periods and also by using median values of five data at each sampling point. Although concentrations of species varied seasonally, distribution patterns were not significantly different. Interpolated distributions of median concentrations of selected VOCs are depicted in Fig. 2. Distributions clearly signify the influence of the emissions from Tupras (refinery) and Petkim (petrochemical complex) on measured VOCs concentrations in the study area. The highest concentrations were observed in the peninsula where the refinery and petrochemical plants are located. This is true not only for the BTEX compounds shown in Fig. 2, but also for most of the VOCs measured in this study. Spatial distribution patterns are different from those for VOCs were obtained for inorganic pollutants. Although refinery and petrochemical industries are important sources for SO₂, precursors of NO₂ and O₃, contribution of these industries on their distributions are not as dominating as in distributions of VOCs concentrations. High concentrations of NO₂ were observed around Izmir − Canakkale highway and at the intersection of that the highway with the Aliaga − Foca road. Median NO₂ concentrations as high as 46 μg m⁻³ were measured in this area (at sites 29 and 30). Contribution of traffic emissions on NO₂ distribution in the region is fairly obvious from the figure. However, it should be noted that the intersection of the two roads
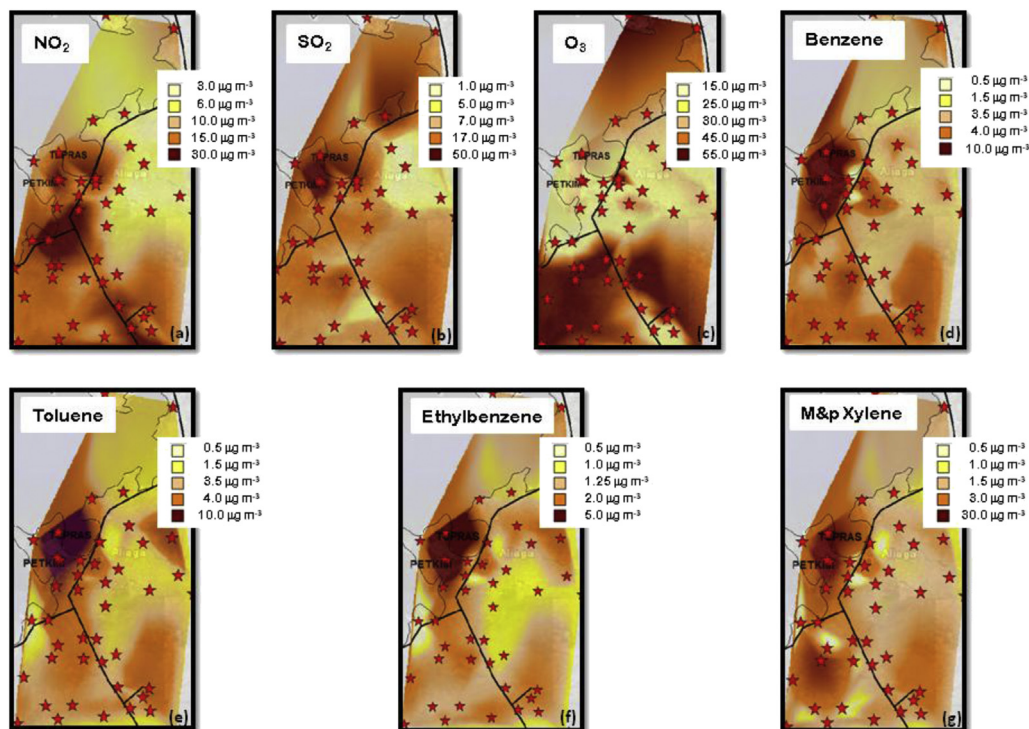
Fig. 2. Interpolated spatial distributions of median concentrations of inorganic pollutants and BTEX compounds in the study area.

where the highest NO_2 concentrations were measured is also the industrial area, where six iron and steel plants are located. Although it is not possible to resolve relative contributions of these plants and traffic on high concentrations of NO_2 measured in those two stations from Fig. 2a, traffic turned out to be the main NO_2 source in the PMF study that will be discussed later in the manuscript.

The refinery and the petrochemical plants are important sources of SO_2 in the area. However, contribution of these industries to SO_2 distribution in the study area was not as dominating as their contribution to distributions of VOCs. Relatively high SO_2 concentrations were also observed at stations, which are close to settlement areas, such as the city of Aliaga and several villages.

Distribution of O_3 concentrations are depicted in Fig. 2c. Ozone concentrations are low in the industrial zone, at the city of Aliaga, and around major roads, but high to the south of the study area, which is downwind from the industrial zone. Similar distribution, with low ozone concentrations at polluted areas and higher concentration at neighboring suburban and/or rural areas has been frequently reported in literature (Wang et al., 2006; Xu et al., 2011) and explained by ozone distillation (O_3 + NO reaction), which inhibits ozone built up at polluted atmosphere with high NO concentrations (Wang et al., 2006; Yang et al., 2011).

Distribution patterns observed in SO_2 and NO_2 concentrations demonstrated a significant change in their sources since 1992. Concentrations of SO_2 and NO_2 were measured on an hourly basis at 7 locations in Aliaga region in a one-year-long monitoring program conducted in 1991. Two of these stations were located at the same point with two passive sampling sites used in this study. One of the stations used in 1991 study was located in the vicinity of the Horozgedigi village, which is located at approximately 7 km to the south of Petkim and Tupras (station number 34 in Fig. 1) and the second one is the Turkelli village, which is located approximately 15 km to southeast of Petkim and Tupras (station number 54 in Fig. 1). Annual average of SO_2 and NO_2 concentrations at

Horozgedigi station in 1991 were 57 ± 42 and 9.1 ± 13 μg m^{-3}, respectively. Those measured in this study at the passive sampling station in 2006, which is approximately at the same location are 22 ± 1.2 μg m^{-3} and 16 ± 3 μg m^{-3}, respectively. A similar trend was also observed at Turkelli station. Concentrations of SO_2 and NO_2 measured in 1991 were 33 ± 38 μg m^{-3} for SO_2 and 7 ± 12 μg m^{-3} for NO_2. Those in 2006 at the same site were 12 ± 5 and 15 ± 12 μg m^{-3}, respectively. Similar variations observed in both stations suggest that SO_2 concentrations decreased and NO_2 concentration increased in last 20 years in Aliaga region. The increase in NO_2 concentrations is probably due to the increase in number of motor vehicles in the last 20 years.

The decrease in SO_2 concentrations between 1991 and 2005 is due to change in mode of energy production. Main source of energy for the industries in Aliaga region was oil and coal combustion in 1991 (electricity for iron and steel plants). However, the situation had changed after year 2000 natural gas replacing both coal and oil as an energy source, which reduced SO_2 emission in the area. Similar variations in two stations that are approximately 7 km apart suggest that changes in fuel type in industries affected SO_2 levels not only in the industrial zone, but it reduced SO_2 concentrations in the whole Aliaga region.

Sampling sites were grouped into four categories as industrial, residential, traffic-impacted, and rural, depending on their locations relative to the main emission sources in the study area (See Fig. 1). Concentrations of VOCs averaged for each group are given in Table 2. Highest concentrations were observed in the industry group while the lowest concentrations were generally associated with rural stations. Although these were consistent with expected patterns, VOCs concentrations measured in the industrial stations were not as high and concentrations measured in rural stations were not as low as expected. These inconsistencies between expected and observed concentrations were due to strong influence of anthropogenic sources to some, but not all of the rural stations and lack of VOCs emissions from all industrial sources. This is

Table 2
Mean concentrations (μg m^{-3}) of the BTEX compounds and inorganic pollutants measured at the sampling sites in Aliaga classified depending on the characteristics of the locations.

Pollutants	Industry		Residential areas ($n = 13$)	Roadsides ($n = 16$)	Rural areas	
	Petroleum refinery and petrochemicals complex ($n = 9$)	Iron-steel industries ($n = 3$)			Downwind ($n = 8$)	Upwind ($n = 6$)
Benzene	4.7 ± 9.9	0.42 ± 0.28	0.68 ± 0.68	0.53 ± 0.51	1.9 ± 8.4	0.36 ± 0.23
Toluene	3.9 ± 4.1	1.2 ± 0.71	1.6 ± 1.1	1.1 ± 0.93	3.9 ± 16.8	0.74 ± 0.55
Ethylbenzene	0.99 ± 1.0	0.13 ± 0.13	0.25 ± 0.17	0.39 ± 0.60	0.66 ± 4.3	0.12 ± 0.12
m + p-Xylene	2.0 ± 4.0	0.20 ± 0.18	0.31 ± 0.28	2.0 ± 3.3	0.77 ± 3.0	0.15 ± 0.15
o-Xylene	0.76 ± 0.92	0.08 ± 0.08	0.16 ± 0.13	0.06 ± 0.06	0.20 ± 0.73	0.06 ± 0.06
SO$_2$	54 ± 44.5	18.8 ± 8.3	29.4 ± 10.0	16.0 ± 10.4	13.9 ± 14.6	14.6 ± 8.2
NO$_2$	20 ± 11.1	21.0 ± 9.9	26.5 ± 6.2	20.6 ± 16.8	6.9 ± 2.5	11.7 ± 4.4
O$_3$	75.3 ± 33.0	67.1 ± 32.1	77.4 ± 36.5	74.8 ± 34.0	81.8 ± 33.6	83.5 ± 32.8

confirmed in Table 2, where industrial stations were divided into two subgroups, including sampling points close to Petkim and Tupras and stations in the vicinity of iron and steel plants. Similarly, rural stations were also divided into two groups as upwind and downwind of the industrial area. Concentrations of BTEX compounds were high in the stations located around Petkim (petrochemical complex) and Tupras (refinery) and low around iron and steel plants. Note that VOCs concentrations around the iron and steel plants were lower than those around residential areas and roads. This also explains why average VOC concentrations, in "industrial" subgroup are not as high as expected.

There is also large difference between VOC concentrations measured in the rural stations that are downwind and upwind from Petkim and Tupras (see Table 2). Concentrations of almost all of the VOCs including BTEX compounds were found to be higher in the rural stations that are downwind from industrial zone, when compared with those corresponding levels at the rural stations that are upwind from industrial zone.

Similar results were obtained for inorganic gases as well. Concentrations of SO$_2$ were high around Petkim and Tupras, but low in iron and steel zone, because electricity is the mode of energy used in all iron and steel plants. Note that average SO$_2$ concentration in residential stations was 29 μg m^{-3}, which was higher than average concentrations measured in road-side, rural stations, and stations located in and around iron and steel plants. This was significantly different from the situation 20 years ago, when SO$_2$ concentrations in whole region were dominated by strong emissions from Petkim and Tupras complexes.

Concentrations of NO$_2$ were approximately at the similar level in industrial, traffic-impacted, and residential sites, but low in rural stations, both upwind and downwind from industrial zone, demonstrating that industries are not strong sources of NO$_2$ in Aliaga region. This result is consistent with the NO$_2$ distribution map discussed earlier in the manuscript.

3.3. Temporal variation of VOCs and inorganic gases

Two of the sampling campaigns were performed in summer months (June and August) and two during winter season (December and February) to evaluate seasonal variations in concentrations of VOCs, NO$_2$, SO$_2$ and O$_3$. Average summer and winter concentrations of measured parameters and their winter-to-summer concentration ratios are depicted in Fig. 3. Winter-to-summer concentration ratios of VOCs vary between ~5 for dodecane and 0.7 for undecane.

For twenty out of twenty-nine VOCs, winter concentrations were higher than summer concentrations. Concentrations in the two seasons were comparable for the remaining five compounds. This pattern is partly due to meteorology, which favors higher

pollutant concentrations in winter season, owing to reduced mixing height and ventilation coefficient (Chou et al., 2007; Parra et al., 2009) and partly due to enhanced photochemical degradation of VOCs in summer season (Hoque et al., 2008).

It should be noted that, since concentrations of a pollutant was expected to be higher in winter if its emission rate would not change between summer and winter seasons due to meteorology. Several VOCs that had comparable concentrations in both seasons and the ones with slightly higher concentrations in summer, including 3-methylhexane, o-xylene, 1,2,4-trimethylbenzene, n-octane, and undecane, likely due to the increase vehicular emissions, as Aliaga is on the road that connect Izmir, which has a metropolitan population of 3.5 million, to holiday resorts on the Aegean coast of Turkey, and evaporative emissions during summer.

Similarly, summer and winter concentrations were found to be at comparable levels for NO$_2$ and SO$_2$, probably due to increased traffic-related NOx emissions during summer (Fig. 3). Ozone was the only pollutant that had significantly higher concentration in summer. Winter to summer concentration ratio for ozone was 0.1, as a result of its enhanced photochemical production with increased solar flux in summer.

3.4. Source apportionment

Positive Matrix Factorization receptor model (EPA PMF v.3.0) was employed to apportion contributions of possible sources on VOCs, NO$_2$, and SO$_2$ concentrations measured at 55 locations in Aliaga. Median concentrations of individual pollutants measured at each station during 5 sampling periods were used as inputs to the PMF model, since the chi-square test indicated that most of the 29 VOCs measured in this study were log-normally distributed with 95% or higher confidence. Uncertainties for each data point were set to 5% of the measured concentration plus MDL. Data below MDL were substituted with MDL/2 and their uncertainties were set as 5/6 of the detection limits. The missing data were substituted with median concentrations and their uncertainties were set as 4 times the geometric mean values (Polissar et al., 2001). The weak and bad variables identified by the signal/noise (S/N) ratios need to be down-weighted to reduce their effects on the solution (Paatero and Hopke, 2003). The "weak" variables were downweighted appropriately in the analysis, while "bad" variables were omitted from the analysis. A total of 27 species were used in the data analysis while seven species (2methylhexane, 3methylhexane, 1,3,5-trimethylbenzene, 1,3-dichlorobenzene, benzylchloride, 1,4-diethylbenzene and ozone) having very low S/N (⩽0.2) were excluded from the PMF analysis by assigning to their category as "bad".

Model optimization was based on an analysis of residuals, the difference between theoretical Q (Q$_{th}$) and calculated Q (Q$_{calc}$)
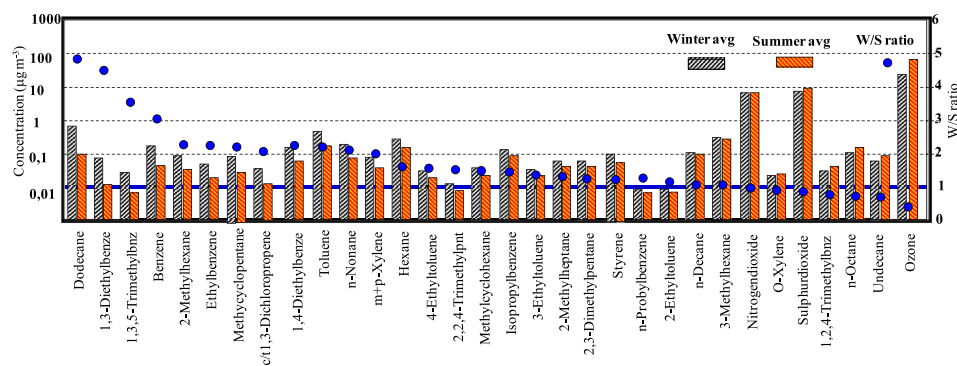
Fig. 3. Winter and summer concentrations and winter-to-summer ratios of measured parameters.

values, calculated uncertainties, and physical interpretability of the factors and contributions. The model was run 20 times with a random seed to determine the stability of goodness-of-fit values; the Q values were stable (see Figure S2 in SI). Calculated Q values were minimized by running the model with random seed values (Belis et al., 2013) and trying to keep scaled residuals within 0 ± 2 (Li et al., 2013). Most of the residuals were within the range and running the model with different seed values had fairly limited effect on Q_{th}. The most influential factor to reduce the Q_{th} was to increase the number of factors retained. However, running the model with more than six factors violated the interpretability criteria. Finally six factor solutions were found to be the most appropriate.

Fig. 4 shows the factor loadings, which represent concentrations of species in each factor and percent contribution of factors to concentrations of species, corresponding to "explained variance" in conventional factor analysis. Beside average G-scores of VOCs from urban, industrial, roads and rural stations are depicted at different graphs in the same figure. Since (G) scores of each factor represent the source contributions, samples with high factor scores, for a particular factor, are expected to be closer to the emission source or sources represented by that factor (Guo et al., 2004a). Spatial distributions of factor scores for each source mapped out using a GIS software (MapInfo with Vertical Mapper) are depicted in Fig. 1.

Factor 1 isolated by PMF accounts for large fractions of the concentrations of most heavy hydrocarbons including 1,2,4,5-tetramethylbenzene, dodecane, 2-ethyltoluene, and ethylbenzene (Fig. 4a). Heavy hydrocarbons are shown to be good markers for exhaust emissions from heavy duty vehicles with diesel engines (Liu et al., 2008). Average factor 1 scores are the highest in sampling points in the proximity of roads, as shown in Fig. 4b. There is a dense transportation activity of trucks carrying scrap iron between the ship dismantling facilities and iron-steel plants in the industrial zone, as well as a dense traffic on the highway and on the main roads. Contribution of roadway emissions to spatial distribution of factor 1 scores is also clear in Fig. 5a. With all these considerations, factor 1 was identified as "diesel exhaust", representing emissions from heavy vehicles with diesel engines operating in the study area.

Factor 2 is heavily loaded with styrene. The factor accounts for approximately 70% of the measured styrene concentration and approximately 20% of the concentrations of some of the heavy hydrocarbons, such as 3-ethyltoluene, trimethylbenzene and n-decane (Fig. 4c). Styrene is the best known monomer in plastic industry (Miller et al., 1994). The petrochemical complex in Aliaga is expected to be its main source. However, average factor 2 scores were found to be fairly low in sampling locations around petrochemical complex and refinery, and high in and around residential locations (Fig. 4d). High factor 2 scores around the town of Aliaga

and villages are also obvious in Fig. 5b. The reason for low factor 2 scores at sampling stations around the petrochemical complex is probably due to the lack of styrene production during this study. There is a styrene plant in the Petkim complex, which produces styrene monomer for other plants in the complex, but it was not operational during our sampling campaigns. Factor 2 scores were high in residential areas probably because of the emissions from styrene sources, such as, new plastic materials that are produced from styrene monomer (Lithner et al., 2009), thermal degradation of used plastic ware that contains styrene monomer (Miller et al., 1994), and photocopiers (Henschel et al., 2001). High styrene emissions and a similar styrene factor were also found at an urban site in Bursa (Yurdakul, 2014). Thus, factor 2 was identified as a styrene source representing "domestic activities in settlement areas" in the Aliaga region.

Factor 3 was characterized by its high fractional contribution to BTEX compounds, 2,3 dimethylpentane, methylcyclohexane, n-octane, n-nonane, and n-decane (Fig. 4e). In an urban atmosphere gasoline-powered light duty vehicle traffic emissions is the dominating source of BTEX compounds (Baltrenas et al., 2011). However, petroleum industries, particularly refineries are also strong sources of not only BTEX compounds, but also heavy hydrocarbons that are associated with factor 3 (Song et al., 2008). Higher average factor 3 scores in refinery category in Fig. 4f, and very high scores found in the peninsula where petrochemical complex and refinery is located in Fig. 5c also supports that factor 3 is associated with emissions from the refinery and petrochemical complex.

Doğan (2013) placed an online GC-FID system between the refinery and petrochemical complex and monitored concentrations of approximately 60 VOCs continuously with 30 min resolution for 15 days. He then generated separate VOCs profiles for both the refinery and petrochemical plants by relating measured data with wind direction during measurements. We compared factor 3 loadings with the refinery and petrochemical profiles generated by Doğan (2013). The regression plots between factor 3 profile and profiles generated by Doğan (2013) are given in Fig. 6a and b. Statistically significant R^2 values for the linear regression between factor 3 profile and the Petkim ($R^2 = 0.43$, P[r,n] < 0.05) and Tupras ($R^2 = 0.52$, P[r,n] < 0.05) profiles also support the hypothesis that factor 3 is associated with "emissions from Tupras refinery and Petkim petrochemical complex" in Aliaga region.

Factor 4 accounts for approximately 50% of methylcyclopentane concentration and 20%–40% of the concentration of hexane, methylcyclopentane, 2-methylhexane, 2,3-dimethylpentane, 2,2,4-trimethylpentane, toluene, 2-methylheptane, and n-nonane (Fig. 4g). These C_4–C_6 compounds are solvents used in various industrial activities (Borbon et al., 2002). This is supported by relatively high average factor 4 score in the refinery category in Fig. 5d,
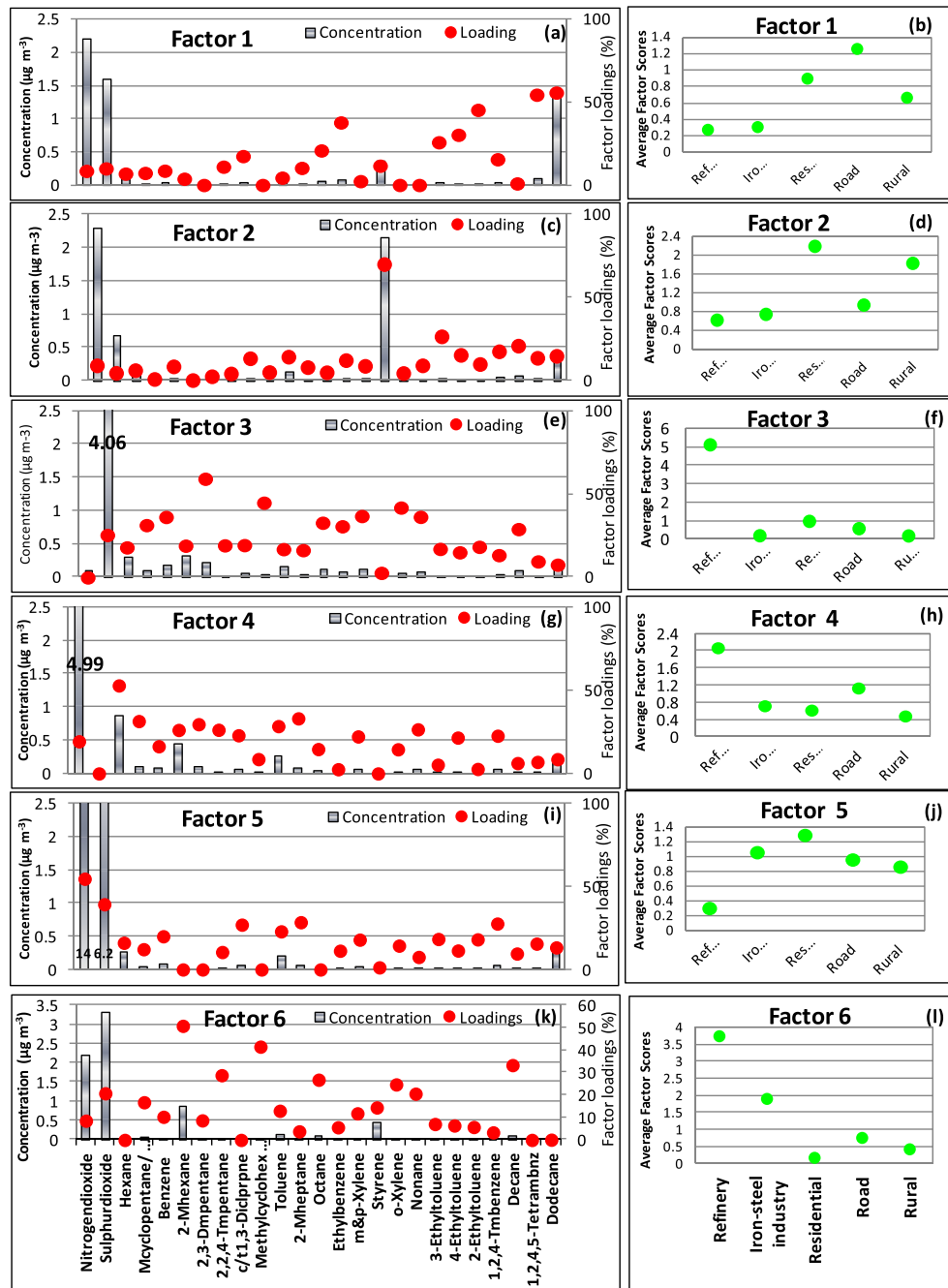
Fig. 4. Factor loadings, fractions of VOC concentrations accounted by factors and average scores for different station categories generated in PMF exercise.

and high factor 4 scores at the peninsula where refinery and petrochemical complex are located, as shown in Fig. 4h. Linear regression between factor 4 loadings and refinery and petrochemical plant profiles generated by Doğan (2013) demonstrated that factor 4 correlates well with petrochemical profile $R^2 = 0.73$, P [r,n] < 0.05) but does not correlate as well with the refinery profile. This factor is identified as "petrochemical" factor.

Factor 5 is loaded with well documented gasoline markers, such as, benzene, toluene, ethylbenzene, xylene, NO_2 and SO_2 (Fig. 4i). Average values of factor 5 scores for different station groups are given in Fig. 4j, which indicate that average factor 5 scores are low in refinery − petrochemical category, and high in all other station groups. Particularly high values of factor 5 scores are found in the

city of Aliaga and in the part of the study area where most of the iron-and steel plants are located, as shown in Fig. 5e. These VOCs are not expected to be emitted from iron and steel plants. High values of factor scores around iron and steel plants are probably due to presence of roads with heavy traffic in the same area. Composition of the factor 5 (loadings) were compared with two light duty vehicle exhaust profiles from USEPA SPECIATE database (profile IDs 2536 and 2538) (USEPA, 2006). Correlations between factor 5 loadings and SPECIATE profiles were reasonably good ($R^2 = 0.77$, P [r,n] < 0.05 with profile 2536 and $R^2 = 0.67$, P[r,n] < 0.05 for profile 2538). Consequently, factor 5 was identified as "gasoline vehicle exhaust emissions" in the study area.

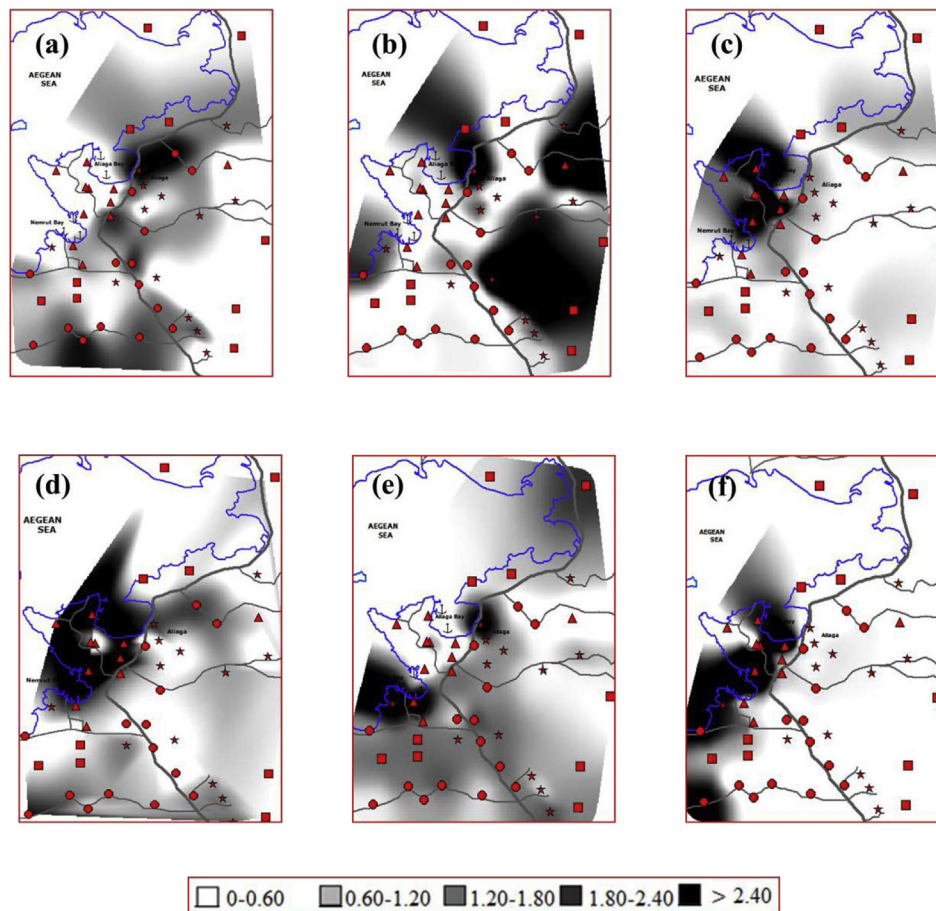Factor 6 accounts for a >20% of the measured concentrations of 2

Fig. 5. Spatial distributions of PMF factor scores of (a) Factor 1, (b) Factor 2, (c) Factor 3, (d) Factor 4, (e) Factor 5, (f) Factor 6.

methylhexane, 2,2,4-threemethylpentane, methylcyclohexane, n-octane, o-xylene, n-nonane, and n-decane (Fig. 4k). It is difficult to assign a specific source for factor 6, by looking to these VOCs, because they are associated with a variety of sources including vehicle exhaust (Liu et al., 2008), various domestic activities (Guo et al., 2004a), gasoline evaporation (Yamada, 2013), solvent evaporation (Watson et al., 2001), surface coatings (Afshari, 1999), and diesel exhaust (Srivastava et al., 2005). Although VOCs included in factor 6 are not ideal source tracers, their spatial distributions shown in Figs. 4l and 5f provide information on potential sources of this factor. Average factor 6 scores were significantly higher in Petkim- Tupras category and iron and steel category, but low in road, residential, and rural categories. Similarly, distribution map for factor 6, which is given in Fig. 5f depict high scores in both of the industrial zones, where petrochemical plants, refinery, and iron — steel industries are located. Furthermore factor 6 profile showed statistically significant correlation (within 95% confidence level) with the refinery profile (Doğan, 2013) but not with the petrochemical profile. Therefore, this factor was attributed to emissions originated from "petroleum refinery and iron-steel industries".

Contributions of 6 factors extracted by the PMF model to the measured VOC, NO$_2$, and SO$_2$ concentrations are illustrated in Fig. 7. PMF exercise revealed that light and heavy duty vehicle exhaust emissions were the highest contributors to VOCs levels in the area, accounting for 50% of the measured $\sum_{29}$VOCs concentration. Industrial activities, particularly petrochemical industries and refinery were the second highest contributors. These two industries account for approximately 40% of the total VOC levels in the study

area. However, it should be pointed out that contribution of each factor to measured VOC concentrations showed dramatic differences depending on the receptor location. Although traffic emissions were the highest contributor on the average, contribution of Petkim and Tupras were much higher than light and heavy duty traffic emissions in the sampling points located that are in the vicinity of these facilities. Strong variability of VOCs concentrations around industries is expected and documented in the literature (Parra et al., 2009; Civan et al., 2011), which is due to strong spatial variations in source contributions around industries. This highlights the most important advantage of determining source contributions using spatially distributed passive sampling data over assessments based on data generated at few permanent stations. Source contributions determined from one or two permanent stations would probably not be representative for the study area where VOCs concentrations and source contributions show such strong spatial variability. Iron and steel industries turned out to be insignificant VOCs sources as expected and emissions from domestic activities in villages were important only in their very close proximity.

3.5. Lifetime carcinogenic risk estimation for benzene

A life-time cancer risk assessment was conducted for benzene based on measured concentrations and data obtained from two questionnaires. One of the questionnaires was to generate time–activity data, and the second one to generate demographic–personal data for people living at the Aliaga region. Details of
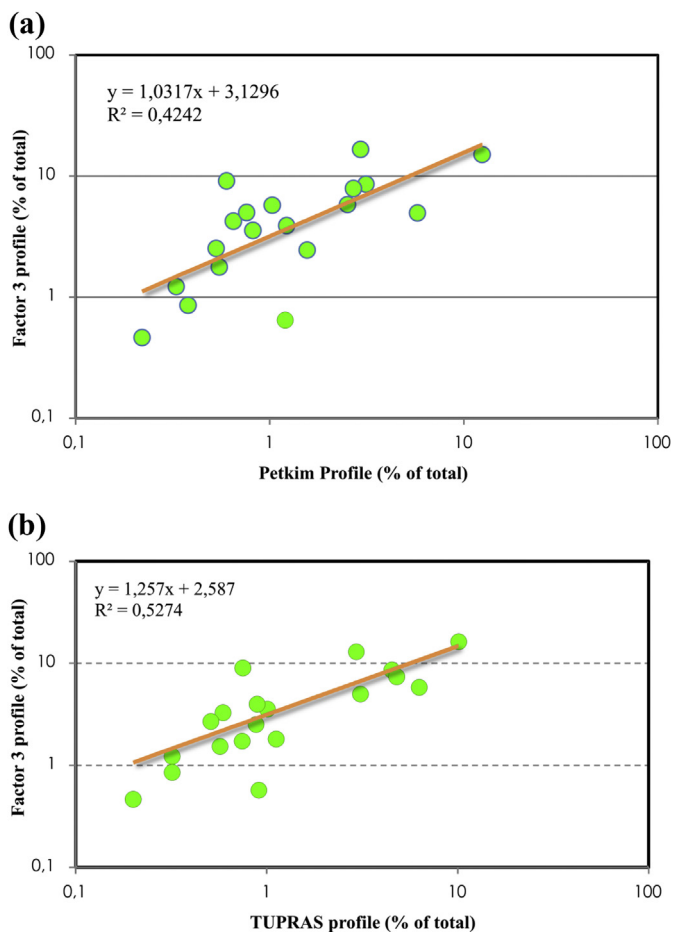
(a)

$y = 1,0317x + 3,1296$
$R^2 = 0,4242$

(b)

$y = 1,257x + 2,587$
$R^2 = 0,5274$

Fig. 6. Comparison of factor 3 profiles with profiles generated for a) Petkim and b) Tupras.

benzene are given in Fig. 8. Mean, median, standard deviation of the distribution and the 95th percentile level are marked on the graph.

The mean and median carcinogenic risks were 12.9 and 3.7 per one million population. These risks can be compared with USEPA benchmark value of 1 per one million population. The difference between median and mean estimates pointed out the distribution of the carcinogenic risks was skewed (Zhou et al., 2011), which is probably due to lognormal distribution of benzene concentration. The estimated mean carcinogenic risk levels are within the range of those calculated based on ambient measurements in Bejing, China (Zhang et al., 2012), in Seattle, USA (Wu et al., 2009), and in Portland, USA (Tam and Neuman, 2004) which were reported as 15.3, 8.8, and 41.9 per one million, respectively. It should be noted that, like benzene concentration, carcinogenic risk due to benzene inhalation also showed large spatial differences between sampling points. It was significantly higher in the regions close to Petkim and
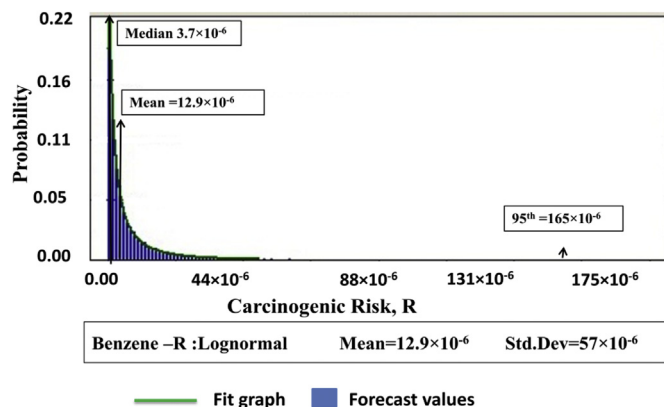

Fig. 8. Statistics, frequency and fitted distributions of cancer risk for benzene.

Fig. 7. Pie chart illustrating the contributions of 6 factors isolated by the model to receptor VOCs, NO$_2$, and SO$_2$ levels averaged for the sampling periods.

these questioners are given in SI. Statistical evaluation of questionnaire data showed that people living in the study area spend 79% of their time within buildings for purposes, such as, living, working, resting and studying. This percentage is fairly similar with the corresponding values reported by Guo et al. (2004b) and Dodson et al. (2007) for people living in urban locations in Hong Kong and in sub-urban/urban locations in Boston, US, respectively. The participants naturally ventilated their indoor environment by opening the windows for 176 min/day, on average.

The lifetime cancer risk for benzene was estimated using Monte Carlo simulation method. Probability distributions of cancer risk for

Tupras, but lower than calculated average risk in stations far from industries and roads. The PMF modeling results demonstrated that 68% of benzene concentrations in the study area is due to emissions from Petkim and Tupras, suggesting that at least half of the cancer risk due to inhalation of benzene can be attributed to these two plants.

4. Summary and conclusion

Spatial and temporal variations of concentrations of 32 VOCs, NO$_2$, SO$_2$ and O$_3$ were determined at Aliaga, Turkey, which is a

densely populated industrial zone on the Aegean cost of Turkey, using passive samplers. Fifty-five passive sampling tubes were placed in approximately 30 km × 30 km study area. Distribution maps of measured compounds were prepared by interpolating VOCs concentrations at each sampling station using a GIS software. High concentrations of SO_2 and most of the VOC were observed in the industrial zone where petrochemical complex and the refinery are located. Concentrations of NO_2 and some of the BTEX compounds were also high around major roads. Ozone concentrations were the highest at rural stations that are not under direct influence of any source. This is attributed to destruction of O_3 by NO in places where NO concentration is high (also known as NO distillation).

Concentrations of most of the VOCs were high during winter season due to lower mixing height. However, this observation was not true for all VOCs. Compounds that have evaporative sources and those of which generation depends on solar flux (like O_3) have higher concentrations in summer season, or comparable concentrations in both seasons.

The PMF was run after averaging data from five campaigns at each station. Six factors that were associated with emissions from heavy duty vehicles (diesel emissions), emissions from domestic activities in settlement areas, combined emissions from Tupras and Petkim, emissions from Petkim, gasoline exhaust and emissions from Petkim and iron and steel plants, were extracted by the model. Among these, traffic emissions (light and heavy duty vehicles) were the largest contributor to the measured VOC concentrations, accounting for approximately 50% of the total VOCs concentrations. Tupras and Petkim accounted for approximately 40% of $\sum_{29}$VOCs. Remaining 10% is accounted for by factor 2, representing domestic activities in towns and villages in the Aliaga region.

Distribution of factor scores suggested that source contributions are highly variable, depending on the distance between the receptor site and point sources. Consequently, although contribution of traffic to the measured VOCs concentrations were higher than combined contributions of Petkim and Tupras on the average, contributions of these facilities were dominating in the peninsula where they are located. We believe that this is an important advantage of determining source contributions with a spatially distributed data, because sources and source contributions calculated with data generated at one or two permanent stations does not represent the whole area. More control measures should be developed to mitigate the VOCs and inorganic pollutants resulting from these two clusters of sources, namely Petkim and Tupras.

Potential cancer risk at Aliaga region, due to inhalation of benzene was calculated using a probabilistic approach, based on the assumption of lifetime exposure to benzene. Hence calculated risk was probably to be underestimated mainly as only limited number of species was monitored and there were no indoor measurements that should be included in data set. The mean and median carcinogenic risks of benzene were 12.9 and 3.7 per one million population. Based on the source apportionment results the petrochemical complex and refinery found to be largest contributors (67%) to the benzene concentration in the region, followed by vehicular exhaust (27%). Despite a possible underestimation, the estimated risks still exceeded the acceptable level, suggesting that the pollutants with health hazards in this region are worth further investigation. The source apportionment and estimated lifetime cancer risk results presented in the paper can provide the guidance for future health risk managers to design the risk reduction strategy more effectively.

Acknowledgement

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2014.12.031.

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