Background atmospheric levels of BTEX in a medium-sized city and surrounding area in Southern Italy

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Abstract

Background atmospheric levels of BTEX in the suburb of Caserta (41° 04' N, 14° 20' E), a Southern Italian city with about 75,000 inhabitants and a low level of industrialization, were measured during weekdays in 2005. The average annual concentrations (μg m^{-3}) were 8.7 benzene, 26.0 toluene, 6.5 ethylbenzene, 14.4 (m+p)-xylene and 12.5 o-xylene, with higher values during summer. The average daily concentrations of the different BTEX hydrocarbons were strongly correlated (average correlation coefficients = 0.93). The (m+p)-xylene/ethylbenzene concentration ratio was relatively low (2.2) and did not show statistically significant seasonal variations. In Naples, a densely populated city on the coast, 25 km from Caserta, the ratio was significantly higher (3.3). Intermediate ratios were recorded in sampling sites located between the two cities. The results suggest that BTEX tend to stagnate in Caserta area, producing relatively high levels with low X/E value, or, alternatively, that they are in greater part produced elsewhere, very likely in Naples, and are transported towards Caserta. To discriminate between these two hypotheses analysis of the patters of local winds is in progress.
Keywords: monitoring, BTEX, urban air quality, medium-sized city, Caserta City.

1 Introduction

BTEX (benzene, toluene, ethylbenzene and xylenes) are traffic-related air pollutants with well-documented adverse effects on human health. In particular, benzene is known to be a carcinogenic agent [1] whilst toluene strongly affects

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the nervous system [2]. As these monoaromatic hydrocarbons react in the mesosphere with different rate constants, their ratio can be used to evaluate their age in an air mass [5].

BTEX levels in big cities have been the object of extensive investigation throughout the world. On the other hand, the information on the pollution level in small- and medium-sized cities is rather scanty [3, 4].

This paper reports an investigation on BTEX background levels in Caserta, a medium-sized city of Southern Italy (41° 04' N, 14° 20' E, about 75,000 inhabitants) and its surrounding area. Large industrial or thermo-electric plants are absent in this area. On the coast, about 25 km South to Caserta and in the same plain, there is Naples, a city with about 1,000,000 inhabitants and high traffic density.

2 Experimental

2.1 Sampling sites

The location of sampling sites is indicated in Fig. 1. The main site (M) is located in the suburb of Caserta city. At about 200 m from this site there are agricultural fields. Because of the absence of large industrial or thermo-electric plants, this sampling site can be referred to as a "suburban background" station. The sampling was performed on weekdays from February to December 2005, except August, 8 times per month. The data relative to samples collected on rainy days were not included in this study. In the reference sites the sampling was carried out five times, 24-hours each time and contemporaneously in all the sites, during October-December 2005. The sites 1 to 4 are located in Naples, the sites 5-12 in the suburb of a small town (5,000 – 40,000 inhabitants), the site 13 near a green park in the suburb of a small town (< 5,000 inhabitants) and sites 14 and 15 in agricultural fields. All the sampling points were about 5 metres above the ground level and were not located in proximity to major cross-roads.

2.2 Analytical procedures

Monoaromatic compounds (benzene, toluene, ethylbenzene, o-xylene and (m+p)-xylene were collected by Radiello® diffusive samplers, patented by Foundation *Salvatore Maugeri* (FSM), exposed for 24 hours. The samplers were stainless steel cylinders with a 100-mesh-grid opening, packed with a cartridge of 530 mg activated charcoal. Exposed cartridges were extracted with carbon disulphide for VOC (J.T. Baker, Instra-Analysed) using 2-fluorotoluene as an internal standard. Analyses were performed on a Clarus 500 Perkin-Elmer gas chromatograph equipped with a split injector (25/1), an Elite 5 Perkin-Elmer capillary column (crossbond 5% diphenyl - 95% dimethyl polysiloxane, 60 m x 0.32 mm ID x 0.25 μm df) and a FID detector. One-μl samples were injected at a constant temperature of 240 °C. The oven temperature program was 40 °C for 5 min, to 80° at 8 °C/min and to 250 °C at 20 °C/min. The carrier gas was He at 20 psi.

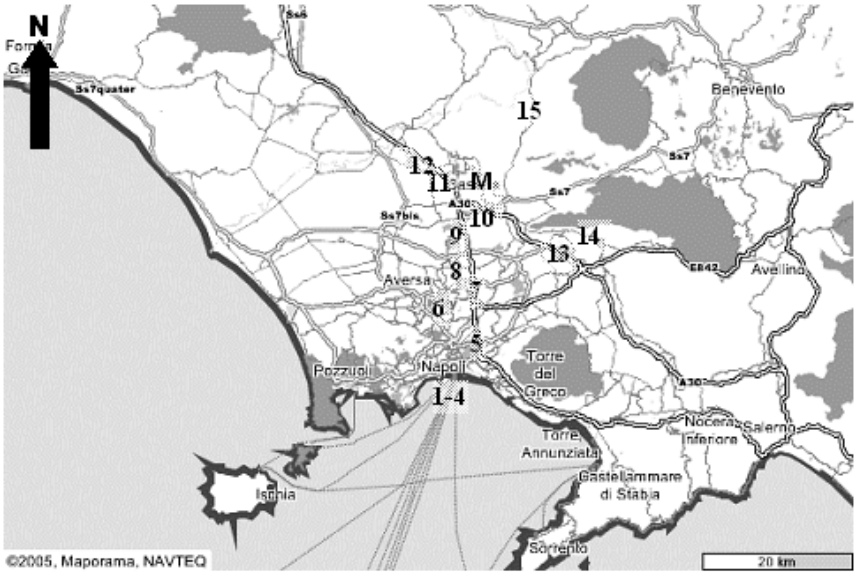

Figure 1: Geographical distribution of the sampling sites. M indicates the main sampling site, numbers 1 to 15 indicate the reference sites, the grey areas indicate hills.

3 Results and discussion

Table 1 reports the statistical data for BTEX concentrations recorded in the main sampling site, located in the suburb of Caserta. The data are from 70 analyses of diffusive adsorbing cartridges.

As a general trend, the levels of pollutants in the air exhibited a bell-shaped profile with the maximum values in June. This pattern indicates that emissions from domestic heating plants (operating in the winter season) did not significantly contribute to the BTEX levels measured. A possible explanation for the higher concentrations detected in summer could be transport of pollutants from the coast by sea breezes, that are of regular occurrence during summer days. It has been shown, for example, that during summer the air in central Iberian Peninsula contains recirculated pollutants from previous days or emitted from densely populated along coast [6].

The 24-hour average BTEX concentrations correlate rather well (Tab. 2), with no statistically significant seasonal variation.

The good correlation observed is a strong indication that BTEX in the suburb of Caserta are produced by a common source with most the same characteristics throughout the year. The best possible candidate is emission from vehicular traffic. Conversely, contribution by sources with a seasonal dependence can be excluded.

Table 1: Average levels of BTEX recorded in the suburb of Caserta.

Pollutant	24-hour average concentration ($\mu g/m^3$)	Standard deviation ($\mu g/m^3$)	Minimum value ($\mu g/m^3$)	Maximum value ($\mu g/m^3$)
Benzene	8.7	2.6	3.2	16.3
Toluene	26.0	7.7	9.2	49.6
Ethylbenzene	6.5	1.6	2.3	9.7
(m+p)-Xylene	14.4	3.3	5.1	20.4
o-Xylene	12.5	2.9	4.4	18.4

These levels are relatively high and in the range expected for a metropolitan area. The average benzene concentration is close to the limit value fixed by the EU Air Quality Directive EC/30/1999 for 2006. This Directive fixes lower limits for the following years.

Figure 2 reports the monthly average concentrations of BTEX.

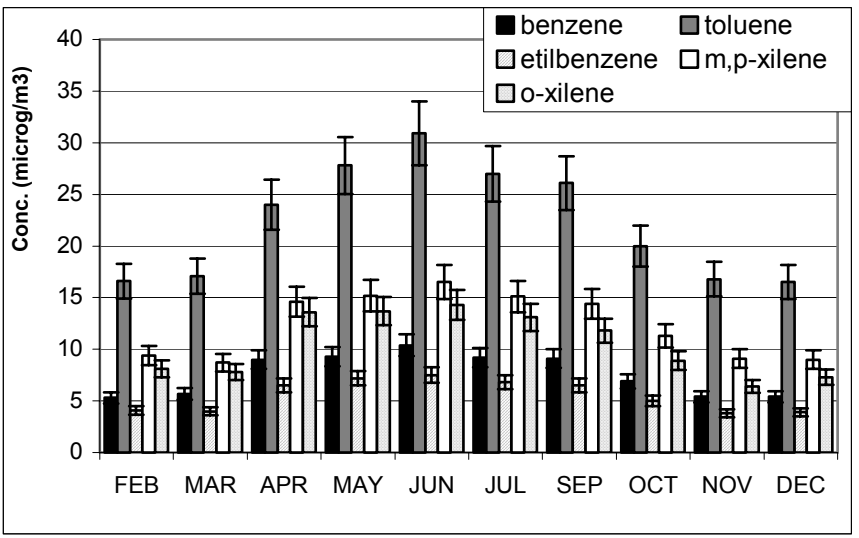

Figure 2: Monthly average concentrations of BTEX recorded in the suburb of Caserta in 2005.

Nelson and Quigley [7] proposed the use of [(m+p)-xylene]/[ethylbenzene] ratio and [o-xylene]/[ethylbenzene] ratio (X/E) to evaluate the age of urban plumes. Because ethylbenzene has a longer lifetime, lower values of X/E indicate an older plume. In our study we found a X/E value of 2.2 ($\sigma = 0.1$, max value = 2.3, min. value = 2.0) in the suburb of Caserta (the main sampling site), with no statistically significant monthly dependence as shown in Fig. 2. This

X/E value is relatively low if compared to the range of values reported in literature, from 1.3 to 4.5 [8]. X/E values in Rome were 3.1 [9], 3.0 and 3.3 [8].

Table 2: Correlation coefficients between the 24-hours average BTEX concentrations recorded during 2005 in the suburb of Caserta.

Variable	Benzene	Toluene	Ethylbenzen	(m+p)-Xylene	o-Xylene
Benzene	1	0.97	0.96	0.95	0.88
Toluene		1	0.95	0.94	0.85
Ethylbenzene			1	0.98	0.91
(m+p)-Xylen				1	0.93
o-Xylene					1

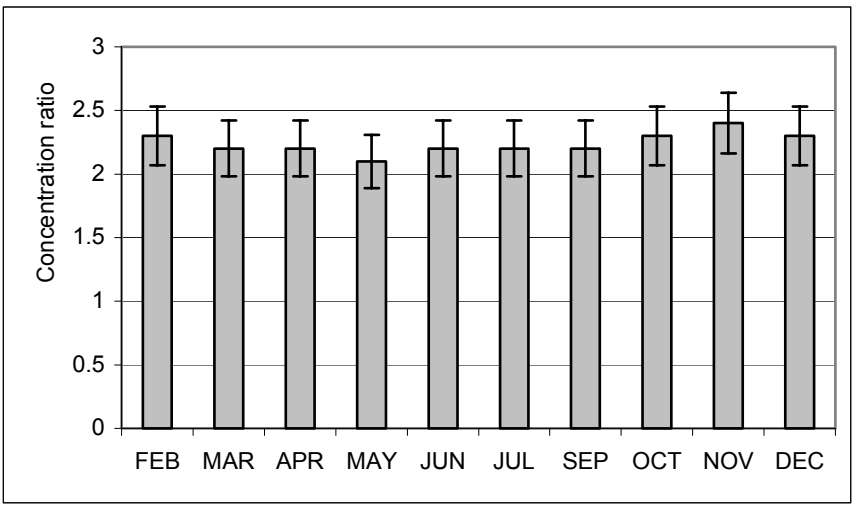

Figure 3: Monthly average (m+p)xylene / ethylbenzene concentration ratio recorded in the suburb of Caserta.

Table 3 reports the average values of BTEX concentrations recorded in the reference sites indicated in Fig. 1 (five samplings for each site).

The BTEX concentrations, as expected, were higher in the sites 1-4, located in Naples.

Figure 4 reports the X/E, [benzene]/[ethylbenzene], [toluene]/ [ethylbenzene] and [o-xylene]/[ethylbenzene] ratios *versus* the distance from Naples.

The [(m+p)-xylene]/[ethylbenzene] and [o-xylene]/ [ethylbenzene] ratios decrease markedly from Naples to Caserta, indicating a parallel increase in the age of the BTEX. No marked dependence on the distance from Naples was observed for the [benzene]/[ethylbenzene], [toluene]/[ethylbenzene] ratios. It is worth noting that the reactivity of these hydrocarbons in the troposphere

decreases in the order m-xylene > p-xylene > o-xylene > ethylbenzene > toluene > benzene [10].

Table 3: Average values of BTEX concentrations (μg/m^3) in the reference sites.

Site	Benzene	Toluene	Ethylbenzene	(m+p)-Xilene	o-Xilene
1 (0)*	10.9	31.6	6.7	22.8	11.4
2 (0)	10.8	30.4	7.8	27.6	14.7
3 (0)	8.7	27.8	7.5	24.8	16.4
4 (0)	9.4	28.5	8.1	28.3	15.5
5 (10)	6.9	22.1	6.2	19.2	9.6
6 (15)	7.3	22.3	6.7	20.8	11.3
7 (17)	6.5	19.4	5.9	17.8	9.5
8 (20)	6.7	21.5	6.1	16.5	9.8
9 (25)	5.1	12.5	4.2	10.1	5.2
10 (26)	6.0	20.2	4.9	11.8	6.6
11 (32)	4.6	13.0	3.9	9.0	5.1
12 (34)	5.1	15.8	4.7	11.3	5.1
13 (35)	4.9	11.3	3.6	7.9	4.2
14 (36)	4.8	10.7	3.3	6.9	3.1
15 (50)	4.9	15.3	4.1	8.6	3.7

* The figures in parenthesis indicate the distance in km from Naples.

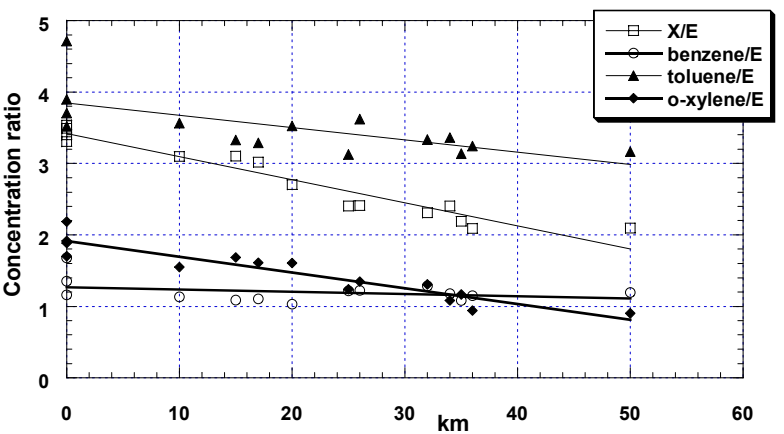

Figure 4: Dependence of X/E, [benzene]/[ethylbenzene], [toluene]/[ethylbenzene] and [o-xylene]/[ethylbenzene] ratios on the distance from Naples.

4 Conclusions

Salient features of the BTEX levels in Caserta and surrounding area are as follows:

(a) BTEX concentrations in the suburb of Caserta were higher than expected, considering the relatively low level of local traffic and industrial activities; moreover, BTEX concentrations were significantly higher in summer than in winter;

(b) the concentrations of the different pollutants were strongly correlated, indicating a common source, and/or different sources with strictly correlated activities, whose characteristics do not change significantly throughout the year;

(c) [(p+m)-xylene]/[ethylbenzene] (X/E) and [o-xylene]/[ethylbenzene] ratios were relatively low and progressively increase from Caserta to Naples.

The relatively high levels of BTEX with low X/E value present in the Caserta area could be explained in terms of stagnation of locally-produced BTEX pollutants. However, the possibility that BTEX are produced elsewhere and then drift to Caserta area cannot be excluded. If so, a likely source of BTEX is the densely populated areas on the coast (Naples), wherefrom these pollutants might be transported to the interior by sea-land breezes. A detailed analysis of the pattern of local winds is in progress to establish the prevalence of either mechanism

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