

Assessment of Air Pollution, by the Urban Traffic, in University Campus of Bucharest

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Abstract

This study aims to measure traffic-related air pollution of vehicles with internal combustion, the main source of emissions of BTEX, organic compounds and NO_x, NO₂, NO, O₃, CO, SO₂, PM₁₀ and PM_{2.5}, inorganic compounds, in three sites of the University campus, surrounded by residential areas. According to the University data, around 8000 students are being exposed daily to the measured level of pollution, in all 3 studied places of campus. A mobile laboratory was used, which continuously measures above mentioned pollutants and meteorological parameters. The diurnal variation of BTEX, in a sunny and rainy day showed two peaks of BTEX concentration in the morning and evening. In the rainy days, the non-polar (hydrophobic) compounds as BTEX are mechanically trained by rain into the ground, where either they enter into the groundwater, or volatilized and re-enter in the air. Particulate matter such as PM₁₀ and PM_{2.5} is, in a large part, carried by the rain into the soil. The polar compounds (hydrophilic, NO_x, SO₂) dissolves in the rainwater and are absorbed in the soil (increasing soil acidity) and evaporated towards the clouds (leading to acid rain). In our study, BTEX compounds removed by the rain varied between 62% - 75%, NO_x and SO₂, 80% and 77% respectively. Particulate matters were washed out up to 68% for PM₁₀, and 42% for PM_{2.5}. In the sunny days the air pollution with measured concentrations of O₃ (121.66 ± 7.02, 123.56 ± 4.89 μg/m³) remained for 7 hours close to the limit value (120 μg/m³). The maximum of solar radiation, with corresponding low concentrations in NO_x and xylene, corresponds to photochemical reactions in the atmosphere, generating photochemical smog. In a sunny day and high traffic, we found the maximum value 5.4 μg/m³ for benzene, for 30 min., a known human carcinogen, exceeding the annual limit value de 5 μg/m³. The average background, from benzene, in three University campuses daily visited by around 8000 students was 0.97 μg/m³, exposed to 1.46 μg/m³ and the cancer risk is 1/100,000.

Keywords

University Campus Outdoor Air Quality, BTEX, Mobile Laboratory, PM10, PM2.5

1. Introduction

Transport related emissions, deforestation, agriculture and fertilizer used and recurrent forest burning are some of the factors that have increased atmospheric pollutant emissions [1]. The fast growth in vehicular traffic means that air pollution might continue to rise in the future.

Vehicles with gasoline and diesel engines emit a wide variety of air pollutants, such as: CO, NO₂, SO₂, volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs) and particulate matter (PM) [2].

Volatile organic compounds (VOCs) significantly contribute to the photochemical reactions in the atmosphere. Their reaction with NO_x in the presence of sunlight generates secondary pollutants and photochemical smog such as OH radical and ozone [3] [4]. VOCs contribute to O₃ formation through a series of photochemical reactions, including the hydroxyl radical (OH) initiated oxidation of VOCs, nitrogen cycling driven by peroxy (RO₂) and hydroperoxy (HO₂) oxidation and photolysis, and the combination of oxygen atom (O) with molecular oxygen (O₂) [5] [6]. VOCs are important ozone precursors that contribute to the formation of photochemical smog and secondary organic aerosols.

74 VOC species were detected from the tested vehicles, including 22 alkanes, 6 alkenes, 1 alkynes, 16 aromatics, 3 cyclanes, 10 halohydrocarbons, 12 carbonyls and 4 other compounds [7].

The BTEX (benzene, toluene, ethylbenzene, m,p-xylene and o xylenes) ratios in total VOCs identified were: 60% in Hong Kong [8], 70% of the ambient VOCs in summer in Beijing [9], 33% in Dinghu Mountain and Beijing [7] [10] etc.

The percentage of BTEX (by weight) in gasoline is 18% compared to the others and the components, in BTEX, of benzene, toluene, ethylbenzene, m, p-xylene and o xylenes are 11%, 26%, 11%, 40% and 12%, respectively [11]. Volatilities as benzene and toluene are close to that ratio B/T, in emissions, of 1/2.

Comparing the lifetime of toluene and benzene in air it was estimated at 2 and 12.5 days, respectively, while xylenes were only 7.8 h [12]. The photo-oxidation reactions in the air occur at different rates: benzene reacts more slowly with OH radicals, while toluene/m-xylene reacts 5 times and 19 times as fast as benzene, respectively [13].

The photolysis of BTEX to radicals OH and NO₃ is important in summer, due to the high level of available temperature and solar radiation. This may be the reason why the BTEX values were lower in the summer than in the rainy season [14]. Since BTEX has low solubility and it will not be incorporated into clouds or rain, wet deposition might not affect their depletion. This might result in almost no difference between their concentrations in rainy and summer seasons, as

observed in some studies [15].

Benzene is a known toxic carcinogen [16] [17] and epigenetic modifications were related to benzene low dose exposures [18]. Toluene is less toxic and causes drowsiness, impaired co-ordination, and liver and kidney damage [19]. Usually, many pollutants coexist in the ambient air, several of which may have additive or even synergistic effects; both benzene and toluene can affect the central nervous system and they usually coexist with each other in the air due to several common resources [2].

The traffic-generated emissions were estimated to account for more than 50% of the total emissions of particulate matter (PM₁₀ and PM_{2.5}), in the urban areas, in highly industrialized countries [20]; in London more than 80% of particulate matter results from road traffic [2].

If indoor air pollution can be reduced by treatment of incoming fresh air intake, for example, by adsorption on activated carbon filters [21] [22], urban outdoor air pollution can be reduced only by normative measures and the coordination of road traffic.

It was demonstrated that exposure to BTEX was very high for the students living in the urban traffic site [23].

In this paper we assess the traffic-related air pollution, in three different areas of the University campus (noted PP-66 Pache Protopopescu, TE-122-124 Lacul Tei and PL-59 Plevnei), using a mobile laboratory which continuously measures chemical parameters (BTEX, O₃, NO_x, NO, NO₂, CO, SO₂, PM₁₀ and PM_{2.5}) and meteorological parameters. The three places of the campus (different locations in Bucharest) are near urban traffic and are surrounded by residential areas. The outcomes shall give indications to the local government in order to implement measures to improve outdoor air quality and decrease human health risks.

2. Materials and Methods

The traffic policemen and drivers are much more exposed to traffic-related air pollutants, but it's difficult to measure their exposure using large-scale cost-saving methods, since stationary monitoring is not feasible for these highly mobile groups [2].

The analytical procedure usually adopted for the determination of BTEX compounds in urban air used a pre-concentrated probe by active or passive sampling, using adsorption, thermal desorption and following analysis on gas chromatography technique (GC), with FID, PID or MS detectors [6] [9] [10] [24] [25] [26] [27].

The introduction of portable measuring equipments made personal exposure assessment feasible; measurements of the BTEX compounds and selected inorganic compounds (CO, NO_x, O₃ and SO₂) were conducted using measuring techniques and devices installed in automatic monitoring stations.

In recent years, a great number of researchers began to use the portable emission measurement systems (PEMS) to study the emission characteristics of motor vehicles because of their ability to reflect emissions under real-world condi-

tions [7] [28].

To analyse pollutants' concentration levels it is important to have information about weather, meteorological parameters (air temperature, humidity, atmospheric pressure, wind speed and direction, solar radiation and precipitation), but also detailed descriptions of sampling locations with the indications of potential emission sources.

The objective of this study is to evaluate the traffic-related concentrations of pollutants in urban air (BTEX, NO_x, O₃, SO₂ and CO, PM₁₀, PM_{2.5}), with a mobile laboratory equipped with continuously monitoring devices (Table 1). The mobile laboratory was placed in three University campuses areas, visited daily by around 8000 students. The chosen places to be measured inside the University campuses were close to the University entrance. The ambient air was continuously drawn through a Teflon tube placed on the mobile laboratory rooftop at about 3m up from the ground, and all the pollutants described in Table 1 were simultaneously measured. Data acquired quality is guaranteed by the periodic calibration of equipment.

The GC/FID has a capillary column, with a length of 60 m, the separation being made by the temperature program: an isothermal of 50°C holds 3 min, a heating rate of 8°C/min to 180°C/min holds 5 min; the total time for analysis was 18 min.

The concentration of particles PM_{2.5} was measured with a Portable Environmental Dust Monitor 11-E (manufactured by GRIMM) with a 5 min. time step [29] [30] [31]. Dust concentration PM₁₀ was measured using a Verewa device, which is not able to measure simultaneously both PM₁₀ and PM_{2.5}.

The results can be processed and transmitted remotely using IOVIS software.

3. Results and Discussions

The present study indicates that the levels in the ambient air are directly related

Table 1. Characteristics of the mobile laboratory devices.

Pollutant	Name	Measurement principle	Measuring range	Detection limit	Accuracy %
BTEX	GC 5000 AMA	GC/FID	0 - 50 µg/m ³	0.03 ppb	±1.0%
NO _x (NO + NO ₂)	APNA 370 Horiba	Chemi-luminescence	0 - 1.0 ppm	0.5 ppb	±1.0%
O ₃	APOA 370 Horiba	Ultraviolet absorption	0 - 1.0 ppm	0.5 ppb	±1.0%
CO	APMA 370 Horiba	Non-dispersive infrared absorption	0 - 100 ppm	0.05 ppm	±1.0%
SO ₂	APSA 370 Horiba	Ultraviolet fluorescence	0 - 0.5 ppm	0.5 ppb	±1.0%
PM ₁₀	F701-20 Verewa	Beta radiation adsorption	0 - 10 mg/m ³	0.001 mg/m ³	±2.0%
PM _{2.5}	Dust Monitor 11-E Grimm	Laser radiation	0.25 - 32 µm	0.1 µg/m ³	±2.0%

to the intensity and magnitude of the vehicles' number and type; the studied sites showed that their industrial surroundings and traffic compositions are different from each other (Figure 1). The concentrations are also indirectly related to dispersion, stability and wind speed. Thus the toxic air compounds can pose special threats in urban areas, because of the large number of students and people living near roads and facing heavy traffic.

The ratio of benzene to toluene (B/T) is commonly used to identify the BTEX emission sources. A ratio B/T value of around 0.5 (wt./wt.) is found to be characteristic of vehicular emissions in many urban areas worldwide [31] [32].

However, when the source of emissions of organic compounds from the BTEX group is located at a close distance from the measuring/monitoring station (a "fresh" source of emissions), the value of the m, p X/E parameter is higher than 3.3 [34] [35]. Under ideal conditions, where the only source of emissions of BTEX compounds is vehicle traffic, the numerical values of the $B \div T \div E \div X$ parameter is $3 \div 4 \div 1 \div 5$ and $B \div E < 5$, and $T \div E < 6$ [36] [37].

In our study, the main source of pollution with BTEX is vehicular emission (Table 2).

In the diurnal variation of BTEX, during a sunny and rainy day (Figure 2), two peaks of BTEX concentration were observed in the morning and in the

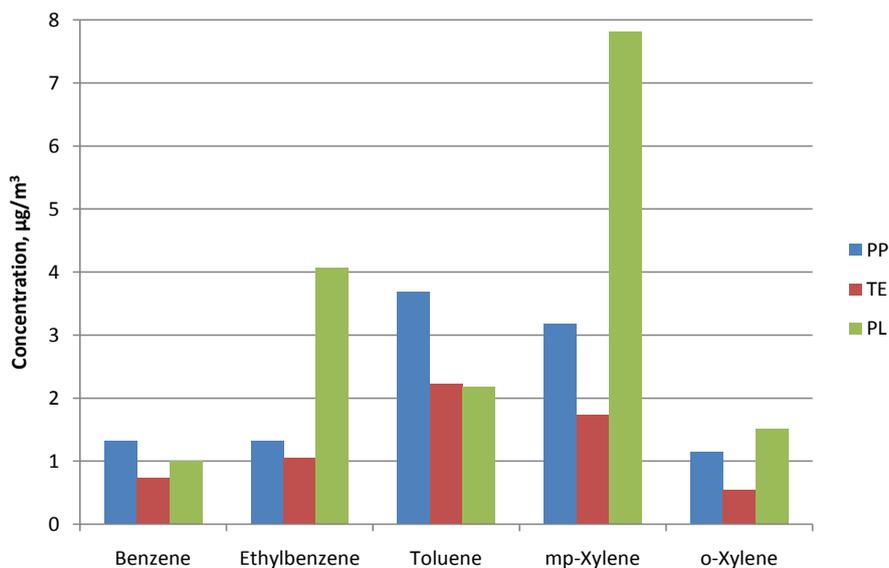


Figure 1. Comparison of mean concentration levels of BTEX from the three sites of campus.

Table 2. Ratio B/T, B/E, T/E, m,p X/E and $B \div T \div E \div X$, in 3 sites of university campus from Bucharest.

Site*	B/T	B/E	T/E	m,p X/E	$B \div T \div E \div X$
1	0.3	1	3.4	3.3	$1 \div 3.4 \div 1 \div 5.5$
2	0.3	1	3.8	3.3	$1 \div 3.7 \div 1 \div 4$
3	0.5	0.2	0.5	3.4	$0.2 \div 0.5 \div 1 \div 4$

*PP-1; TE-2; PL-3.

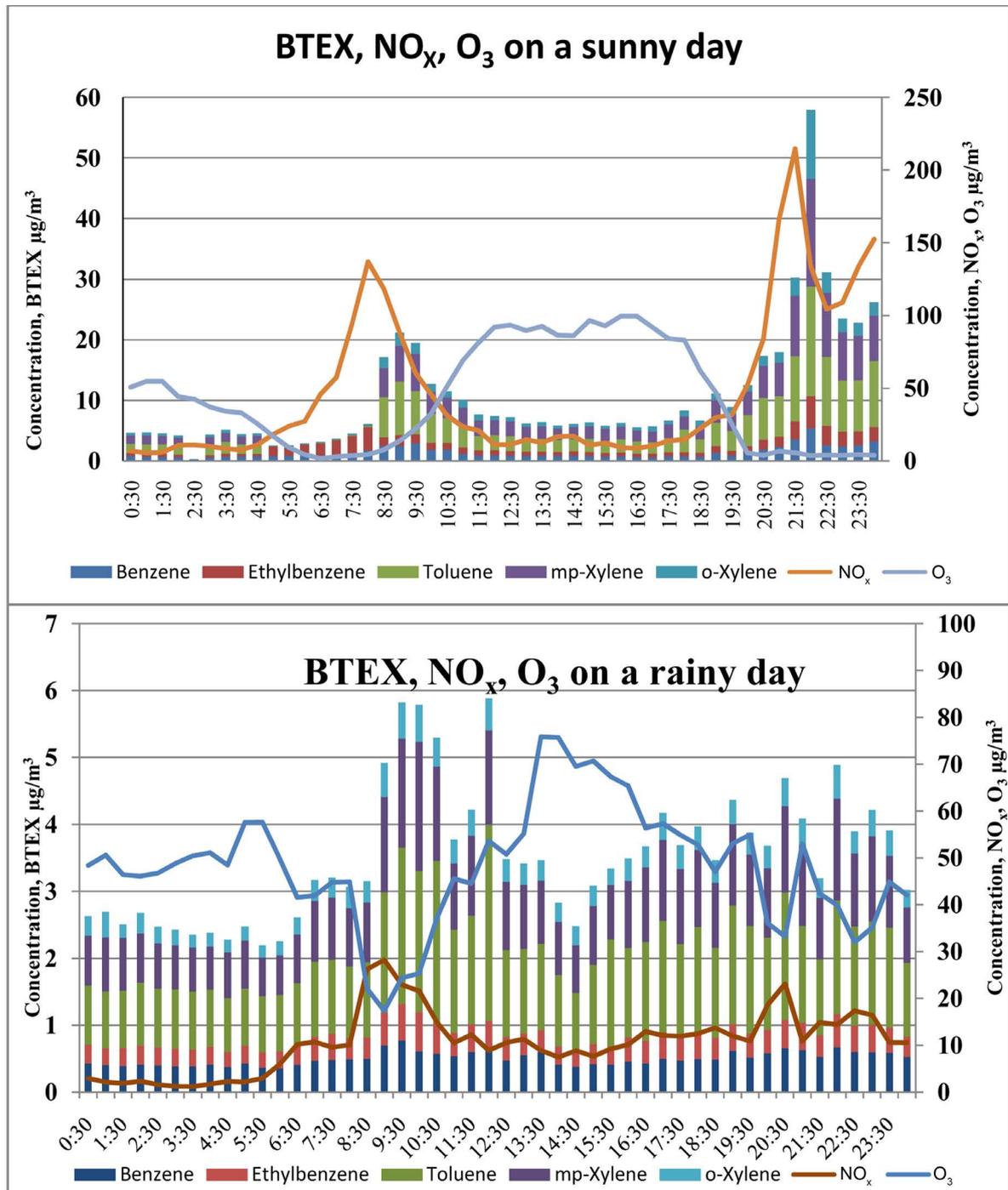


Figure 2. A typical sunny and rainy day, indicating levels of BTEX species, in the 1st site (PP).

evening. The maximum concentration was recorded from 7:00 to 10:00 in the morning, and then decreased at around 15:00. Thereafter, the concentration increased again from 17:00 until 22:00, when the second BTEX peak occurred. This trend is very similar to the diurnal trends found in other urban areas [9] [38].

In the rainy days, the rain washes out the pollutants, thus the accumulation of BTEX is smaller than in the sunny days (Figure 2, Table 3). In the weekend day

Table 3. Comparison of emissions, by Average \pm SD (n = 48), in a sunny day, a cold/rainy day and a weekend day in the site 1*, $\mu\text{g}\cdot\text{m}^{-3}$.

Pollutant	Sunny day	Cold/rainy day	Weekend day
Benzene	1.32 \pm 1.01	0.50 \pm 0.10	0.56 \pm 0.26
Toluene	3.68 \pm 3.73	1.34 \pm 0.47	1.56 \pm 0.97
Ethylbenzene	1.33 \pm 1.04	0.34 \pm 0.08	0.47 \pm 0.23
m,p-Xylene	3.18 \pm 3.34	0.99 \pm 0.29	1.35 \pm 0.72
o-Xylene	1.15 \pm 1.70	0.32 \pm 0.09	0.43 \pm 0.21
NO	32.0 \pm 49.8	1.1 \pm 1.5	1.6 \pm 1.8
NO ₂	41.2 \pm 26.4	18.5 \pm 11.1	18.1 \pm 15.8
NO _x	47.2 \pm 52.1	10.6 \pm 6.6	10.8 \pm 9.1
O ₃	42.9 \pm 35.8	48.1 \pm 12.8	61.3 \pm 24.6
CO**	0.5 \pm 0.4	0.3 \pm 0.05	0.3 \pm 0.1
SO ₂	1.3 \pm 1.0	0.3 \pm 0.2	0.8 \pm 0.7
PM ₁₀	84.4 \pm 43.1	19.7 \pm 3.1	33.3 \pm 10.4
PM _{2.5}	23.5 \pm 5.4	10.5 \pm 1.2	13.5 \pm 7.4

*PP -1; **mg/m³.

the traffic is low so the pollution follows same trend (**Table 3**).

The non-polar (hydrophobic) compounds as BTEX are mechanically carried by rain to the ground where they either enter in the groundwater, with a piston effect, or volatilized and re-enter the atmospheric air [39].

In **Table 4** benzene was 9% in the BTEX_{total} in all three sites while o-xylene was found to be the most abundant species, with 43% of BTEX_{total}.

The maximum value of benzene, found in the studied sites, was 5.4 \pm 1.01 $\mu\text{g}/\text{m}^3$ (**Table 4**). It is a matter of concern due to its carcinogenic effects, even in lower concentrations [41] [42]. In the Directive 50/EC, 2008 [43], on ambient air quality, the legislator recommends that the average annual concentration in the atmospheric air must not exceed 5 $\mu\text{g}/\text{m}^3$ in the urbanized areas (**Table 5**). Benzene has a relatively long life span, low reactivity and is stable in the atmosphere.

The maximum value of toluene, ethylbenzene and xylenes (m, p xylene and o-xylene) was found to be 18.07 \pm 3.73, 8.86 \pm 2.68, (17.78 \pm 3.34 and 11.38 \pm 1.7) respectively (**Table 4**), but that group are characterized by a very short life time in the atmospheric air in the urbanized area (in particular xylenes); these compounds undergo photochemical reactions more easily with the participation of strong oxidisers such as the hydroxyl radical $\cdot\text{OH}$, than benzene [33].

Table 4 shows high concentrations in O₃ (123.56 $\mu\text{g}/\text{m}^3$), above the limit values (120 $\mu\text{g}/\text{m}^3$, **Table 5**). High concentrations in O₃ corresponds to low concentrations in NO_x and xylene as can be observed in **Figure 3**, for a sunny day, due to photochemical reactions in the atmosphere, generating photochemical smog. During midday (10.00 - 18.00) (**Figure 3**), the solar radiation becomes strongest while BTEX and NO_x decrease, which could be interpreted as a photochemical reaction, producing O₃ [45]. There is a delay of 2 hours between the maximum solar radiation and the maximum produced O₃ concentration linked

Table 4. Measurement statistics in 3 sites of Campus from Bucharest, in $\mu\text{g}/\text{m}^3$.

Pollutant	Site*	Mean	Standard deviation	Maximum	Minimum
Benzene	1	1.32	1.01	5.40	0.08
	2	0.74	0.36	1.73	0.35
	3	0.84	0.25	1.45	0.51
Ethylbenzene	1	1.33	1.04	5.31	0.00
	2	1.05	1.05	4.14	0.34
	3	4.74	2.68	8.86	2.38
Toluene	1	3.69	3.73	18.07	0.05
	2	2.22	1.39	5.92	0.12
	3	1.17	0.93	3.04	0.05
mp-Xylene	1	3.18	3.34	17.78	0.00
	2	1.74	0.99	4.26	0.05
	3	5.33	4.12	9.82	0.10
o-Xylene	1	1.15	1.70	11.38	0.01
	2	0.55	0.25	1.32	0.20
	3	1.02	0.55	1.80	0.30
CO**	1	0.54	0.43	1.92	0.25
	2	0.37	0.14	0.74	0.22
	3	0.43	0.14	0.76	0.24
NO	1	32.06	49.78	207.80	0.00
	2	18.09	30.81	126.30	0.09
	3	3.77	2.90	10.81	0.00
NO ₂	1	41.23	26.41	92.75	10.44
	2	40.45	23.28	87.80	12.31
	3	23.30	8.33	34.68	4.12
NO _x	1	47.23	52.13	214.80	5.40
	2	35.65	28.63	122.10	8.03
	3	15.21	6.35	25.73	2.07
O ₃	1	54.34	49.06	121.66	1.63
	2	55.12	49.23	123.56	0.38
	3	28.42	10.62	47.07	5.77
SO ₂	1	1.28	1.06	5.07	0.00
	2	2.86	1.52	6.45	0.86
	3	2.34	2.15	11.30	0.81
PM ₁₀	1	58.49	27.10	164.06	29.36
	2	29.12	10.41	46.00	15.00
	3	16.17	3.49	22.00	10.00
PM _{2.5}	1	18.28	3.68	29.26	12.08

*PP-1; TE-2; PL-3; ** $\mu\text{g}/\text{m}^3$.

Table 5. Limit values and alert thresholds, directive 50/2008/EC (ambient air quality) [43].

Pollutant	Limit values				Alert thresholds
	1 hour	8 hour	1 day	Annual	
SO ₂ , µg/m ³	350		125		500
NO ₂ , µg/m ³	200			40	400
CO, mg/m ³		10			
O ₃ , µg/m ³		120			240
Benzene, µg/m ³				5	
PM ₁₀ , µg/m ³			50	40	
PM _{2.5} , µg/m ³				24	

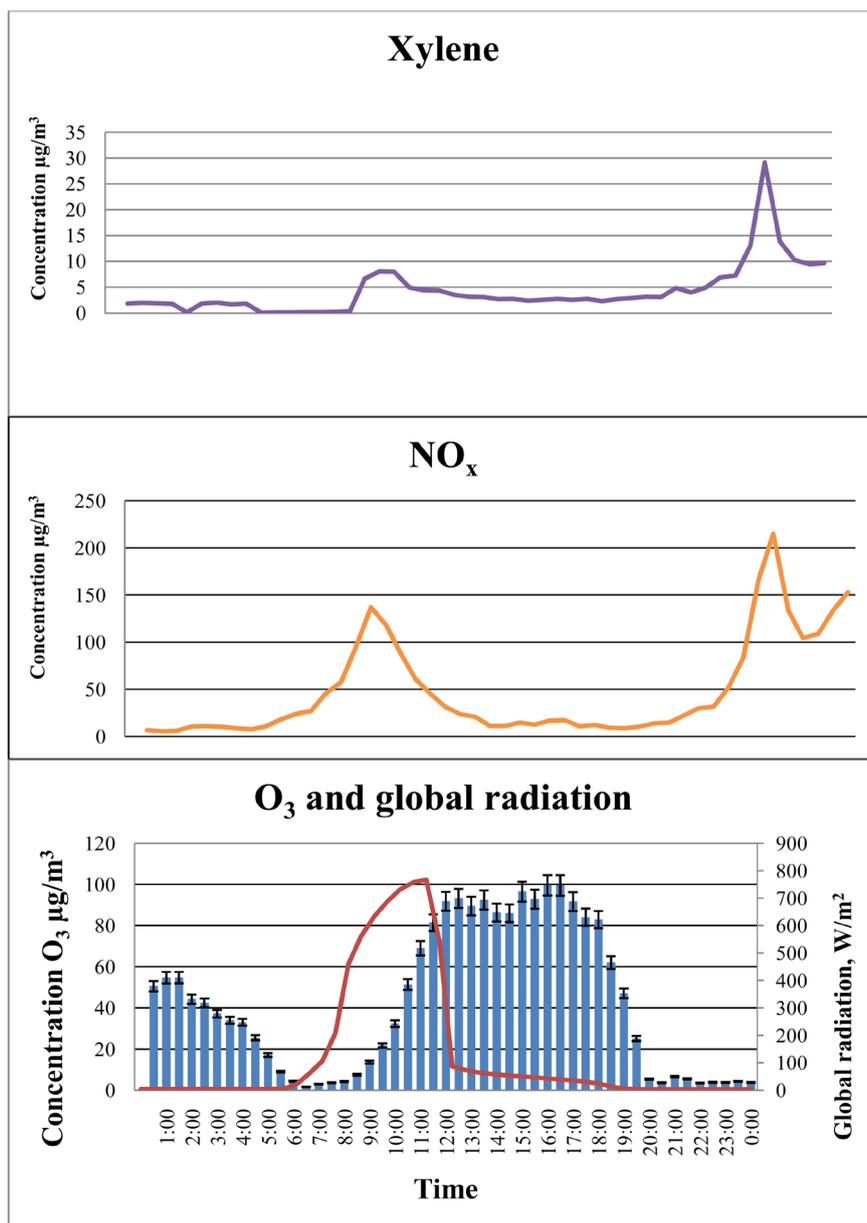


Figure 3. Diurnal variations of total xylene, NO_x, global radiation and O₃ from a typical sunny day.

to the photochemical reaction conditions.

Toluene and xylenes have a lower toxicity level than benzene. When exposed to photochemical reactions in the atmosphere they also can react to form new toxic compounds (peroxybenzoyl nitrates, carbonyl compounds etc.) which can result in adverse health effects [44].

The BTEX present in air can affect the environment in two ways, directly & indirectly. After BTEX are discharged into the atmosphere, they cause not only pollution problems on a local scale, but also play an important role on a regional scale, having effects such as acid rain, photochemical ozone formation introduced by the reaction with OH radicals in the troposphere, in the presence of nitrogen oxides and sunlight and increased risk of cancer [40].

CO results from an incomplete combustion of diesel fuel or gasoline in traffic engines; high concentrations of CO, generally, result from poor vehicle maintenance and an insufficient use of vehicle emission control systems [2]. In our study the concentration in CO was lower than the limit value.

Vehicles can also be a source of SO₂ emissions. However, the condition must be met that the fuel used in vehicles is contaminated with sulphur compounds. Interpretation of data summarized in **Table 4** shows that sulphur dioxide concentration in the atmospheric air in the 3 sites is very low. This can result from the fact that high-quality liquid fuels are used in vehicles, which are virtually free from sulphur compounds.

The seasonal variations of meteorological conditions may influence the dispersion, photochemical reactions, and emissions of air pollutants. The wind speed, for example, was very low (1.4 ± 0.7 m/s; 1.6 ± 1.4 m/s and 1.6 ± 1.1 m/s in the three sites), implying the dominance of local air masses at the monitoring site.

Particulate matters such as PM₁₀ and PM_{2.5} are, in a large part, carried by rain into the soil. The polar compounds (hydrophilic, NO_x, SO₂) dissolve in rainwater and are absorbed into the soil (increasing soil acidity) or evaporates to the clouds (leading to acid rain). **Figure 4** shows that measured PM₁₀ concentrations in site 1 during the sunny days are above the one day limit values according to Directive 50/2008/EC for ambient air quality (**Table 5**).

In our study, BTEX compounds were removed by the rain between 62% - 75%, NO_x and SO₂ 80% and 77% respectively. Concerning the particulate matters, they were washed out in a percentage of 68% - 85% for PM₁₀ and 42% - 69% for PM_{2.5} (**Figure 4**).

4. Conclusions

The interpretation of the results, in the monitoring study, obtained for the three sites of the University campuses, related to the atmospheric air pollution produced by urban traffic, showed that:

- in a sunny day with normal traffic we found that the maximum value 5.4 µg/m³ for benzene, a known human carcinogen, for 30 min., exceeding the annual limit value of 5 µg/m³; high concentrations in O₃ were determined for

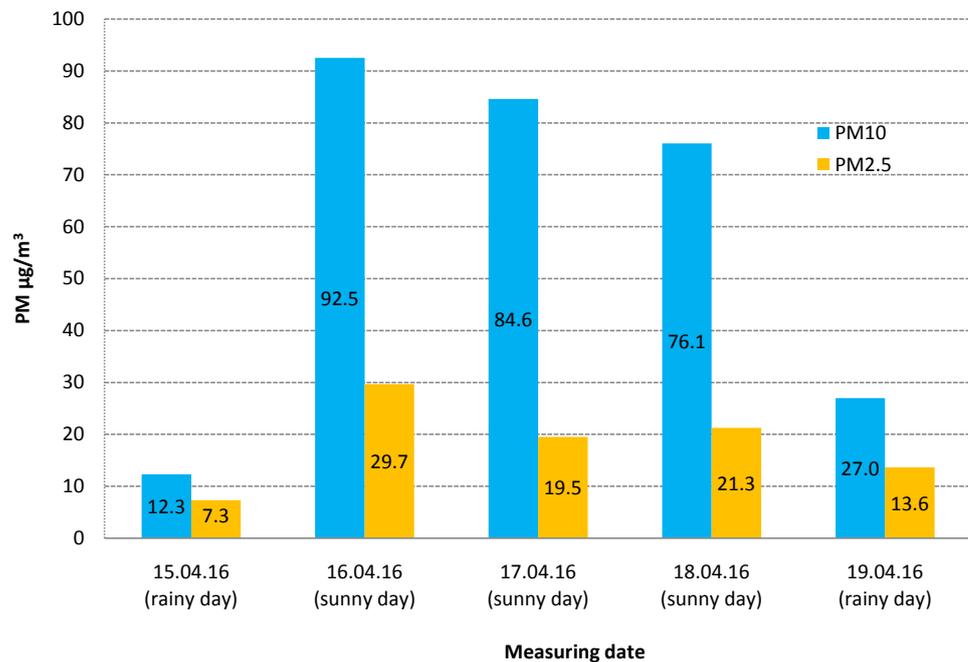


Figure 4. Comparison of PM₁₀ and PM_{2.5} in a sunny and rainy day in the site 1 (PP).

a 7 hours period (121.66 ± 7.02 , $123.56 \pm 4.89 \mu\text{g}/\text{m}^3$) being above the limit value ($120 \mu\text{g}/\text{m}^3$). The maximum of solar radiation, with corresponding low concentrations in NO_x and xylene, involves the formation of photochemical smog;

- in a rainy day, the rain washed out 62% - 75% of BTEX, 80% NO_x, 77% SO₂ and 68% PM₁₀, 42% PM_{2.5}.

The study of Ballesta [46] showed that background ambient air quality defines a baseline for exposure of the population upon which emissions related to activities or locations are superimposed. Daily average values of human exposure, for a non-smoking population, were approximately 1.5 times the level of urban background.

The average background, from benzene, in our 3 sites, was $0.97 \mu\text{g}/\text{m}^3$ and the exposure for students was $1.46 \mu\text{g}/\text{m}^3$.

The U.S. EPA (2005) [47] cancer risk analysis estimates that an individual exposed to benzene levels between 1.3 and $4.5 \mu\text{g}/\text{m}^3$ faces an increased risk to 1/100,000, which corresponds to our monitored case.

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