

CONSIDERATIONS CONCERNING AIR POLLUTION WITH PAHs OF PARTICULATE MATTERS FROM URBAN AREAS WITH INTENSE ROAD TRAFFIC

Elena Bucur; Ileana Nicolescu

National Research and Development Institute for Industrial Ecology –**ECOIND**,
90-92 Panduri St., sector 5, Bucharest, Romania,
ecoind@incdecoind.ro, poluare.aer@incdecoind.ro

Abstract:

From the potential air pollutants from big urbane areas in the last years special attention is given to particulate matters, which are found among the “six criteria pollutants” as they were named by the United States Environmental Protection Agency (EPA) next to the ozone, carbon oxide, nitrogen dioxide, sulphur dioxide and lead, due to the risk they can pose to human health and the environment.

Of interest to the environment and population health are the PM 10 (particulate matter with an aerodynamic diameter of up to 10 μm) and PM 2.5 (particulate matter with an aerodynamic diameter of up to 2.5 μm) dust fractions, and their monitoring in the environmental air is controlled by the legislation all around the world, the PM 2.5 falling in the category of breathable dusts which can enter and accumulate in the respiratory system at the pulmonary alveolus level, causing serious health problems [1].

The toxic degree of the particulate matters is amplified by the presence in their structure of other harmful chemical compounds from which the most important are heavy metals and PAH-s[2].

The paper presents the test results in 2010, in two monitoring campaigns for PAHs concentration in particulate matter PM 10, PM 2.5 and total suspended particulates in the air, in Razoare, one of the crowded intersections from Bucharest. Thus, the concentration of polycyclic aromatic hydrocarbons in particulate matter in air varies greatly with temperature, the concentrations being 10 -15 times higher than in winter. In terms of distribution in dimensional fractions, the obtained data showed 90% of polycyclic aromatic hydrocarbons are present in PM2.5 fraction, thus indicating the traffic as the priority source of pollution with polycyclic aromatic hydrocarbons in the areas with heavy urban traffic.

Keywords: Air pollution, PM 10, PM 2.5, HAPs, HPLC

Introduction

Air pollution in big urbane areas is an issue of broad interest to the scientific fields because of its effect that on the population’s health. A particular attention is given in this direction to the pollution with particulate matters and especially to the pollution with PM 10 and PM 2.5; their monitoring in ambiental air is regulated in all the world legislations, PM 2.5 particulate matters fitting in the category of breathable dust that can penetrate and can accumulate in the

pulmonary system, in the pulmonary lobes causing serious health problems [1,3,4].

The latest researches show that emissions from road traffic is the most important source of PM 2.5 dust pollution, along with heavy metals and polycyclic aromatic hydrocarbons adsorbed on these particles.

Because of the recognized carcinogenic nature of these compounds, in order to improve the health of the population living in large crowded cities which are characterized by intense traffic, a high priority is given to the knowledge on the pollution level and its reduction. [6,7]

The information presented in this paper are part of a larger study targeting air pollution in large conurbations. It was conducted in 2008-2010 and it refers to air pollution with polycyclic aromatic hydrocarbons adsorbed on particulate matters and to the distribution in PM 10 (particles with nominal diameter less than 10 micrometers), PM 2.5 (particles with nominal diameter less than 2.5 micrometers) and TSP (total dust) dimensional fraction of these particulates.

Experiments

The tests were developed in one of the crowded intersections in Bucharest, Razoare intersection, in two distinct stages; the first stage was in winter, from 8 to 18 February 2010 and it was characterized by heavy precipitation (snow and rain) and lack of traffic (the traffic was stopped from 8th to 11th February 2010) and the second stage was in summer, from 26 July to 3 August 2010 and it was characterized by moderate temperatures (20°C) and high humidity in the first period.

With the respect of SR EN 12341/2002 and EN 14907/2006 for the equipment location and to ensure a representative sampling for particulate matters, in order to determine the actual concentration of dust, ambient air samples were taken and analyzed.

Daily samplings and measurements of total dust content PM_{2,5} and PM₁₀ particulate matters were performed using samplers Ingenieurbüro GmbH Sven LECKEL equipped with impactor inlets with exchangeable jets for PM₁₀ and PM_{2,5} retaining them on the of 47mm diameter fibreglass filter; sampling flow was 2.3 m³/h for a sampling time of 24 hours. Before and after exposure the glass fibre filters were weighed with a Mettler Toledo Analytical balance with accuracy of 0.00001 g, after 24 hours of conditioning at 20°C and 50% humidity. The increased weight of the filter represents the amount of particulate matters corresponding to the sampled volume air.

Before the extraction of the polycyclic aromatic hydrocarbons adsorbed on particulate matters, the filters were kept in Petri dishes, in cold and dark conditions.

Extraction, separation and quantification of the polycyclic aromatic hydrocarbons adsorbed on the particulate matters were achieved in accordance with ISO 16362:2005 [3]. For extraction was used an ultrasonic extraction bath and acetonitrile as solvent extraction in two steps of 30 minutes, followed by proper analysis by HPLC / FL type Agilent Technologies 1200. To establish the calibration curves and quality assurance of the results a certified reference material PAH MixturePM - 613a containing 16 PAHs in acetonitrile with concentrations from 5 to 100µg/ml was used.

Figure 1 show the chromatogram obtained for a 1:200 dilution's CRM-HAP. MixturePM - 613a.

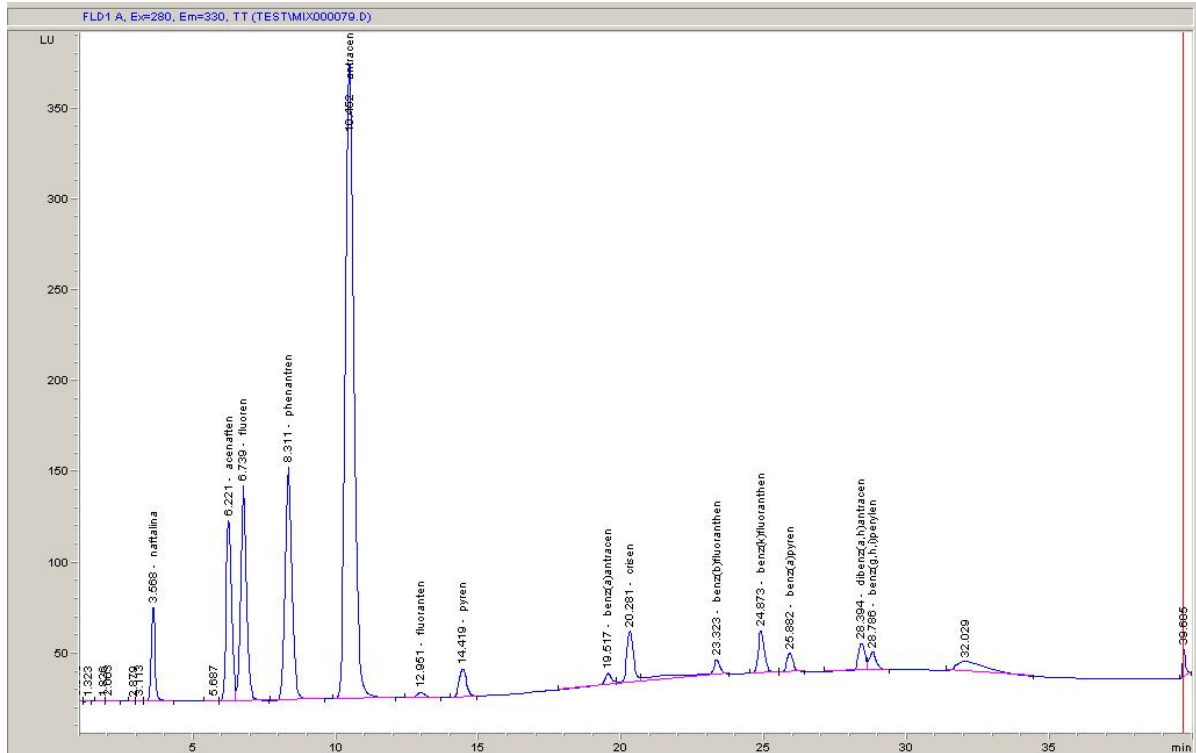


Figure no.1. 1:200 dilution chromatogram of PAH's MRC MixturePM - 613a.

Results and discussions.

Test results for particulate matters in ambient air conducted in those two seasons are presented in Table 1 and diagrams in Figure no. 2.

Data obtained from the sampling performed in 8 to 18 February 2010 indicates a mean content of particulate matters in ambient air of $45.1 \pm 12.64 \mu\text{g}/\text{m}^3$ for total dust, $40.4 \pm 14.42 \mu\text{g}/\text{m}^3$ for PM 10 and $36.9 \pm 12.56 \mu\text{g}/\text{m}^3$ for PM 2.5; the limit is exceeded only for PM 2.5; data obtained in 26 July to 3 August 2010 indicates a mean content of particulate matters in ambient air of $63.9 \pm 14.08 \mu\text{g}/\text{m}^3$ for total dust, $41.9 \pm 8.64 \mu\text{g}/\text{m}^3$ for PM 10 and $32.9 \pm 6.13 \mu\text{g}/\text{m}^3$ for PM 2.5, very closed values of maximum permissible limit for particulate matter PM 10 and exceeding the annual limit value for PM 2.5 corresponding to the year 2011 ($30 \mu\text{g}/\text{m}^3$).

Table no.1. Dust content in ambient air, Razoare, Feb. 8-18 and 26 July-3 August 2010.

Perioada	PM 2,5 µg/m ³	PM 10 µg/m ³	TSP µg/m ³	Perioada	PM 2,5 µg/m ³	PM 10 µg/m ³	TSP µg/m ³
8-9 febr 2010	31.5	32.3	39.6	26-27 iul 2010	25.3	27.6	43.5
10-12 febr 2010	21.9	23.7	30.45	27-28 iul 2010	27.5	37.1	55.8
12-15 febr 2010	41.3	43.1	48.5	28-29 iul 2010	36.9	46.7	80.9
15-16 febr 2010	34.1	40.7	42.6	29-30 iul 2010	31.4	42.8	57.8
16-18 febr 2010	55.6	62.3	64.5	30-2 aug 2010	34.2	44.6	69.1
				2-3 aug 2010	41.9	52.6	76.4
media, µg/m ³	36.9	40.4	45.1	media, µg/m ³	32.9	41.9	63.9
st.dev, µg/m ³	12.56	14.42	12.64	st.dev, µg/m ³	6.13	8.64	14.08
CMA, µg/m ³	30	50	150	CMA, µg/m ³	30	50	150

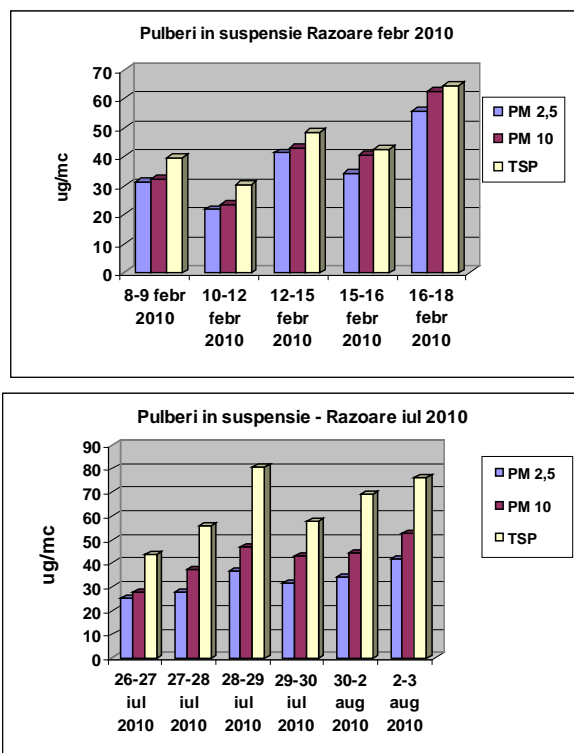


Fig.nr. 2 Dust content in ambient air, Razoare, 2010.

Particulate matters sampled in the special conditions of heavy precipitation (snow and rain) and lack of traffic, are composed predominant of small dust, like PM 2.5. Thus, the tests conducted in February 2010 show that the particulate matters PM 10 contain 92.1% PM 2.5 of its composition being in a proportion of 88.9% of total suspended particulates, while in July 2010 particulate matters in the air show an increase and also a different distribution of the dimensional fractions such as an increasing of the proportion of higher dimensional fractions, one of the possible causes being a suspension of the sediment.

The test results for polycyclic aromatic hydrocarbons concentrations adsorbed on particulate matters in those two periods of time at Razoare intersection are compared in Table 4; the most abundant compound is benz (k) florante whose concentration in dust is in a mean, 10 times higher than other compounds identified.

Indifferent of the period of time when dust sampling was conducted, high vapour pressure hydrocarbons such as naphthalene, acenaphthene, fluorene, phenanthrene, anthracene and fluoranthene were not identified; it is assumed that they have passed in the gas phase, or their concentration is below of the detection limit of the method.

Due to the volatility of the compounds and emissions from fuel burning for heating homes, concentrations of PAHs are 10-15 times higher in winter than in summer (Figure no. 3), as it was expected.

Table 4. The content of PAHs [ng / m] in ambient air particulate matters, Razoare, 2010

HAP \ PS	PM 2,5 , ng/mc		PM 10, ng/mc		TSP, ng/mc	
	feb. 2010	july 2010	feb. 2010	july 2010	feb. 2010	july 2010
pyren	1.61	0.41	1.63	0.44	1.21	0.35
benz(a)anthracene	1.78		1.61		1.25	
crisen	2.31	0.16	2.33	0.23	1.68	0.21
benz(b)floranten	2.74	0.29	2.62	0.32	1.93	0.26
benz(k)floranten	22.51	1.83	22.17	1.97	15.87	1.96
benz(a)pyrene	1.91	0.13	1.83	0.15	1.27	0.15
dibenz(ah)anthracene	1.88		1.83		1.29	
benz(ghi)perilen	2.44	0.19	2.25	0.2	1.7	0.21

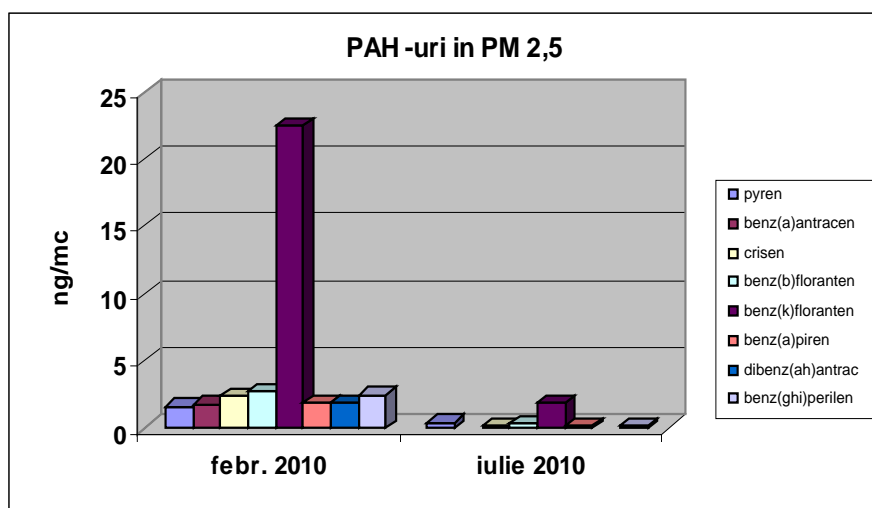


Figure no. 3. PAHs content in PM 2,5 [ng/mc] - Razoare, 2010

Distribution analysis of these polycyclic aromatic hydrocarbons in the three dimensional fractions of particulate matter shows that polycyclic aromatic hydrocarbons are found mainly in particulate PM 2.5, in other fractions

dimensional polycyclic aromatic hydrocarbons exist in low amounts due to the dilution caused by the larger particulate matters presence, but with low PAHs.

Regarding to the limits imposed by in force legislation, the only compound for which environmental legislation has imposed an annual limit value is 1ng/m^3 for benzo [a] pyrenul in PM 10 particulate matters. Test results made in February 2010 indicate a mean value of 1.83 ng/m^3 in PM 10 particulate matters and 1.91 ng/m^3 in PM 2.5, pretty much for a daily mean, compared to the annual mean of 1 ng / m^3 (Figure no. 4).

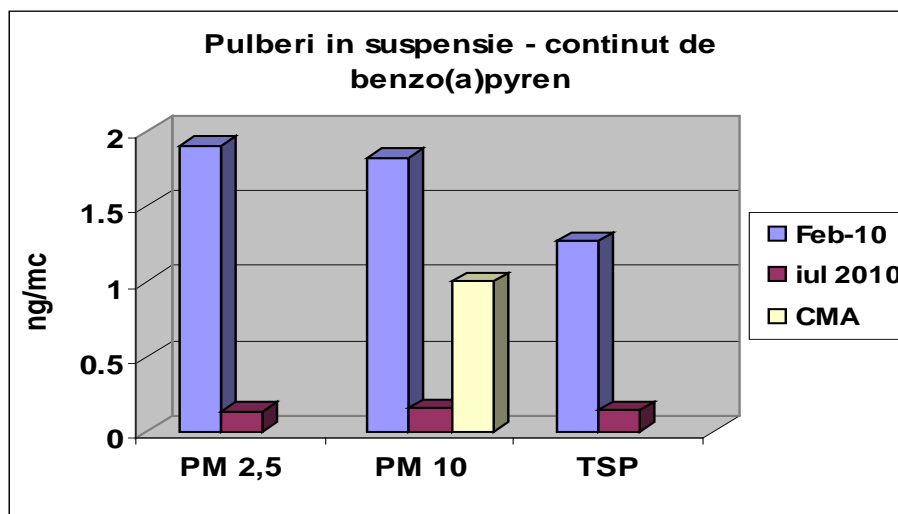


Figure no. 4. The content of benzo (a) pyrene in PM 2.5, PM 10, TSP - Razoare, 2010

Conclusions

Tests conducted in two periods of time in 2010, from February 8 to 18, respectively 26 July -3 August 2010 in Razoare intersection area demonstrates a high level of pollution with PM 10 and PM 2.5 particulate matters, total dust concentration being under limit.

In specific periods of weather when the tests were conducted it was found that particulate matters are consisting mostly of small particles, PM2.5 being 85-90% in particulate matter PM 10; PM 2.5 also accumulates 90% of the total polycyclic aromatic hydrocarbons present in total particulate matters.

Among the most abundant polycyclic aromatic compounds is benzo (k) whose concentration in dust floranten is on mean 10 times higher than the other identified compounds. Naphthalene, acenaphthene, fluorene, phenanthrene, anthracene and fluoranthene are not found in any of the dimensional fractions - it is assumed that they have passed in gas phase, or their concentration is below of the detection limit of the method.

As expected in summer compared with winter, many of polycyclic aromatic hydrocarbons volatilise and much smaller amounts of these compounds are found particulate matters. The test made in cold season show that PAHs concentrations are 10-15 times higher than in summer due to the reduced volatility of compounds and to the emissions from fuel combustion for heating in homes.

Analyzing the distribution on dimensional fraction of particulate matter and the presence of polycyclic aromatic hydrocarbons in these fractions, was found a preponderance of PM 2.5 particulate matters and also 90% of the amount of polycyclic aromatic hydrocarbons are contained in these fractions indicating in this way road traffic as a source of pollution emissions.

References

1. S. Manescu, M. Cucu, M. L. Diaconescu, “Sanitary Environmental Chemistry”, Ed Medical, Bucharest, 1994;”;
2. X. Querol, M.Viana, A. Alastuey, “Source origin of trase elements in PM from regional background, urban and industrial sites of Spain”, *Atm. Env.*(**41**), 2007, 7219-7231;
3. L. Trasande, G.Thurston, “The role of air pollution in asthma and other pediatric morbidities” *Jallergy Clin Immunol* 2005,689-696;
4. S. W. See, S. Karthikeyan,R. Ralassubramanian “Health risk assessment of occupational exposure to particulate-phase polycyclic aromatic hydrocarbons associated with Chinese, Malay and Indian cooking” *Jour.Envir. Monit.*,(**8**) 2006, 369-376;
5. ISO 16362:2005 Ambient air. Determination of particulate polycyclic aromatic hydrocarbons using High Performance Liquid Chromatography.
6. V. Kaunelienė, A. Cicėnaitė, I. Jegorova, “Tentative Air Concentrations of PAHs and PCBs in Urban Area of Lithuania” *Env. Res.Eng. Man.*,**No.2(28)**, 2004, 33-39;
7. J.Masih, A.Masih, *Characteristics of polycyclic aromatic hydrocarbons in indoor and outdoor atmosphere in the North central part of India*, *J. Haz. Mat.*, (**177**) 2010, 190-198.