



“Gheorghe Asachi” Technical University of Iasi, Romania



AROMATIC HYDROCARBON LEVELS AND PM_{2.5} CHARACTERIZATION IN ROME URBAN AREA: PRELIMINARY RESULTS

Carla Fanizza^{1*}, Silvia Baiguera¹, Federica Incoronato¹, Cinzia Ferrari²,
Marco Inglessis², Marcello Ferdinandi², Roberto Schirò¹, Barbara De Berardis²

¹INAIL – Research Area, Department of Technological Innovations and Safety of Plants, Products and Anthropic Settlements,
220E Via Alessandria, 00198 Rome, Italy

²Italian National Institute of Health (ISS), Department of Environmental Health and Primary Prevention, 299 Viale Regina Elena,
00161 Rome, Italy

Abstract

The preliminary results of aromatic hydrocarbon (AR) levels and PM_{2.5} physico-chemical characterization in Rome urban air throughout the 2014 are reported. A gas chromatograph was used for continuous measurements of AR concentrations with 30 minute time intervals. PM_{2.5} was collected by PM swam Dual Channel. Metal content was determined by ICP-MS. Single particle characterization was performed by Scanning Electron Microscopy equipped with a thin window system for X-ray microanalysis by energy dispersion spectrometry. X-ray microanalysis data were used to classify the particles into clusters of similar chemical composition. Results showed variations in seasonal AR levels, higher concentrations in winter and lower in summer. Toluene was the most abundant compound, followed by *m,p*-xylene and benzene. The compounds showed similar correlations in winter and summer. According to T/B ratio and meteorological analysis, AR levels were under the influence of vehicular sources. Seasonal variation of different inter-species ratios showed a decreasing trend from winter to summer and an increase from August to December. ICP-MS analysis revealed Fe, Al and Zn as the most abundant elements, decreasing from March to July (except Zn). PM_{2.5} single particle characterization detected four particle clusters: C-rich particles, metal particles, sulphates and soil dust. C-rich particles were constituted of a large number of spherule aggregates carrying trace of S, Na and K. Metal particles are the second significant component, including Fe, Pb, Cu, Zn, Ni and Ti. Further studies must be performed to better understand the processes of transformation that undergo the carbonaceous particles in the atmosphere.

Key words: analytical electron microscopy, aromatic hydrocarbons, physico-chemical characterization, PM_{2.5}

Received: December, 2014; Revised final: June, 2015; Accepted: June, 2015

1. Introduction

Volatile organic compounds (VOCs) attracted much attention due to their wide occurrence and health impacts, especially in urban area. Quantification of VOCs in the ambient air is important for air quality assessment and for understanding the photochemical formation of smog. Aromatic hydrocarbons (ARs) usually represent a

significant fraction of total VOCs, and they are emitted by fuel combustion and evaporation of fuels and solvents. Among ARs, benzene, toluene and xylene are well known as major components with a potential health risk (Lawryk and Weisel, 1996; Leung and Harrison, 1999). Atmospheric ARs participate in complex chemical reaction to form secondary pollutants. Several studies suggest that 10%-60% of fine particulate matter (PM_{2.5}) is

* Author to whom all correspondence should be addressed: e-mail: c.fanizza@inail.it; Phone: +39 0697892610; Fax: +39 0697892590

composed of organic compounds (Pandis et al., 1992; Seinfeld and Pandis, 1998; Zhang et al., 2011). $PM_{2.5}$ is composed of a wide variety of organic and inorganic components of primary and secondary origin. Atmospheric hydrocarbons may contribute to particulate matter generation via semi-volatile reaction products that undergo gas-to-particle conversion.

In particular, aromatics typically contribute with 0.1 to 0.45 $\mu\text{g}/\text{m}^3$ to the observed $PM_{2.5}$ concentrations as shown in several studies (Kleindienst et al., 2010; Lewandowski et al., 2008; Offenberger et al., 2011; Stone et al., 2009).

Epidemiological studies have linked ambient particulate matter (PM) levels to an increased incidence of adverse cardiovascular events. Numerous epidemiological studies have associated short-term and long-term PM exposures to increased mortality (Dockery et al., 1993; Hart et al., 2015; Kloog et al., 2013; Peters et al., 2005; Pope et al., 2006; Samet et al., 2000). Moreover, several studies have shown that iron and other transition metals leaching from particles or by their presence on particle surfaces play a role in the generation of reactive oxygen species (ROS) in biological systems (Ghio et al., 2000) and ROS production activate cellular inflammatory response pathways (Heal et al., 2005).

Rome has a surface area of 1300 km^2 , 2.5 million inhabitants and the highest number of vehicles (~1.8 millions in 2013) among Italian cities.

In the present work are reported the preliminary results of a collaboration, started in January 2014, between the Italian National Institute of Health (ISS, Department of Environmental Health and Primary Prevention) and National Institute for Insurance against Accidents at Work (INAIL, Department of Technological Innovations and Safety of Plants, Products and Anthropic Settlements) whose main purpose is to undertake very in-depth studies on fine particulate matter through the physical-chemical characterization of individual particles and the study of the processes of transformation that undergo the particles in the atmosphere. For these reasons the AR levels, the concentration of several trace metals in $PM_{2.5}$ and single particle characterization of $PM_{2.5}$ have been evaluated in the urban air of Rome.

Moreover, natural radioactivity has been used as a reliable tracer of the dilution properties of the lower atmosphere.

2. Experimental

2.1. Sampling site description

The measurements presented in this work were carried out at the monitoring station located in the front yard of the Italian National Institute of Health (ISS) (2 km east of the city center) on the right side of the ISS main building central entrance.

The station is about 8 m from the curb of the street, a large road with medium-high traffic intensity.

2.2. AR monitoring and analytical method

Continuous measurements of AR concentrations were carried out between January 1 and December 10, 2014. The January data were not taken into account because the measurements for most of the days did not cover more than 90% of the daily hours. A Syntech Spectras 955 gas chromatograph (GC) was used for continuous measurements of 7 aromatic hydrocarbon concentrations with 30 minute time intervals, in 2014. A detailed description of the analytical system can be found elsewhere (Fanizza et al., 2014; Xie et al., 2008; Wang et al., 2004). The GC was calibrated according to Syntech recommendations; one complete full dynamic calibration was performed before each seasonal campaign by using a standard certified calibration gas mixture, containing 28 target species with mixing ratios of 1 ppm in nitrogen (Sapio, Italy), prepared by the gravimetric method (SR ISO 6142/2001). The calibration gas was diluted with zero air (quality 5.0) to prepare six calibration spans; the dilutions were prepared using a calibration system (Calibration System CMK5, MCZ, Umwelttechnik, DE). For every concentration (3, 5, 10, 15, 30, 50 ppbV) at least 6 samples was analyzed.

For each analysis, an air sample with a volume of 250 mL was sampled. The height of air intake was at road level. The daily averages were taken into account when the measurements covered more than 90% of the daily hours. The detection limits are estimated to be 0.03 to 0.05 $\mu\text{g}/\text{m}^3$, and the uncertainty is estimated to be 5%.

2.3. Natural radioactivity

The knowledge of the low atmosphere dilution properties layers makes possible to understand the accumulation of pollutants as well as the temporal evolution of all air pollution processes. We applied the technique based on the monitoring of a chemically stable compound (Radon) with an emission flow in order to get information about dilution potential of the Planetary Boundary Layer that can be considered constant in the space-time scale of interest.

The Radon gas is produced in the ground by the ^{222}Rn and the ^{220}Rn isotope (Thoron) radioactive decay and it is released in atmosphere where it disperses prevalently by turbulent scattering. Therefore, the concentration of Radon in atmosphere is mostly dependent on the vertical dilution factor, while the Radon products could be seen as natural tracers of mixing properties for low PBL layers. In case of convective mixing or advection, the natural Radon accumulation is allowed in the low PBL layers (Perrino et al., 2009). A sequential automatic system, namely PBL Mixing Monitor (FAI

Instruments, Fontenuova, Italy) was used to assess the mixing ratio of low PBL layers.

The instrument samples on hourly basis the atmospheric particulate matter where Radon progeny fixes and, by a Geiger-Muller counter, determines the sample radioactivity level. The instrument manufacturing characteristics allow getting 24 averages per hour of the natural radioactivity values per every sampling day.

2.4. PM_{2.5} sample collection and metal content determination

PM_{2.5} was collected by PM swam Dual Channel FAI Instruments, operating at 2.3 m³/h flow rate. Six particulate sampling for metal content determination and single particle physico-chemical characterization by analytical electron microscopy, were conducted from March 2014 to July 2014.

For the determination of metal content PM_{2.5} was collected on mixed cellulose ester membrane (pore size 1.2 µm) during 24 h; for single particle characterization by electron microscopy particulate matter was collected on polycarbonate membranes (pore size 0.8 µm) during 8 h. In a quartz tube sampled cellulose filters were added with 3 ml HNO₃ (67-69% Romil, ICP grade, metallic impurities less than 5 ppb), put in a closed vessel and mineralized by Microwave Digestion System (START D - Milestone). The obtained solutions were diluted with purified water (MilliQ Integral A10 System – Millipore) and analyzed using ICP-MS (Elan 9000 - Perkin Elmer) for 9 elements. The elemental concentrations were obtained by external calibration (3 points each element) using indium as internal standard.

A blank's elemental concentration has been subtracted in order to obtain the final values. The analytical uncertainty for each elemental concentration was determined. The minimum detection limit (MDL) for each element was defined as 3 times the blank's standard deviation.

2.5. Physico-chemical characterization of PM_{2.5}

Single particle characterization of PM_{2.5} was performed by SEM equipped with a thin –window system for X-ray microanalysis by energy dispersion spectrometry. A semi-automatic analysis system (Particle Analysis, EDAX) was used.

For each particle morphological parameter (mean diameter, Feret Diameter, Aspect ratio, shape factor) and chemical composition were determined (De Berardis et al., 2007). The intensities of the characteristic X-ray lines, collected from each particle and converted to the corresponding atomic concentration by standardless ZAF correction method, were analyzed by hierarchical cluster analysis (HCA) to determine the principal components of PM_{2.5} (Paoletti et al., 2003).

2.6. Data analysis

Pearson correlation test was carried out to study the relationship between compounds. $p < 0.05$ was considered significant, $p < 0.001$ highly significant.

3. Results and discussion

3.1. AR monitoring

The seasonal mean concentrations of ARs are given in Table 1. AR levels ranged from 19 µg/m³ in the winter period to 4.4 µg/m³ in the summer. The fall AR concentrations (7.3 µg/m³) were lower than spring levels (8.6 µg/m³), which can be linked to atmospheric conditions. Generally, VOC concentrations were higher in winter and autumn than in spring and summer, as found in many other cities (Batterman et al., 2002; Fanizza et al., 2014; Kourtidis et al., 2002; Pankow et al., 2003; Zou et al., 2015). Because November 2014 has been the hottest since 1800 and the wettest from 1926 (Brunetti, 2014), the correlations (hourly averages) between concentrations and temperature during spring, summer and fall were carried out to verify the influence of temperatures on AR levels. The AR/T winter correlations were not developed because of the lack of data related to hourly average temperature.

All ARs had highly significant ($p < 0.01$) negative correlations with temperature during the periods taken into account. These results are consistent with the effects of photochemical reactions, in summer these reactions must proceed faster than in winter. The average temperature during spring and fall period was 20°C and 18°C, respectively.

Table 1. Seasonal and annual AR concentrations (µg/m³)

Aromatic hydrocarbons	WINTER		SPRING		SUMMER		FALL		2014	
	Avg	Max-Min	Avg	Max-Min	Avg	Max-Min	Avg	Max-Min	Avg	Max-Min
Benzene	1.95	4.55-0.83	1.39	3.66-0.34	1.16	2.52-0.37	1.06	10.28-0.46	1.28	10.28-0.34
Toluene	6.86	23.49-1.34	2.58	14.03-0.32	1.39	9.47-0.15	2.27	22.41-0.17	2.57	23.49-0.15
Ethylbenzene	1.15	6.95-0.21	0.46	5.21-0.04	0.16	1.08-0.04	0.36	4.53-0.04	0.40	6.95-0.04
<i>m, p</i> -xylene	6.04	23.86-1.09	2.47	19.40-0.28	1.04	6.94-0.04	2.22	24.63-0.15	2.32	24.63-0.04
<i>o</i> -xylene	1.68	7.41-LOD ^a	0.70	6.33-0.07	0.31	2.13-0.04	0.66	7.62-0.04	0.67	7.62-LOD ^a
1,3,5 -TMB ^b	0.60	3.49-0.06	0.26	10.35-0.02	0.12	2.80-0.05	0.22	3.17-0.05	0.25	10.35-LOD ^a
1,2,4 -TMB ^b	1.24	7.70-0.16	0.72	16.01-0.07	0.28	4.27-0.05	0.59	8.65-0.05	0.60	16.01-0.05
Total	18.97	69.23-4.27	8.55	64.09-1.37	4.39	20.36-0.67	7.25	69.88-0.78	7.87	69.88-0.67

^aLOD = below the limit of detection, estimated to be 0.03 to 0.05 µg/m³; ^bTMB = trimethylbenzene

However, other atmospheric parameters have probably contributed to the low AR concentrations in fall as rain and relative humidity. During summertime the AR total concentration reduced of 77%. The minimum concentrations during summer months are probably due to the seasonal variation in the reactivities of ARs and to the higher mixing height in summer period.

Fig. 1 shows variations of all measured AR seasonal averages (mean, minimum and maximum values, standard deviation). All AR showed the same seasonal variation (Fig. 1), registering the highest concentration during winter and the lowest concentration during summer. Toluene was the most abundant ARs with an annual mean concentration of 2.57 µg/m³, the second and third ARs measured were m,p-xylene (2.32 µg/m³) and benzene (1.28 µg/m³) (Table 1). Toluene was found the most abundant AR in other cities around the world, such as Rome (Fanizza et al., 2014; Fuselli et al., 2010), Weldgeund (South Africa) (Jaars et al., 2014), and Pamplona (Parra et al., 2009).

AR concentrations measured in this study are smaller than levels reported for Asiatic urban areas

(Ran et al., 2009; Song et al., 2007), Pamplona, Spain, (except for m,p-xylene) (Parra et al., 2009), Kocaely, Turkey, (Pekey et al., 2011), Mexico City (Sosa et al., 2009) and for an urban area located in a relatively medium-size town from Mures County, Romania (Roba et al., 2014). On the contrary AR concentrations were higher than London levels (Russo et al., 2010) and tend to follow within the range of the Los Angeles measurements (Warneke et al., 2012). These differences can be attributed to particular characteristics of the studied cities.

The Pearson's correlations among AR measured, during winter and summer period, are reported in Table 2.

The evaluated correlations resulted to be highly significant (p<0.01) and positive and remained quite similar in both periods, even if the correlations were slightly higher in summer than in winter, which could be due to range of atmospheric and traffic conditions. Most AR concentrations were very strongly correlated (r≥0.61) in both seasons, suggesting that they came from the same sources during both periods, like vehicular traffic (Khoder, 2007).

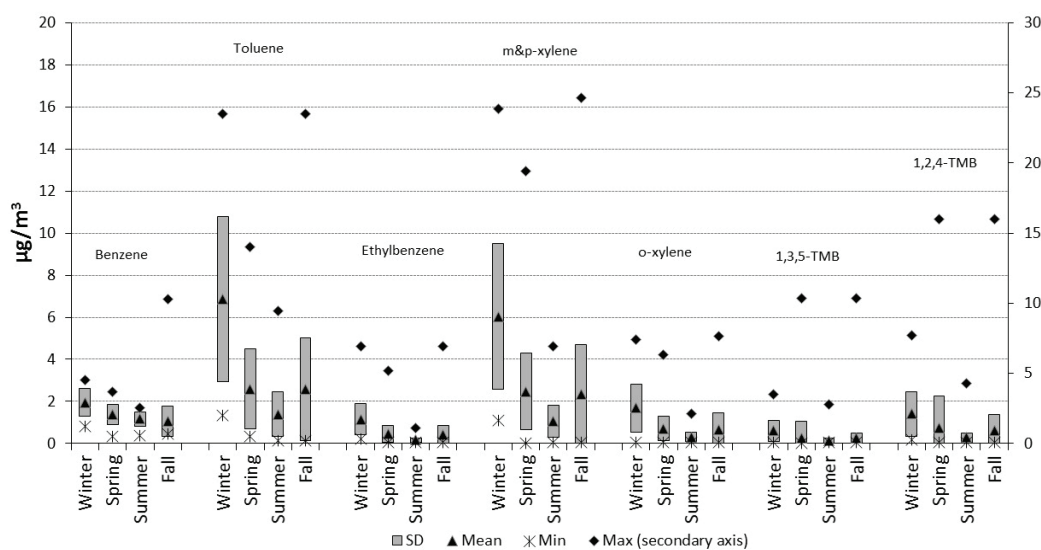


Fig. 1. AR seasonal variations during this study

Table 2. Pearson Correlation Coefficients

	WINTER					
	toluene	ethylbenzene	m, p-xylene	o-xylene	1,3,5-TMB	1,2,4-TMB
Benzene	0.58	0.48	0.53	0.53	0.35	0.35
Toluene		0.87	0.95	0.94	0.69	0.66
Ethylbenzene			0.93	0.96	0.84	0.83
m, p-xylene				0.99	0.85	0.83
o-xylene					0.85	0.83
1,3,5-TMB						0.96
	SUMMER					
Benzene	0.61	0.61	0.67	0.64	0.30	0.45
Toluene		0.76	0.85	0.81	0.40	0.54
Ethylbenzene			0.92	0.90	0.57	0.69
m, p-xylene				0.97	0.67	0.79
o-xylene					0.68	0.79
1,3,5-TMB						0.91

The inter-compound ratios can also be used to determine possible sources for ARs and the age of the air masses (Hoque et al., 2008). The T/B ratio is usually high close to anthropogenic emissions and decreases with an increase of distance from the sources and, based on T/B ratio, several studies individuate the possible sources (Lan and Minh, 2013). A $T/B < 3$ was characteristic of fresh emissions originating from traffic. In our study the T/B ratio was 2 highlighting that vehicular emissions are the main source of VOCs in Rome urban air. Seasonal variation of different inter-species ratios is graphed in Fig. 2. AR concentrations in ambient air are higher in winter than in summer period.

The inter-species ratios showed a decreasing trend from winter to summer, with the lowest value in August, and an increase from August to December.

The lowest values observed during the hottest months were due to enhanced photochemical reactions: the abundance of more reactive species decreased leading to reduction in inter-species ratios. Diurnal variations of all sampling days, monitored throughout the four seasons, showing the evolution of aromatics are presented in Fig. 3. AR levels followed every week day a similar pattern that changed during the weekends, e.g., Fig. 4 shows a typical week for each season.

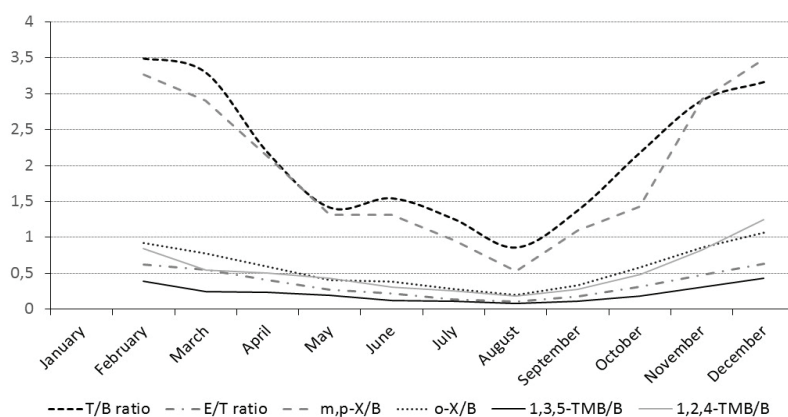


Fig. 2. Seasonal variations of AR inter-species

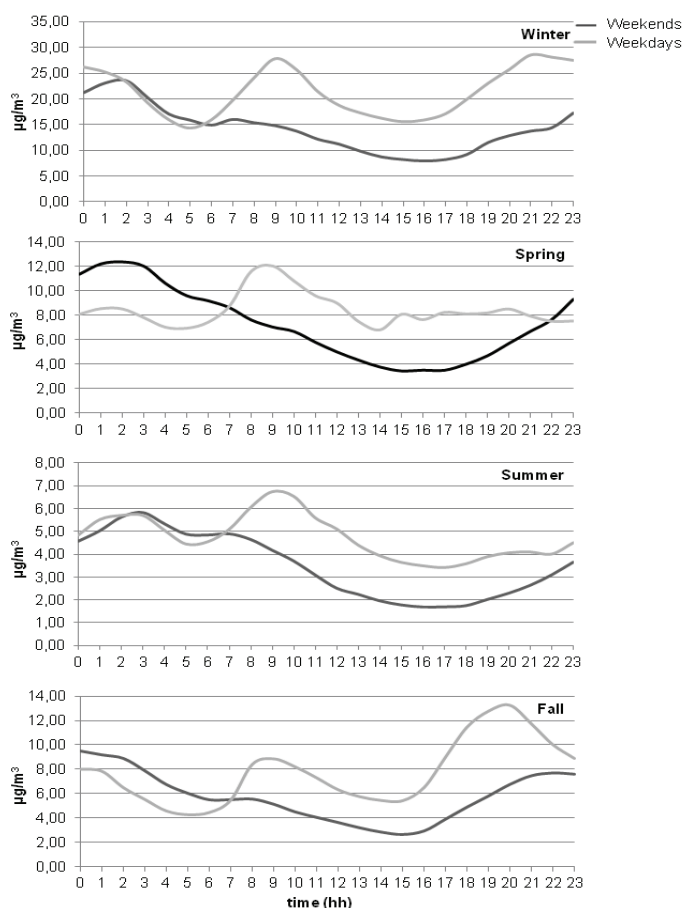


Fig. 3. AR diurnal variations during the monitored days

The AR concentrations were not the same throughout the day. Higher concentrations were recorded in the morning and in the evening and lower ones during the first afternoon on working days. The AR concentrations were cyclically lower during weekends than on working days in all four seasons, reflecting reduced levels of vehicular emissions on weekends, as it can be observed in Figs. 3-4. At weekends, there were slight increases in concentrations on evening.

These increases in concentrations coincided with traffic rush hours usually registered in the morning and in the evening on working days. A similar trend was found in previous studies developed in Rome urban air (Brocco et al., 1997; Fanizza et al., 2014).

Observed seasonal variations in AR concentrations are probably due to two different reasons: the seasonal variation in the reactivities of ARs and the height of the mixing layer that influences the dilution or the concentration of volatiles. In cold seasons (winter and fall) the thinning of the mixing layer and the occurrence of temperature inversion layers near the ground inhibits the vertical dilution of pollutants at night causing an increase of pollutants.

Consequently, AR trend follows mainly traffic emissions. In winter the second peak was slightly higher than the first, while in fall the peak in the late afternoon was considerable higher. In these periods the lowest values are found in the early morning around 5 a.m. During spring and summer, photochemical reactions are more rapid during the day and in the afternoon than in the morning, then the first concentration peak in the morning is higher than that in the late afternoon. Moreover the increase of mixing layer in the warmest hours of the day lead to a pollution dilution and a decrease of pollutant level in late afternoon.

The monthly variations of AR concentrations expressed as media, median, minimum and maximum values are graphically presented in Fig. 5a.

The AR concentration decrease, registered during the hottest months (July-September), was due to photochemical activity resulting from enhanced solar flux, temperature and higher OH radical concentrations in summer period. Traffic activity also contribute to observed seasonal variation in AR concentration, indeed a decrease in vehicular traffic volume was generally observed during the warmest months (July-August) compared to other months of the year in the center of Rome.

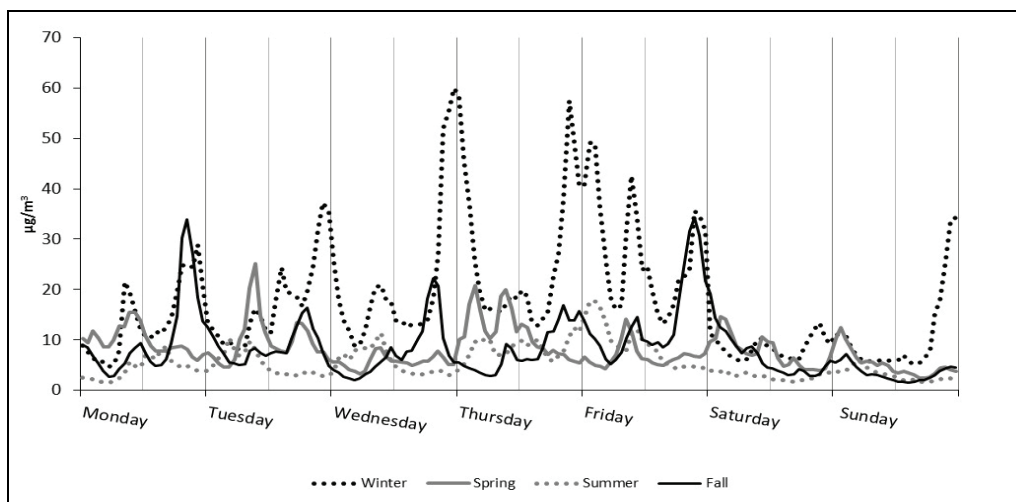


Fig. 4. Weekly averages of AR concentrations

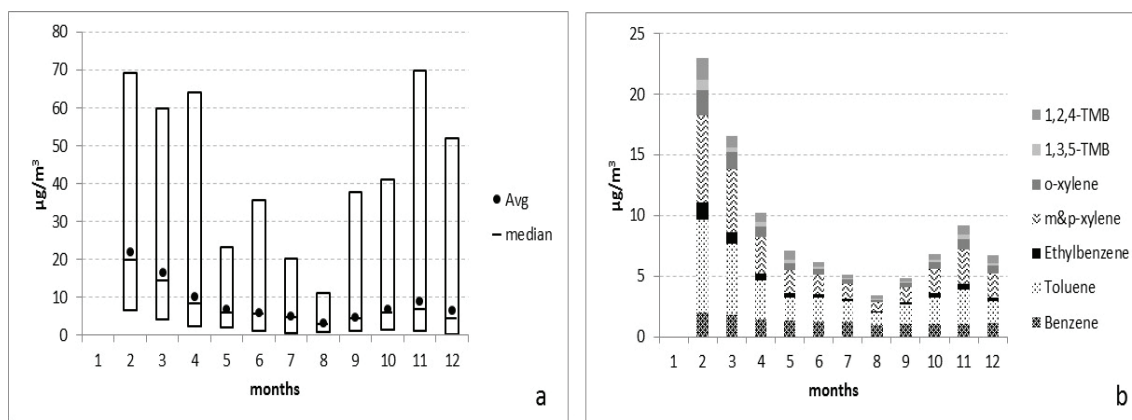


Fig. 5. (a) Monthly variations in AR concentrations during the period of study; (b) the contribution of individual compounds in the different months of the year

The highest concentrations of ARs were found in February and March. In November, AR concentration was lower than April, this was probably due to abnormal weather condition registered in this month. As above mentioned, in November temperatures higher as the seasonal averages were recorded and this month was particularly rainy.

The contribution of individual compounds in the different months of the year is shown in Fig. 5b. The maximum monthly average concentrations of all measured compounds were found in February, whereas the minimum were observed in August. Monthly average concentrations varied from 2.03 µg/m³ to 1.00 µg/m³ for benzene, from 7.64 µg/m³ to 1.76 µg/m³ for toluene, from 1.45 µg/m³ to 0.35 µg/m³ for ethylbenzene, from 7.15 µg/m³ to 1.99 µg/m³ for *m,p*-xylene, from 2.05 µg/m³ to 0.61 µg/m³ for *o*-xylene, from 0.85 µg/m³ to 0.23 µg/m³ for 1,3,5-TMB and from 1.84 µg/m³ to 0.69 µg/m³ for 1,2,4-TMB.

Moreover, Fig. 6 shows examples of typical sequences for summer and winter periods of natural radioactivity, which can be considered a good natural tracer of the mixing properties of the lower atmosphere. The variation with time of the radon concentration provides immediate information on current atmospheric conditions and on their changes. During summer the pattern indicated high nocturnal stability and low values from early morning to late evening (Fig. 6). The mixing period typically starts early in the morning and lasts until the late evening. During wintertime the pattern indicated an alternation between atmospheric stability (high nighttime radon values and daytime minima) and advection (steady low radon values) (Fig. 6).

To estimate the potential health risk of benzene in our monitoring site, formulas recently reported by Zhang et al. (2015) were used. Based on our collected data, benzene concentrations was 1.28E-03 mg/m³, the average daily exposure was 3.92E-04 mg/kg per day, the lifetime cancer risk (LTCR) resulted 1.13E-05, while the non-cancer risk of benzene (HQ) was estimated to be 0.04. According to USEPA, the acceptable LTCR for adults is 1E-06, and the HQ should be lower than 1 (USEPA, 2009). In our case, LCTR exceed the limit, implying that the potential cancer risk due to ambient benzene exposure should be a health concern in the urban Rome area. Moreover, calculated HQ indicated that non-cancer risk of benzene is not as distinctive as its cancer risk, as already reported also for four background sites in China (Zhang et al., 2015).

3.2. PM_{2.5} metal content analysis

Table 3 shows the concentration's mean value, expressed in ng/m³, for the six campaigns of PM_{2.5} sampling. Fe was the most abundant element, followed by Al and Zn in agreement to chemical composition of fine particulate particles collected in

areas heavily impacted by traffics, as Milan and New York (Perrone et al., 2010; Song and Gao, 2011).

Table 3. Mean value (SD) of elemental concentration expressed in ng/m³

<i>Analyzed Metal</i>	<i>Mean value (SD)</i>
Al	2.671 (2.704)
Cd	0.006 (0.005)
Cu	0.450 (0.162)
Fe	6.589 (3.172)
Ni	0.093 (0.042)
Pb	0.241 (0.141)
Ti	0.098 (0.069)
V	0.103 (0.056)
Zn	0.615 (0.123)

As in sampling site industrial plants or thermo electrical sites were absent and vehicular traffic was the main source of pollution the metals were attributed to fuel combustion, tyre and brake wear (Kumar et al., 2013; Pant and Harrison, 2013). Many study showed that abrasion particles contribute significantly to fine particulate (Lin et al., 2005; Narvaez et al., 2008; Song and Gao, 2011). In Fig. 7 the concentrations of metals in PM_{2.5} collected from March 2014 to July 2014 are displayed. Generally, metal's concentrations decreased from March to July; Zn, instead, remained mostly constant during the sampling period.

3.3. PM_{2.5} characterization by SEM/EDX

HCA allow us to classify the PM_{2.5} into four principal components or cluster with similar chemical composition: C-rich particles, sulphates, soil dust and metals (Fig. 8). C-rich particles were the most important component of PM_{2.5} making up 90% of PM_{2.5}. Many authors showed the prevalence of C-rich particles in PM_{2.5} in different urban environments (Baulig et al., 2004; He et al., 2001; Longhin et al., 2013; Pipal et al., 2011).

This kind of particles were mainly spherules with size ranging from 40 to 70 nm showing two different morphologies: chains of spherules with dimensions up 2 µm and aggregates of large number of spherules ranging from 360 nm to 4 µm. Our data on morphological characteristics of this type of particles are in agreement with Longhin et al. (2013). These authors showed that carbon soot particles were mainly aggregates constitute by round-shaped nanoparticles of 40 nm in diameter.

Moreover analytical electron microscopy characterization showed that C-rich aggregates act as carrier, on their surface, of different elements. X ray microanalysis data showed traces of S, Na, and K on 12% of aggregates, suggesting that carbonaceous particles act as vehicles of alkaline metal sulphates, produced by SO₂ photochemical oxidation catalysed by C-rich particles themselves. 18 % of C-rich aggregates showed traces of S and heavy metals, as Fe, V, Zn and Pb.

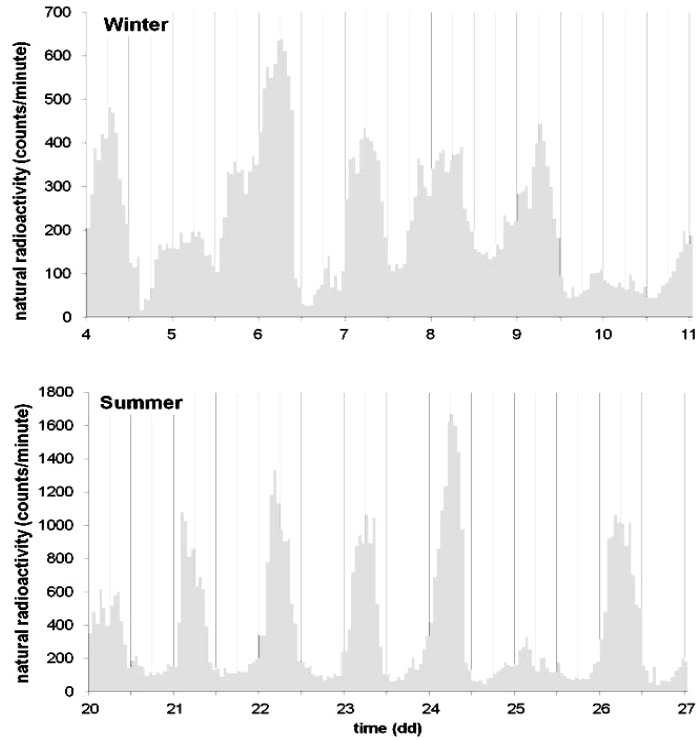


Fig. 6. Natural radioactivity trends in winter and summer periods

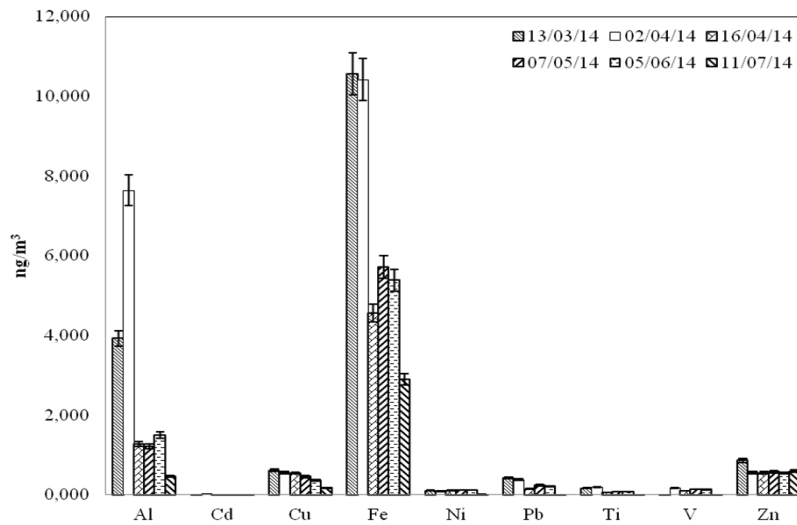


Fig. 7. Metal concentration (ng/m^3) for each sampling day

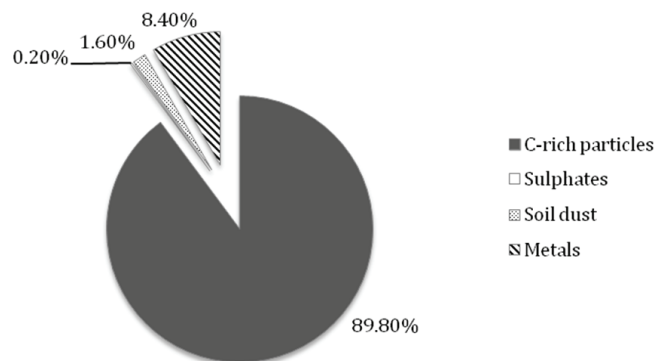


Fig. 8. Abundance of principal component identified in $PM_{2.5}$ by HCA on SEM/EDX physico-chemical characterization data

These carbonaceous particles, coming from fuel oil combustion (Chen et al., 2005, Moldanova et al., 2009), showed an average size of 512 nm. In addition, larger and pure spherical carbonaceous particles (in the size range 200-600 nm), deriving from incomplete fuel oil combustion, were rarely observed.

Metal particles are the second more important cluster of PM_{2.5}. They showed a size distribution ranging from 670 nm to 200 nm. This component includes oxides and metal compounds of Fe, Pb, Cu, Zn, Ni, Ti. Iron oxides are the most abundant particles in this cluster. The cluster of soil dust consists of silica and clay (Si, Al or Si, Al, Fe) particles. This component made up only 1.6% of PM_{2.5}.

4. Conclusions

AR concentrations in this work showed values comparable to those reported for Los Angeles, while resulted lower than other cities like Pamplona and Mexico City. AR seasonal variations showed the highest concentrations during winter, decreasing during warmer seasons and registering the lowest value during summer. Moreover, AR fall concentrations were lower than spring levels due to the particular meteorological conditions during this period. According to T/B ratio and the meteorological analysis, AR levels were under the influence of vehicular sources.

Vehicular traffic was the most important source of PM_{2.5} as shown by the main components (C-rich particles and metals) identified in the particulate by physico-chemical characterization. Moreover X-ray microanalysis data focused out a coating of alkaline metal sulphates on the carbonaceous particle surfaces, due to the catalytic action of particles themselves. However, it is necessary to carry out further studies in this site on ozone, nitrogen oxides, carbon monoxide and sulphur dioxide analysis in order to better understand the processes of transformation that undergo the carbonaceous particles in the atmosphere.

Acknowledgments

This work was supported under the grant INAIL/P20 "Studio dell'inquinamento primario e secondario in un'area urbana in funzione delle sorgenti emissive e delle condizioni meteo-climatiche (Study of the primary and secondary pollution in the urban area in function of the emission sources and of the meteo-climatic conditions)" L04, 2013-15.

Authors thanks Dr.ssa Daniela Lega (Department of Technological Innovations and Safety of Plants, Products and Anthropic Settlements, INAIL) for providing the scanning electron microscopy.

References

Batterman S.A., Peng C.Y., Braun J., (2002), Levels and composition of volatile organic compounds on

commuting routes in Detroit, Michigan, *Atmospheric Environment*, **36**, 6015–6030.

- Baulig A., Poirault J.J., Ausset P., Schins R., Shi T., Baralle D., Dorlhene P., Meyer M., Lefevre R., Baeza-Squiban A., Marano F., (2004), Physicochemical characteristics and biological activities of seasonal atmospheric particulate matter sampling in two locations of Paris, *Environmental Science Technology*, **38**, 5985-5992.
- Brocco D., Fratarcangeli R., Lepore L., Petricca M., Ventrone T., (1997), Determination of aromatic hydrocarbons in urban air of Rome, *Atmospheric Environment*, **31**, 557-566.
- Brunetti M., (2014), 2014 is the hottest year, (in Italian), On line at: http://www.stampa.cnr.it/documenti/comunicati/italiano/2014/Dicembre/83_DIC_2014.HTM
- Chen Y.Z., Shah N., Rraun A., Huggins F.E., Huffman G.P., (2005), Electron microscopy investigation of carbonaceous particulate matter generated by combustion of fossil fuels, *Energy & Fuels*, **19**, 1644-1651.
- De Berardis B., Incocciati E., Massera S., Gargaro G., Paoletti L., (2007), Airborne silica levels in an urban area, *Science of Total Environment*, **382**, 251-258.
- Dockery D.W., Pope C.A. III, Xu X., Spengler J.D., Ware J.H., Fay M.E., Ferris B.G. Jr, Speizer F.E., (1993), An association between air pollution and mortality in six US cities, *New England Journal of Medicine*, **329**, 1753-1759.
- Fanizza C., Incoronato F., Baiguera S., Schiro R., Brocco D., (2014), Volatile organic compound levels at one site in Rome urban air, *Atmospheric Pollution Research*, **5**, 303–314.
- Fuselli S., De Felice M., Morlino R., Turrio-Baldassarri L., (2010), A three year study on 14 VOCs at one site in Rome: levels, seasonal variations, indoor/outdoor ratio and temporal trends, *International Journal of Environmental Research and Public Health*, **7**, 3792–3803.
- Ghio A.J., Richards J.H., Carter J.D., Madden M.C., (2000), Accumulation of iron in the rat lung after tracheal instillation of diesel particles, *Toxicologic Pathology*, **28**, 619–627.
- Hart J.E., Liao X., Hong B., Puett R.C., Yanosky J.D., Suh H., Kioumourtzoglou M.A., Spiegelman D., Laden F., (2015), The association of long-term exposure to PM_{2.5} on all-cause mortality in the Nurses' Health Study and the impact of measurement-error correction, *Environmental Health*, **14**, 1-9.
- He K., Yang F., Ma Y., Zhang Q., Yao X., Chan C.K., Cadle S., Chan T., Mulawa P., (2001), The characteristics of PM_{2.5} in Beijing, China, *Atmospheric Environment*, **35**, 4959 - 4970.
- Heal M.R., Hibbs L.R., Agius R.M., Beverland I.J., (2005), Total and water-soluble trace metal content of urban background PM₁₀, PM_{2.5} and black smoke in Edinburgh, UK, *Atmospheric Environment*, **39**, 1417-1430.
- Hoque R.R., Khillare P.S., Agarwal T., Shridhar V., Balachandran S., (2008), Spatial and temporal variation of BTEX in the urban atmosphere of Delhi, India, *Science of Total Environment*, **392**, 30–40.
- Jaars K., Beukes J.P., van Zyl P.G., Venter A.D., Josipovic M., Pienaar J.J., Vakkari V., Aaltonen H., Laakso H., Kulmala M., Tiitta P., Guenther A., Hellén H., Laakso L., Hakola H., (2014), Ambient aromatic hydrocarbon

- measurements at Welgedund, South Africa, *Atmospheric Chemistry and Physics*, **14**, 7075-7089.
- Khoder M.I., (2007), Ambient levels of volatile organic compounds in the atmosphere of greater Cairo, *Atmospheric Environment*, **41**, 554-566.
- Kleindienst T.E., Lewandowski M., Offenbergh J.H., Edney E.O., Jaoui M., Zheng M., Ding X., Edgerton E.S., (2010), Contribution of primary and secondary sources to organic aerosol at SEARCH network sites, *The Journal of the Air & Waste Management Association*, **60**, 1388-1399.
- Kloog I., Ridgway B., Koutrakis P., Coull B.A., Schwartz J.D., (2013), Long- and short-term exposure to PM_{2.5} and mortality: using novel exposure models, *Epidemiology*, **24**, 555-61.
- Kourtidis K.A., Ziomas I., Zerefos C., Kosmidis E., Symeonidis P., Christophilopoulos E., Karathanassisa S., Mploutsosb A., (2002), Benzene, toluene, ozone, NO₂ and SO₂ measurements in an urban street canyon in Thessaloniki, Greece, *Atmospheric Environment*, **36**, 5355-5364.
- Kumar P., Pirjola L., Ketzler M., Harrison R.M., (2013), Nanoparticle emissions from 11 non-vehicle exhaust sources - A review, *Atmospheric Environment*, **67**, 252-277.
- Lan T.T.N., Minh P.A., (2013), BTEX pollution caused by motorcycles in the megacity of HoChiMinh, *Journal of Environmental Sciences*, **25**, 348-356.
- Lawryk N.J., Weisel C.P., (1996), Concentration of volatile organic compounds in the passenger compartment of automobiles, *Environmental Sciences & Technology*, **30**, 810-816.
- Leung P.L., Harrison R.M., (1999), Roadside and in-vehicle concentrations of monoaromatic hydrocarbons, *Atmospheric Environment*, **33**, 191-204.
- Lewandowski M., Jaoui M., Offenbergh J.H., Kleindienst T.E., Edney E.O., Sheesley R., Schauer J.J., (2008), Primary and secondary contributions to ambient PM in the midwestern United States, *Environmental Sciences & Technology*, **42**, 3303-3309.
- Lin C.-C., Chen S.-J., Huang K.-L., Hwang W.-I., Chang-Chien G.-P., Lin W.-Y., (2005), Characteristics of metals in nano/ultrafine/fine/coarse particles collected beside a heavily Trafficked road, *Environmental Science and Technology*, **39**, 8113-8122.
- Longhin E., Pezzolato E., Mantecca P., Holme J.A., Franzetti A., Camatini M., Gualtieri M., (2013), Season linked responses to fine and quasi-ultrafine Milan PM in cultured cells, *Toxicology in Vitro*, **27**, 551-559.
- Moldanova J., Fridell E., Popovicheva O., Demirdijan B., Tishkova V., Faccinetto A., Focsa C., (2009), Characterisation of particulate matter and gaseous emissions from a large ship diesel engine, *Atmospheric Environment*, **43**, 2632-2641.
- Narvaez R.F., Hoepner L., Chillrud S.N., Yan B., Garfinkel R., Whyatt R., Camann D., Perera F.P., Kinney P.L., Miller R.L., (2008), Spatial and temporal trends of polycyclic aromatic hydrocarbons and other traffic-related airborne pollutants in new York city, *Environmental Science and Technology*, **42**, 7330-7335.
- Offenbergh J.H., Lewandowski M., Jaoui M., Kleindienst T.E., (2011), Contributions of biogenic and anthropogenic hydrocarbons to secondary organic aerosol during 2006 in Research Triangle Park, NC, *Aerosol and Air Quality Research*, **11**, 99-108.
- Pandis S.N., Harley R.A., Cass G.R., Seinfeld J.H., (1992), Secondary organic aerosol formation and transport, *Atmospheric Environment*, **26A**, 2269-2282.
- Pankow J.F., Luo W., Bender D.A., Isabelle L.M., Hollingsworth J.S., Chen C., Asher W.E., Zogorski J.S., (2003), Concentrations and co-occurrence correlations of 88 volatile organic compounds (VOCs) in the ambient air of 13 semi-rural to urban locations in the Unites States, *Atmospheric Environment*, **37**, 5023-5046.
- Pant P., Harrison R.M., (2013), Estimation of the contribution of road traffic emissions to particulate matter concentrations from field measurements: A review, *Atmospheric Environment*, **77**, 78-97.
- Paoletti L., De Berardis B., Arrizza L., Passacantando M., Inglessis M., Mosca M., (2003), Seasonal effect on the physico-chemical characteristics of PM_{2.1} in Rome: a study by SEM and XPS, *Atmospheric Environment*, **37**, 4869-4879.
- Parra M.A., Elustondo D., Bermejo R., Santamaria J.M., (2009), Ambient air levels of volatile organic compounds (VOC) and nitrogen dioxide (NO₂) in a medium size city in Northern Spain, *Science of the Total Environment*, **407**, 999-1009.
- Pekey B., Yilma H., (2011), The use of passive sampling monitor spatial trends of volatile organic compounds (VOCs) at one industrial city of Turkey, *Microchemical Journal*, **97**, 213-219.
- Perrino C., Catrambone M., Esposito G., Lahav D., Mamane Y., (2009), Characterisation of gaseous and particulate atmospheric pollutants in the East Mediterranean by diffusion denuder sampling lines, *Environmental Monitoring and Assessment*, **152**, 231-244.
- Perrone M.G., Ferrero L., Lo Porto C., Udisti R., Bolzacchin E., Camatini M., (2010), Seasonal variations in chemical composition and in vitro biological effects of fine PM from Milan, *Chemosphere*, **78**, 1368 - 1377.
- Peters A., von Klot S., Heier M., Trentinaglia I., Cyrus J., Hörmann A., Hauptmann M., Wichmann H.E., Löwel H., (2005), Particulate air pollution and nonfatal cardiac events. Part I. Air pollution, personal activities, and onset of myocardial infarction in a case-crossover study, *Research Report Health Effects Institute*, **124**, 1-66.
- Pipal A.S., Kulshrestha A., Taneja A., (2011), Characterization and morphological analysis of airborne PM_{2.5} and PM₁₀ in Agra located in North Central India, *Atmospheric Environment*, **45**, 3621-3630.
- Pope C.A., Muhlestein J.B., May H.T., Renlund D.G., Anderson J.L., Horne B.D., (2006), Ischemic heart disease events triggered by short-term exposure to fine particulate air pollution, *Circulation*, **114**, 2443-2448.
- Ran L., Zhao C.S., Geng F.H., Tie X.X., Tang X., Peng L., Zhou G.Q., Yu Q., Xu J.M., Guenther A., (2009), Ozone photochemical production in urban Shanghai, China: Analysis based on ground level observations, *Journal of Geophysical Research-Atmospheres*, **114**, ID15301, DOI: 10.1029/2008JD010752.
- Roba C., Ștefănie H., Török Z., Kovacs M., Roșu C., Ozunu A., (2014), Determination of volatile organic compounds and particulate matter levels in an urban area from Romania, *Environmental Engineering and Management Journal*, **13**, 2261-2268.
- Russo R.S., Zhou Y., White M.L., Mao H., Talbot R., Sive B.C., (2010), Multi-year (2004-2008) record of nonmethane hydrocarbons and halocarbons in New

- England: Seasonal variations and regional sources, *Atmospheric Chemistry and Physics*, **10**, 4909–4929.
- Samet J.M., Dominici F., Curriero F.C., Coursac I., Zeger S.L., (2000), Fine particulate air pollution and mortality in 20 US cities 1987-1994, *New England Journal of Medicine*, **343**, 1742-1749.
- Seinfeld J.H., Pandis S.N., (Eds.), (1998), *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, John Wiley & Sons, New York.
- Song F., Gao Y., (2011), Size distributions of trace elements associated with ambient particular matter in the affinity of a major highway in the New Jersey-New York metropolitan area, *Atmospheric Environment*, **45**, 6714-6723.
- Song Y., Shao M., Liu Y., Lu S.H., Kuster W., Goldan P., Xie S.D., (2007), Source apportionment of ambient volatile organic compounds in Beijing, *Environmental Science & Technology*, **41**, 4348–4353.
- Sosa R.E., Bravo H., Mujica V., Sánchez P., Bueno L.E., Krupa S., (2009), Levels and source apportionment of volatile organic compounds in southwestern area of Mexico City, *Environmental Pollution*, **157**, 1038-1044.
- STANDARD, (2001), Gas analysis - Preparation of calibration gas mixtures - Gravimetric method, SR ISO 6142/2001.
- Stone E.A., Zhou J., Snyder D.C., Rutter A.P., Mieritz M., Schauer J.J., (2009), A comparison of summertime secondary organic aerosol source contributions at contrasting urban locations, *Environmental Sciences & Technology*, **43**, 3448–3454.
- USEPA, (2009), Risk assessment guidance for superfund volume I: human health evaluation manual (part F, supplemental guidance for inhalation risk assessment), EPA Report (EPA/540/-R-070/002), United States Environmental Protection Agency, On line at: <http://www.epa.gov/oswer/riskassessment/ragsf/index.htm>.
- Wang J.L., Din G.Z., Chan C.C., (2004), Validation of a laboratory– constructed automated gas chromatograph for the measurement of ozone precursors through comparison with a commercial analogy, *Journal of Chromatography A*, **1027**, 11–18.
- Warneke C., de Gouw J.A., Holloway J.S., Peischl J., Ryerson T.B., Atlas E., Blake D., Trainer M., Parrish D.D., (2012), Multiyear trends in volatile organic compounds in Los Angeles, California: Five decades of decreasing emissions, *Journal of Geophysical Research–Atmospheres*, **117**, ID 00V17, DOI: 10.1029/2012JD017899.
- Xie X., Shao M. Liu Y. Lu S.H., Chang C.C., Chen Z.M., (2008), Estimate of initial isoprene contribution to ozone formation potential in Beijing, China, *Atmospheric Environment*, **42**, 6000–6010.
- Zhang Q., Jiminez J.L., Canagaratna M.R., Ulbrich I.M., Ng N.L., Worsnop D.R., Sun Y., (2011), Understanding atmospheric organic aerosols via factor analysis of aerosol mass spectrometry: a review, *Analytical and Bioanalytical Chemistry*, **401**, 3045–3067.
- Zhang Z., Wang X., Zhang Y., Lü S.L., Huang Z., Huang X., Wang Y., (2015), Ambient air benzene at background sites in China's most developed coastal regions: exposure levels, source implications and health risks, *Science of the Total Environment*, **511**, 792-800.
- Zou Y., Deng X. J., Zhu D., Gong D.C., Wang H., Li F., Tan H.B., Deng T., Mai B.R., Liu X.T., Wang B.G., (2015), Characteristics of 1 year of observational data of VOCs, NO_x and O₃ at a suburban site in Guangzhou, China, *Atmospheric Chemistry and Physics*, **15**, 6625–6636.