Atmospheric BTEX concentrations in the vicinity of the crude oil refinery of the Baltic region

Pranas Baltrėnas · Edita Baltrėnaitė · Vaida Šerevičienė · Paulo Pereira

Abstract Among chemical industries, petroleum refineries have been identified as large emitters of a wide variety of pollutants. Benzene, toluene, ethylbenzene, and xylene (BTEX) form an important group of aromatic volatile organic compounds (VOCs) because of their role in the troposphere chemistry and the risk posed to human health. A very large crude oil refinery of the Baltic States (200,000 bbl/day) is situated in the northern, rural part of Lithuania, 10 km from the town of Mažeikiai (Lithuania). The objectives of this study were: (1) to determine of atmospheric levels of BTEX in the region rural and urban parts at the vicinity of the crude oil refinery; and (2) to investigate the effect of meteorological parameters (wind speed, wind direction, temperature, pressure, humidity) on the concentrations measured. The averaged concentration of benzene varied from 2.12 ppbv in the rural areas to 2.75 ppbv in the urban areas where the traffic was determined to be a dominant source of BTEX emissions. Our study showed that concentration of benzene, as strictly regulated air pollutant by EU Directive 2008/50/EC, did not exceed the limit of 5 ppbv in the region in the vicinity of the crude oil refinery during the investigated period. No significant change in air quality in the vicinity of the oil refinery was discovered, however, an impact of the industry on the background air quality was detected. The T/B ratio (0.50–0.81) that was much lower than 2.0, identified other sources of pollution than traffic.

Keywords Air quality monitoring · BTEX · Crude oil refinery · Passive samplers · PCA · VOCs

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Introduction

In modern societies, the introduction of pollution mitigation measures has progressively reduced the amount of chemicals released into the environment. However, the industrial sector is still an important source of environmental pollutants and thus modern environmental technologies are applied there (Baltrėnas and Zagorskis 2009). Among chemical industries, oil refineries have been identified as large emitters of a wide variety

of pollutants (Nadal et al. 2009). Organic micro-pollutants such as volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs) or polychlorinated biphenyls (PCBs) have been found in ambient air near petrochemical industries (Lee et al. 1996; Pandya et al. 2006; Rao et al. 2008). VOCs, mainly hydrocarbons, originate from production processes, storage tanks, transport pipelines and waste areas (Kalabokas et al. 2001; Cetin et al. 2003; Rao et al. 2007; Ulman and Chilmonczyk 2007). Typical compounds from petrochemical industries are: methane, ethane, propane, benzene, toluene, and xylene (Crosby 1998). In addition, oil refineries are associated with the emission of sulphur compounds, nitrogen oxides and particulate matter (Kalabokas et al. 2001; Cetin et al. 2003; Rao et al. 2007; Ulman and Chilmonczyk 2007).

The crude oil refineries have been linked to an increase of environmental pollution, as well as some adverse health effects for workers and people living nearby. A link between the presence of oil refineries and a varied symptomatology, including respiratory problems, leukemia, birth defects and adverse pregnancy outcome (preterm delivery) in nearby areas has been reported elsewhere (Yang et al. 2004; Park et al. 2006; Yu et al. 2006). Short-term exposure to particular concentrations of some VOCs present in the air is not considered acutely harmful to human health, however, long-term exposure may result in mutagenic and carcinogenic effects. Classic neurological symptoms associated with VOCs are fatigue, headaches, dizziness, nausea, lethargy and depression (ATSDR 1995; Weschler and Shields 1997; Rumchev et al. 2004; Baroja et al. 2005; Ulman and Chilmonczyk 2007). Moreover, benzene and tetrachloroethene have been identified as powerful carcinogenic agents by the World Health Organization (WHO) (Srivastava et al. 2005). A United States study emphasized that ambient VOCs attribute to 35–55% of the outdoor air cancer risk in the United States (US EPA 1990).

Several VOCs (benzene, toluene, ethylbenzene, xylene, isoprene, i, l, n-pentene) are also precursors of ground-level ozone formation (Finlayson-Pitts and Pitts 1993), and they are mainly emitted in areas of intense transport and industrial activity (Payne-Sturges et al. 2004). Today, European air quality standards set the maximum level of benzene, which is 5 μg m^{-3} since January 2010 (EC Directive 2008).

Benzene, toluene, ethylbenzene, and xylene (BTEX) form an important group of aromatic VOCs because of their role in the troposphere chemistry and the risk posed to human health (Hoque et al. 2008). In urban areas, BTEX constitute up to 60% of nonmethane VOCs (Lee et al. 2002). In the process of long-range transport, BTEX are among other VOCs that react with other pollutants such as NO$_x$ and produce secondary pollutants with different reaction rates. Highly reactive species react near the vicinity of the emission sources, while slow reacting ones may be transported to a longer distance from the sources (Srivastava et al. 2005). m- and p-xylene occurs naturally in petroleum. o-Xylene is found in coal tar, petroleum, forest-fire smoke-emissions and plant volatiles (Howard 1990).

When investigating significant sources of BTEX in an industrial city, field measurements of airborne BTEX concentrations would be essential to evaluate the emission sources and characterization of the source. Characteristic ratios of BTEX became gradually useful in identifying emission sources, age of air masses or characterizing the health impact (Ho et al. 2004; Hoque et al. 2008; Liu et al. 2008; Doezema et al. 2010). When considering the effects of BTEX and other pollutants on human health, it is of major importance to study and understand their concentration in the residential areas of the industry impact-zones.

The Mažeikiai crude oil refinery (56°23′15″N, 22°10′34″E) is the only crude oil refinery in the Baltic States, located in the North-West of Lithuania and operating as a typical complex refinery. It was started in 1980s and processes approximately 10 million tons of crude oil per year (200,000 bbl/day) and therefore classified as a very large refinery (McCoy et al. 2010).

In addition, there is a lack of studies in the region on the BTEX concentration spread in the vicinity of the oil refinery. The automatic monitoring station located in the region does not measure BTEX concentration in the air. Also, in order to understand the dynamics, concentrations, and spread of BTEX within the territory, a detailed knowledge of their presence in ambient air over

time and in various seasons is required (Kumar and Viden 2007). The objectives of this study were: (1) to determine of atmospheric levels of BTEX in the region rural and urban parts at the vicinity of the crude oil refinery; and (2) to investigate the effect of meteorological parameters (wind speed, wind direction, temperature, pressure, humidity) on the concentrations measured.

Methodology

Sampling area

In total, we have analyzed 13 stations scattered across the study area of Mažeikiai region. Four stations are located in Mažeikiai city (urban area) and nine sites in rural area. To identify the impact of both urbanization and the refinery on the background quality of atmospheric air sampling sites were grouped into six zones (Fig. 1). Zones 1–5 were organized at a various distance from the oil refinery and the urban zone was located in Mažeikiai city center. Zone 1 is represented by site No 6, which is 3 km north-west of the oil refinery and near the Latvian border.

Mažeikiai municipality receives complaints from local people regarding odors possibly caused by the refinery activities. Zone 2 is formed from the sites No 9 and No 10 in a small town, 3 km east of the refinery. There are no other industries or intense traffic areas close to these sites. Two sites (No 5 and 8) were grouped to form Zone 3 and represented the residential part. This zone is 8 km east-south of the refinery. Zone 4 is represented by the site No 4 which is about 16 km east of the refinery and is located in a residential place. Zone 5 (including sites No 1, 2 and 3) is the most distant area from the refinery. Sites No 7, 11, 12 and 13 represent the urban zone because of they are located near the intense traffic ways and intersections in the centre of the city of Mažeikiai.

Sampling of BTEX

The low cost and easy operation of the diffusive sampling technique makes it an ideal tool for large-scale air pollution monitoring with a high spatial resolution. Passive samplers are widely used to examine the impact of industrial emissions on the spatial distribution of BTEX (Roukos
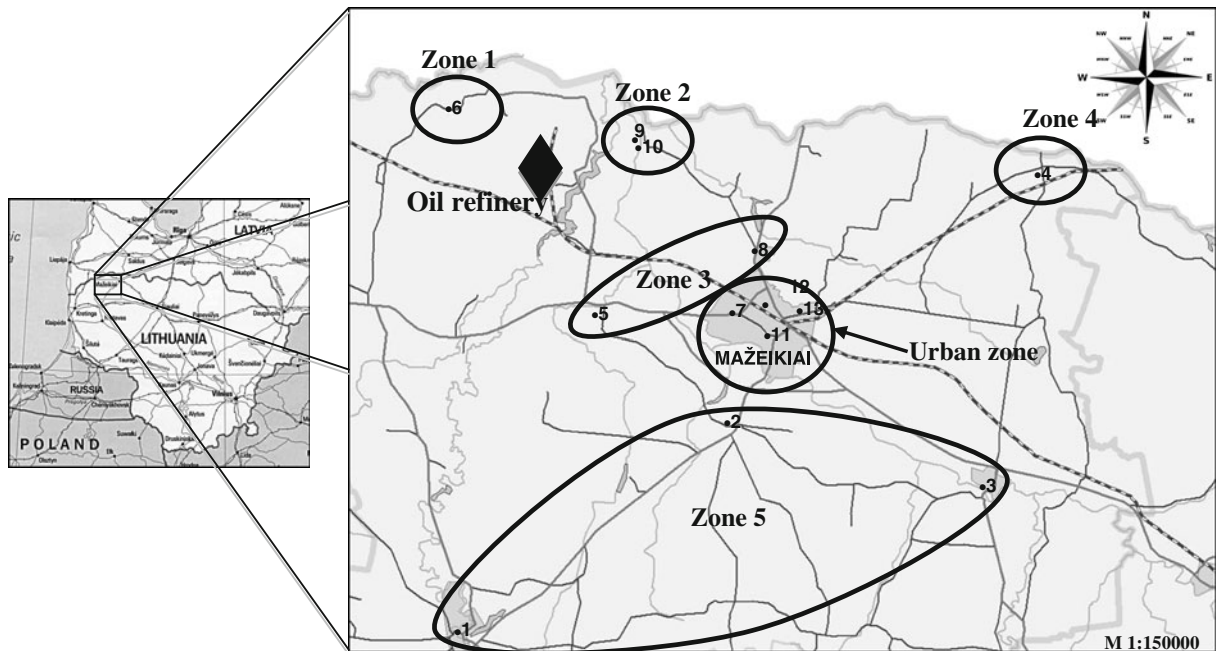

Fig. 1 Air sampling stations in the region of Mažeikiai divided in zones

et al. 2009) or the effects of the traffic activity (Buczynska et al. 2009). Two sampling campaigns for 2 weeks in two seasons—autumn and winter—were conducted: the first campaign was performed in November 2009 (periods of Autumn I and Autumn II) and the second—in February 2010 (periods of Winter I and Winter II). Sampling of BTEX was performed by the means of Passam AG (Switzerland) diffusion tubes. Samplers were exposed at 3 m height and were fixed at streetlight posts about 1 m from the road. The exposure time of an each cartridge was 2 weeks. All samplers were placed in the special shelters to protect them from the rain and minimize the wind influence during the exposure. All samplers were kept in air-tight bags during transportation. After exposure, the samplers were kept in a refrigerator until preparation for analysis. During each campaign, one control tube was kept in a refrigerator and one transport-control was transported, both tightly closed before the analysis.

Meteorological data (wind direction, temperature, humidity, atmospheric pressure and wind speed) were obtained from the meteorological station located in the city of Mažeikiai (Table 1, Fig. 2).

Analytical procedure for the BTEX extraction, apparatus and reagents

The diffusion tube was opened by removing one of the porous buffer layers from the glass tube with a forceps. The activated charcoal was transferred quantitatively (without losses) to a suitable glass vessel which can be closed. A volume of 1.5 ml of carbon disulfide (CS_2) with internal standard was added and the glass vessel was closed. The glass vessels were slightly shaken. After 1 h, the solvent was transferred to an autosampler vial and tightly closed. The calibration curve was prepared daily and up to ten samples were extracted per day. This was done to avoid the storage of extracted solutions as CS_2 is highly evaporative. The analysis was carried out by means of a HP 5890 gas chromatograph comprising a Supelcowax 10 column (0.75 mm in diameter and length 30 m). All the reagents were of the analytical grade. Standard solutions of BTEX were prepared from commercially available solution of 2,000 mg BTEX/ml. CS_2 (99.9%) with low benzene level and 2-fluorotoluene were used.

Statistical analysis

Data normality was tested with the Shapiro–Wilk test (Shapiro and Wilk 1965), and considered normal at a $p > 0.05$. Since many distributions did not respect the normality we transformed data logarithmically (Ln), to achieve the normality. Subsequently, data of each pollutant within each period was compared applying the ANOVA-ONE WAY TEST and considered significant at a $p < 0.05$. If the differences between periods were significant, we applied the TUKEY HSD post hoc test in order to identify the statistical differences within periods, also significant at a $p < 0.05$. Data is presented in original values. In addition, a global analysis was carried out with the principal component analysis (PCA) combining all variables, pollutants and meteorological, based on the correlation matrix. All analyses were performed using the Statistica 6.0 (StatSoft Inc.) for Windows.

Results and discussion

BTEX concentrations in urban zone

Air monitoring, started in 2009 in the Mažeikiai region, was important for the municipality of Mažeikiai and the Environmental Agency of Lithuania to determine BTEX concentrations in

Table 1 Monthly average of meteorological data (wind direction, temperature, humidity, pressure, wind speed)

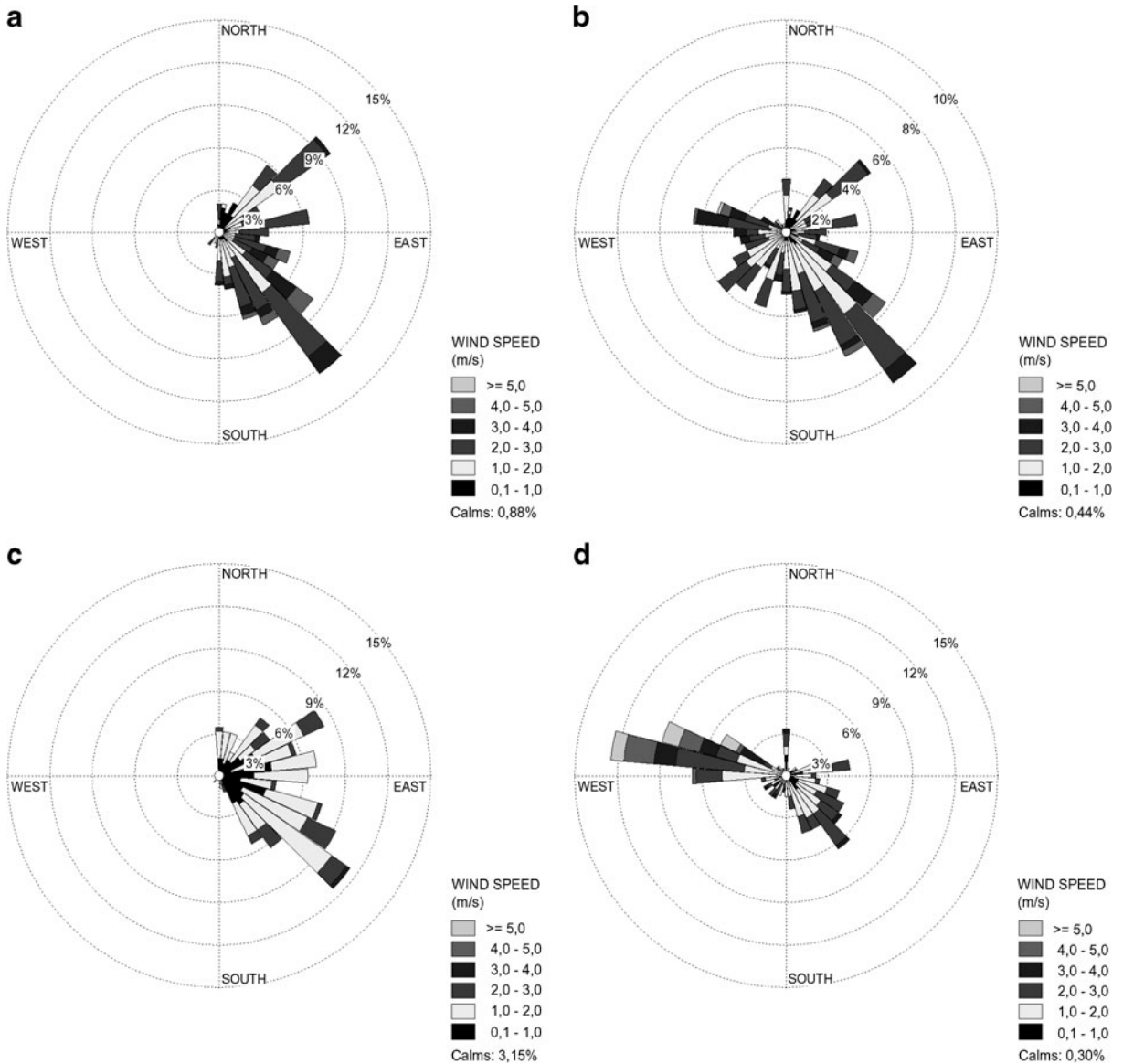| Season	Wind direction radians	Temperature, K	Humidity, %	Pressure, hPa	Wind speed, m s^{-1}
Autumn I	110	276	87.0	1005	1.95
Autumn II	208	281	89.0	998	1.94
Winter I	96	267	82.0	1008	1.20
Winter II	189	273	86.0	992	2.00

Fig. 2 Wind direction during each of two periods within sampling campaigns: **a** Autumn I; **b** Autumn II; **c** Winter I; and **d** Winter II

the region in the vicinity of the crude oil refinery. The main interest was because the European air quality standards regulate the maximum level of benzene and set the value of 5 μg m^{-3} by January 2010 (EC Directive 2008). Benzene is the only compound from BTEX regulated by the European Union.

Concentrations of BTEX in the urban zone and comparison to BTEX values from some of European cities are presented in Table 2. The

average concentration of BTEX in the urban zone within both campaigns was 2.30 ppbv for benzene, 1.95 ppbv for toluene, 0.41 ppbv for *p*-xylene, 0.78 ppbv for *m*-xylene, 0.56 ppbv for *o*-xylene, 0.61 ppbv for ethylbenzene. BTEX concentrations were comparatively similar to those determined in the urban areas of some European cities but much lower than in the traffic-intense areas of the same cities. The exception was the urban area of Vienna city where BTEX concentrations were even lower

Table 2 BTEX concentrations in urban zone of investigated area in comparison with urban and traffic-intense urban areas of some European cities (Monod et al. 2001)

City	Benzene	Toluene	p-xylene	m-xylene	o-xylene	Ethylbenzene
Berlin	2.09	3.84	0.57	1.39	0.76	0.78
Berlin traffic[a]	10.3	23.0	2.6	6.36	3.54	3.60
Bucharest	1.75	3.83	0.39	1.02	0.62	0.63
Bucharest traffic[a]	32.0	50.6	10.7	28.7	17.3	11.0
Krakow	2.43	2.76	0.35	0.91	0.45	0.50
Krakow traffic[a]	31.7	83.8	11.0	27.6	16.1	14.3
London	0.80	2.01	0.27	0.70	0.37	0.40
London traffic[a]	22.0	36.5	5.45	13.5	7.79	6.69
Mažeikiai (Lithuania) urban zone[a]	2.30	1.95	0.41	0.78	0.56	0.61
Prague	2.46	3.49	0.38	0.86	0.48	0.67
Prague traffic[a]	62.7	98.1	21.9	50.5	28.1	25.6
Roma	3.62	9.28	1.49	3.84	2.06	1.77
Roma traffic[a]	8.20	21.4	4.28	10.4	5.77	4.48
Vienna	0.99	1.17	0.19	0.50	0.28	0.25
Vienna traffic[a]	13.3	21.9	4.0	9.43	5.79	4.43

Data is presented in ppbv

[a]One sample

than in the urban zone of Mažeikiai: 0.99 ppbv for benzene, 1.17 ppbv for toluene, 0.19 ppbv for p-xylene, 0.50 ppbv for m-xylene, 0.28 ppbv for o-xylene and 0.25 ppbv for ethylbenzene. It can be expected that the traffic-intense areas of Mažeikiai city, as a comparatively small city (the population of 60,000), may be similar or slightly higher in emissions in comparison with the urban areas of Vienna with a total city population of about 2 million.

During both campaigns, benzene concentration (2.30 ppbv) did not exceed the annual threshold concentration (5.0 ppbv) set by European Union.

In comparison with BTEX concentrations in the rural zones (Zones 1–5), the urban zone was more abundant with benzene, toluene, p-, and m-xylene: 24%, 1.5 times, 3 times, and 3.6 times respectively higher than in the rural areas. This shows that traffic has a high impact on the background concentrations of BTEX in the urban zone of the Mažeikiai city. When traffic has a dominant impact in the background quality of the air, the ratio of benzene:toluene:ethylbenzene:xylene[1] (B:T:E:X) was reported to be 3:4:1:4 (Ho et al. 2004; Na 2006), or 2.3:5.5:1:2.3 (Wang and Zhao

2008). In our study, the ratio was 3:4:1:3 and hence supports the expectations of high impact of traffic on air quality in the urban zone of Mažeikiai city.

Temporal variation of BTEX

To evaluate the temporal variation of BTEX in Mažeikiai region the ANOVA-ONE WAY test for data of the all thirteen sampling sites during each period of both campaigns (Autumn I, Autumn II, Winter I and Winter II) was employed. As it follows from Table 3, the most abundant compounds were benzene and toluene and their concentrations varied significantly within the periods (at $p < 0.001$ for benzene and at $p < 0.05$ for toluene) that represented different meteorological conditions. Both compounds revealed similar patterns of distribution among the periods of investigation. The highest concentrations of both components (3.36 ± 1.13 ppbv of benzene and 2.52 ± 1.26 ppbv of toluene) were observed in Winter I which typical of comparatively high pressure (1,008 hPa), low temperature (267 K) and low wind speed (1.20 m s^{-1}) in the region (Table 1, Fig. 2). These conditions have favored a higher accumulation of BTEX, especially for benzene and toluene which are comparatively less-reactive species due to their longer

[1]Calculated as the sum of p-, m-, and o-xylene

Table 3 Mean concentrations of BTEX (average ± standard deviation), at all investigated sites in each period

Elements	Autumn I (2009)	Autumn II (2009)	Winter I (2010)	Winter II (2010)	F
Benzene	2.05(±0.41)[b]	1.30(±0.26)[c]	3.36(±1.13)[a]	2.38(±0.45)[b]	**
Toluene	1.86(±0.84)[ab]	1.53(±0.77)[b]	2.52(±1.26)[a]	1.88(±0.85)[ab]	*
Ethylbenzene	0.86(±0.34)[a]	0.55(±0.24)[ab]	0.55(±0.33)[ab]	0.47(±0.28)[b]	*
p-xylene	0.34(±0.19)	0.45(±0.24)	0.43(±0.28)	0.39(±0.25)	n.s
m-xylene	0.73(±0.36)	0.73(±0.39)	0.87(±0.67)	0.78(±0.56)	n.s
o-xylene	0.87(±0.37)[a]	0.51(±0.21)[b]	0.42(±0.26)[b]	0.40(±0.21)[b]	**

F value shows the results of the ANOVA-ONE WAY among considered periods, differences significant at a $p < 0.05$* and $p < 0.001$**. *n.s.*(non-significant). Letters showed significant differences within periods. Data is presented in ppbv

atmospheric lifetime (Table 3). Concentrations of ethylbenzene and *o*-xylene were found significantly higher (0.86 ± 0.34 ppbv for ethylbenzene and 0.87 ± 0.37 ppbv for *o*-xylene) in Autumn I. Such an increase in concentrations might have been influenced by meteorological conditions during the period: comparatively low temperature (276 K), low wind speed (1.95 m s^{-1}) and high atmospheric pressure (1005 hPa) in the region. Moreover it may reveal higher emissions during the period. No significant difference was found between concentration of *p*-xylene and *m*-xylene among the periods of investigation.

Spatial variation of BTEX

Figure 3 shows the spatial variation of BTEX in the all Zones. Benzene and toluene were the most abundant among investigated BTEX. Benzene concentration varied from 1.65 to 2.59 ppbv in rural zones and was 2.75 ppbv in the urban zone. Toluene concentration was the lowest in Zone 2 (1.18 ppbv) and the highest in the urban zone (2.14 ppbv). *p*-Xylene and *m*-xylene were found to have the highest difference between averaged value in rural area and the urban zone (2.7 and 2.8 times respectively). *p*-Xylene concentration was the lowest in Zone 1 (0.15 ppbv) and the highest in the urban zone (0.67 ppbv). Similar *p*-xylene concentrations were found in Zones 2, 3, and 4: 0.25, 0.27, and 0.25 ppbv, respectively.

Similar concentrations in Zone 2 (close to the oil refinery) were found of both *o*-xylene and ethylbenzene (0.54 and 0.53 ppbv, respectively) and were the highest among the rural zones. Ho et al. (2004) have found a good correlation between ethylbenzene and *o*-xylene in an industrial area and Hsieh et al. (2006) have found a good correlation between these compounds in the region which was close to the refinery. Apart from the meteorology that had an important impact in the accumulation of benzene and toluene, the increased concentrations of ethylbenzene and *o*-xylene close to the location of the refinery showed its impact on the local air quality.

As it was expected, the urban zone presented the higher concentrations than the rural zone for all investigated BTEX. The difference was 1.4 times for benzene, 2.2 times for toluene, 2.7 times for *p*-xylene, 2.8 times for *m*-xylene, 1.6 times for *o*-xylene, and 2.0 times for ethylbenzene. This suggests that due to urbanization, the air in urban places with population of 60,000 may be 1.4–2.2 times more polluted than in the rural areas.

BTEX characteristic ratios

Characteristic ratios of BTEX are widely used to access the air mass ages, to analyze BTEX origins (Nelson and Quigley 1983; Liu et al. 2008; Roukos et al. 2009) and are less impacted by the difference in sampling protocol (Doezema et al. 2010). The characteristic ratios of toluene/benzene (T/B), benzene/toluene (B/T), *m*-xylene/ethylbenzene (*m*-X/E), and *m*,*p*-xylene/ethylbenzene (*m*,*p*-X/E) were calculated for all zones for two different wind directions: downwind from the oil refinery and downwind from the region centre (Fig. 4).

Toluene and benzene are emitted by automobiles in a ratio of around 2:1 (Staehelin et al. 1998; Conner et al. 1995), therefore, the maximum toluene/benzene ratio (T/B) will be 2 if the traffic emission is the dominant source (Liu et al. 2008; Ting et al. 2008). None of the zones showed T/B close to 2.0, however, the ratio in the urban zone
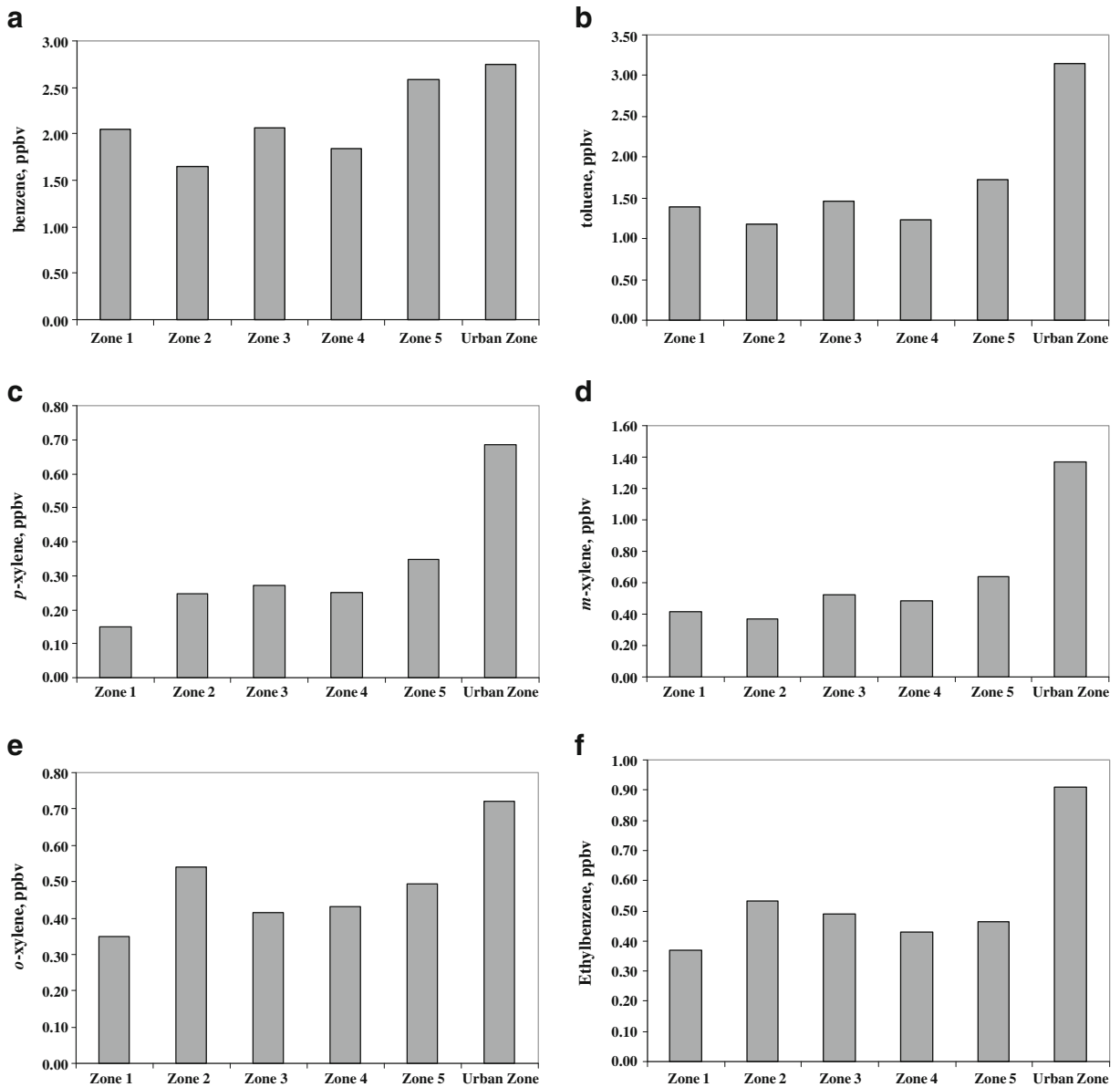
Fig. 3 Averages of **a** benzene; **b** toluene; **c** ethylbenzene; **d** p-xylene; **e** m-xylene and **f** o-xylene concentrations for the whole sampling period

was the highest (1.13–1.29) suggesting that the transport influence in the urban zone is the largest in comparison with the other zones (0.50–0.81) (Fig. 4a).

When comparing the T/B ratios for the different wind directions, the higher values were found downwind from the region centre. The difference varied from 1.1 to 1.4 times and may

explain that the quality of the air brought from the region centre, is more influenced by the traffic. In opposite, the air brought from the oil refinery had T/B ratio much less than 2.0 (thus less impact of traffic) and therefore showing possible contribution of the oil refinery.

The benzene-to-toluene (B/T) ratio is a reverse value of T/B ratio, but it a commonly used as
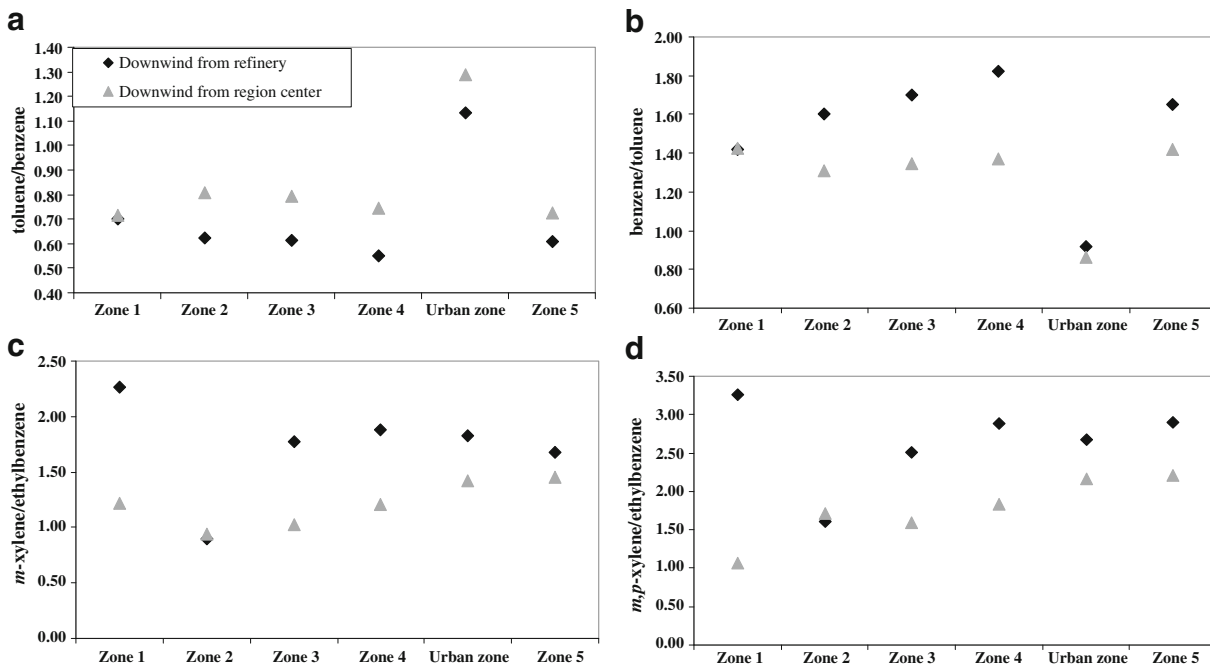
Fig. 4 Average values of BTEX characteristic ratios in zones: **a** toluene/benzene; **b** benzene/toluene; **c** *m*-xylene/ethylbenzene; and **d** *m*,*p*-xylene/ethylbenzene

a tracer to predict long-range transport of pollutants (Srivastava et al. 2005) and as an indicator of the photochemical age of the air (Ting et al. 2008). This is due to the fact that toluene has a much shorter lifetime than benzene (Singh and Zimmermon 1998; Table 3) and during transport toluene will reduce more than benzene because it undergoes photochemical reactions more easily (Prinn et al. 1987). Therefore, the higher the B/T ratio is, the longer distance the emissions were transported. Results of our study showed similar trends of B/T variation. The urban zone presented the lowest B/T ratio (0.86 for wind from the region centre and 0.92—for the wind direction the refinery) showing a short distance from the source of emission that is mainly traffic in the urban zone. In the rural zones B/T ratio increased from the oil refinery towards the region centre. This trend was similar independently of the wind direction, however, more pronounced when the wind was blowing from the refinery (Fig. 4b).

Monod et al. (2001) analyzed air quality in the urban areas and concluded that ratios obtained between *m*-, *p*-, *o*-xylene, and ethylbenzene con-

centrations in many cities in the world had the same sources. In our study, we compared some of theses ratios in the rural zones to study a potential impact of the oil refinery.

The *m*-X/E ratio varied from 0.94 to 2.26 and was the lowest in the Zone 2 (0.90 in downwind direction from the oil refinery and 0.94—downwind from the region centre; Fig. 4c). It was stated that the urban-related sources cause ratios to reach 2.24 ± 0.33 (Monod et al. 2001) thus the lower values exhibit non-urban sources of pollution. Relatively higher ratios in case of wind blowing from the oil refinery indicate higher abundance of pollutants in the territory.

m,*p*-X/E ratio varied with pollutions sources and was found to be close to 3.5 ± 0.5 for the urban pollution (Monod et al. 2001). It varied in the range from 1.3 to 2.9 in the areas where non-traffic sources were active (Truc and Oanh 2007). Similar values were determined in Zone 2 (1.61–1.71; close to the refinery; Fig. 4d) representing the influence of the non-urban source of pollution. *m*,*p*-X/E values were in the range found in the area of petrochemical industry in Southern

Taiwan (1.5–2.6) (Hsieh et al. 2006) and did not change with a changing wind direction. This reveals the impact of the oil refinery as a potential contributor to the background quality of air. Relatively higher ratios in case of wind blowing from the oil refinery indicate higher abundance of pollutants in the territory.

According to studies (Monod et al. 2001; Hsieh et al. 2006; Liu et al. 2008) ratios *m*-X/E and *m*,*p*-X/E had a tendency to decrease with an increase distance from the source, however, the ratios did not follow such a trend in our study. Considering the oil refinery as a source, the distances where ratios were calculated were from 5 to 25 km, therefore other sources, including the railway transporting oil products could have had some influence. Additionally, there is no information about the upsets that often result in 50 times higher emissions than routine emissions and are very likely to occur in such a large refinery (McCoy et al. 2010).

Principal component analysis

Principal component analysis was used to study the relation between BTEX (benzene, toluene, ethylbenzene, *p*-, *m*-, *o*-xylene) within two periods of two campaigns of investigation (Autumn I,
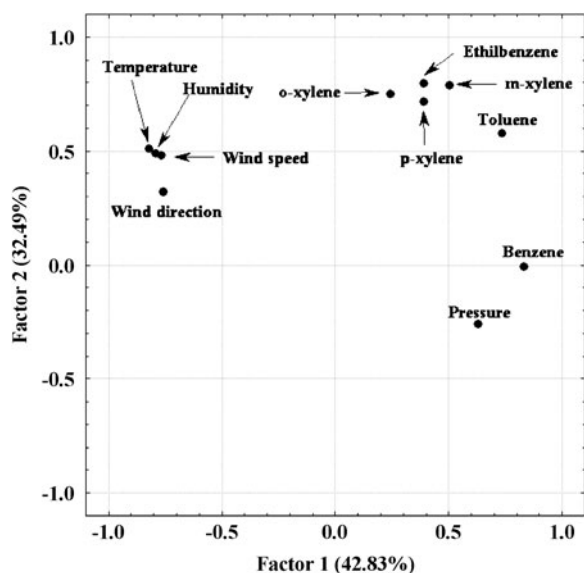
Autumn II, Winter I, and Winter II) in relation to meteorological parameters (wind speed, wind direction, temperature, humidity, pressure). Figure 5 shows the relation between Factors 1 and 2. Both factors explained the total variance of 43% and 32% respectively on the measurements taken for two periods during both campaigns. Results showed in general the correlation between benzene, wind direction, wind speed, humidity and temperature.

We identified three main groups in this study. The first was formed from pressure and benzene. In high-pressure periods, the accumulation of benzene was higher. Wind speed, wind direction, humidity, and temperature felt into the second group of variables. This group is in the opposite side of variables, pressure and benzene, thus explaining that the higher are a wind speed, humidity and temperature the lower is accumulation of benzene. The third group consisted from toluene, *p*-, *o*-, *m*-xylene, and ethylbenzene. This can be explained by the similar lifetime properties of the pollutants. *p*-Xylene, *o*-xylene and *m*-xylene belong to the highly reactive-specie group because of relatively short period of their stay in the atmosphere (Table 4). A higher lifetime is typical for ethylbenzene and toluene and it is generally much lower than benzene (Table 4). The third group variable is located closer to the first group variables and may be explained by the fact that the accumulation of highly reactive species is more influenced by such meteorological variables as
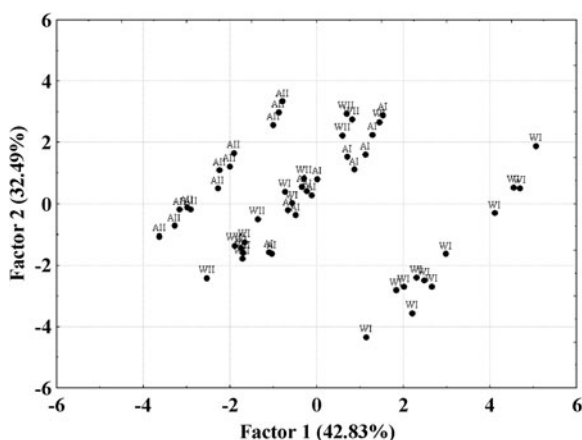

Fig. 5 Relation between Factors 1 and 2 (variables)

Fig. 6 Relation between Factors 1 and 2 (cases)

Table 4 Atmospheric lifetime of BTEX (Monod et al. 2001)

Compound	Atmospheric lifetime[a]
m-xylene	11.8 h
p-xylene	19.4 h
o-xylene	20.3 h
Ethylbenzene	1.6 days
Toluene	1.9 days
Benzene	9.4 days

[a]assuming $[OH] = 10^6$ rad cm^{-3}

higher temperature, lower wind speed, and wind direction.

We found a distinctive difference among periods of investigation in our study Fig. 6. The first period of the winter sampling formed a group apart from the rest of periods projecting different patterns of investigated variables. This period was specific for the lowest values of wind speed, temperature and humidity, as well as the highest pressure. These conditions have favored more stable weather conditions and thus influenced the highest concentrations of benzene and toluene as the relatively less-reactive species.

Conclusions

Study showed that concentration of benzene, as strictly regulated air pollutant by EU Directive 2008/50/EC, did not exceed the limit of 5 ppbv in the region in the vicinity of the crude oil refinery during the investigated period. The averaged concentration of benzene varied from 2.12 ppbv in the rural areas to 2.75 ppbv in the urban areas where the traffic was determined to be a dominant source of BTEX emissions.

Our study showed no significant change in air quality in the vicinity of the oil refinery within the investigated period, however, an impact of the industry on the background air quality was detected. The T/B ratio (0.50–0.81) that was much lower than 2.0, identified other sources of pollution than traffic. Higher T/B values in the rural zones were detected when downwind from the refinery. The B/T ratio increased from the oil refinery towards the region centre had the same

pattern independently from the wind direction and identified increase of the aged air masses. Released from the same source, ethylbenzene and *p*-, *m*-, *o*-xylene showed similar variation patterns in the Zone 2 where local inhabitants often complain of bad odors. Among the rural zones, the higher concentrations of ethylbenzene and *o*-xylene were found in Zone 2. Each of the ratio, *m*-X/E and *m*,*p*-X/E, has shown similar values in Zone 2 independently from the direction of the wind.

The meteorology of Mažeikiai and reactivity behavior of BTEX could be responsible for the seasonal variation. Meteorological properties such as a low wind speed, a high pressure and a low temperature have influenced higher BTEX accumulation patterns in the region, especially for benzene and toluene. Increase of BTEX concentrations is likely to occur in cold periods of a year, from November till February. Apart from the meteorology that had an important impact in the accumulation of benzene and toluene, the increased concentrations of ethylbenzene and *o*-xylene close to the location of the refinery showed its impact on the local air quality.

This study has shown no high influence of the oil refinery on region background air quality, but only trends and implication in relation with meteorological data. The continuous monitoring of BTEX is essential to determine trends of spring and summer meteorological properties for the air quality of Mažeikiai region. Moreover, the oil refinery classified as a very large petrochemical industry is highly subjected to upsets which have to be analyzed. Although this study has not shown significant pollution of the refinery, the refinery upsets which were found to be random events can result in 50 times higher emission rates than the routine emissions (McCoy et al. 2010). Future investigation on the upset emissions would be of high importance and might explain local people complaints.

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