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STUDIES ON THE PRESENCE OF ORGANIC POLLUTANTS SUCH AS POLYNUCLEAR AROMATIC HYDROCARBONS IN THE TREATMENT FLOW OF THE MUNICIPAL WASTEWATER AND THEIR DISTRIBUTION IN DIFFERENT ENVIRONMENTAL FACTORS

- PhD Thesis Summary -

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Keywords: polycyclic aromatic hydrocarbons, wastewater, sewerage system, high performance liquid chromatography, HPLC, sewage sludge, soil, snow.

INTRODUCTION

This thesis aims to determine polynuclear aromatic hydrocarbons in urban wastewaters and soil \sewage sludge from Cluj-Napoca.

The main objectives of the research focused on:

Determining sources of PAHs in urban wastewater, urban runoff and other environmental factors that may contribute to the presence of PAHs in the flow of municipal wastewater treatment plants and their distribution in various environmental factors.

Process analysis of wastewater treatment and sewage sludge and possible measures to prevent pollution at the source.

Determination of factors that influence PAHs behavior.

The thesis has a theoretical part-Chapter 1, which includes data from the literature and a experimental part-Chapters 2-5, which refers to the original contributions in the field that I approached.

Chapter 1 presents a brief characterization of polynuclear aromatic hydrocarbons (PAHs) in the study: the characterization of the physico-chemical properties, the major sources (industrial, transportation, domestic use) and also a synthesis of methods of analysis involved in identifying and quantifying PAHs in wastewater and soil \ sewage sluge.

Chapter 2 presents the results on 14 commonly occurring and/or highly carcinogenic PAH compounds listed as priority pollutants by the United States Environmental Protection Agency and the European Union. Wastewater samples were collected starting from October 2010 until May 2011. Results were expressed by the cumulative amount of 5 from 6 compounds listed in decision No. 2455/2001/CE of the Council of European communities (Council Directive, 1991), ranging from 0.0136 ppb in Floresti sewer to 0.0104 ppb in Cosbuc sewer or from 0.0102 ppb in Someseni sewer to 0.0036 ppb in Napoca sewer (February), being also expressed as cumulative amount of 14 from 16 compounds recommended by the USA Environmental Protection Agency which ranged from 0.5584 ppb in Floresti (February) sewer to 0.3735 ppb (February) in Cosbuc sewer or from 0.3406 ppb in Someseni (February)sewer to 0.3064 ppb (March) in Napoca sewer. The research focuses on two main objectives: to determine the concentrations of PAHs in Cluj Napoca's sewerage system (establishing the contribution of each sewer) and to determine the different potential sources

of PAHs. PAHs were extracted using liquid-liquid extraction with hexane and determined by high performance liquid chromatograph with both diode array and fluorescence detection. The PAH concentration varies significantly, which may in part be due to differences in the catchments areas. The obtained data provided a general picture of PAHs sources for the sewerage system in urban area of Cluj.

Chapter 3 presents some preliminary results on assessment of PAHs contamination of surface soils originating from different locations in Transylvania, covering roadside, residential and agricultural areas. PAHs were determined by high performance liquid chromatography using an Agilent 1100 system with fluorescence detection, able to separate 14 PAHs: naphthalene, acenaphtene, fluorene, phenanthrene, anthracene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(ah)anthracene, benzo(ghi)perylene and indeno(1,2,3-cd)pyrene. This study proved that PAHs are part of the soil mixture, with total concentrations ranging from 0.09 to 81.40 μg/ kg, the highest recorded values being for chrysene (38.70 μg/ kg), pyrene (14.78 μg/ kg) and indeno(1,2,3-cd)pyrene (10.48 μg/ kg); the highest soil contamination was established for soil originating from Cluj Napoca city center (81.40 μg/ kg).

Polycyclic aromatic hydrocarbons (PAHs) are a group of environmentally persistent organic pollutants with various structures and varied toxicity. As the urban snowpack can act as a collector device for atmospheric-deposited PAHs, the objectives of this study were to establish the PAH distribution and to identify their sources based on PAH profile and isomer ratios. The determined PAHs included naphtalene, acenaphtene, fluorene, phenanthrene, anthracene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a) pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene, indeno(1,2,3-c,d)pyrene. Snow samples were collected from three areas located in Cluj Napoca, Romania (Manastur area, city center and Marasti area) during the winter period 2011-2012; meltwater samples were extracted with hexane using liquid-liquid extraction, being then analyzed by high performance liquid chromatography, with an Agilent 1100 system with fluorescence detection, separations being accomplished on an Envirosep PP column in a total run time less than 30 minutes. The obtained results revealed relative high levels pyrene, chrysene and benzo(b)fluoranthene, which are associated with combustion processes in Manastur area, while in Marasti area the major PAHs concentrations (fluorene, phenanthrene and chrysene) are related with traffic.

Based on the general property of aromatic compounds to fluoresce, spectrofluorimetric analysis of PAH's (poly-aromatic-hydrocarbons) from pyrogenic sources mixture in acetonitrile was performed. Pure kits of 5 PAH compounds with condensed aromatic rings, at concentration of 0,5 μg/mL, were mixed in equal quantites and concentrated in 2 ml acetonitrile. The fluorescence spectra due to electronic specific interactions were studied on liquid standard samples using a ABLE & JASCO FP 6500 recording spectrofluorometer, applying an excitation wavelength of 210 nm and monitoring the emission wavelength over the 250–890 nm range. All measurements were performed with excitation/emmission slits of 3/10 μm width. As solvent for the standards was used acetonitrile. Measurements were carried out in a 3.5 mL quartz fluorescence cuvette. Recorded spectra for a set of diluted PAH standard solution of 0,01 μg/mL - 0,05 μg/mL shows constant and proportional maxima at 305,14 nm, 381,41 nm and 407,73 nm respectively. Results shows that PAH's from pyrogenic sources extracted and concentrated in acetonitrile can be directly monitored by spectrofluorimetry. The technique has great potential as a rapid, inexpensive and non-destructive technique for field biomonitoring of PAH's exposure in environment.

In ***Chapter 4*** are analyzed concentrations of these organic compounds in sludge samples from Cluj-Napoca wastewater treatment plant are reported. The objective was to investigate PAHs in sludge from wastewater treatment plant and to assess their potential for land application. Primary sludge, fermented sludge, fermented concentrated sludge, anaerobic-digested dehydrated sludge and rejection water samples were collected monthly from December 2012. Ultrasonic assisted extraction with hexane was used, being followed by filtration and concentration to dryness in a rotary evaporator; the obtained residue was redisolved in acetonitrile. High performance liquid chromatographic analysis was achieved using an Agilent 1100 system consisting in a solvent degasser, a quaternary pumping system, an autosampler, a column oven, a diode-array detector and a fluorescence detector. Separations were accomplished using an Envirosep PP column with acetonitrile:water as mobile phase (45:55 v/v). Detection limit was 0.001 □g/ kg, with good linearities for all PAHs, with correlation coefficients higher than 0.998. PAHs with four rings appeared to be the primary components in most of the tested sludge samples, the highest concentration levels being in anaerobic-digested dehydrated sludge samples. The obtained results can be helpful for the regional policy makers to make proper decisions on treating the increasing amount of sewage sludge, to provide practical reference for establishing threshold values of PAHs for

land application of sludge, knowing that the practice of recycling sewage sludge onto agricultural lands poses an additional risk of soil contamination with PAHs.

Another objective of this study was to assess the polycyclic aromatic hydrocarbons' (PAH) contamination of urban sewage sludge – a potential agricultural fertilizer, as a result of the increasing environmental concern regarding the fate of biodegradable solid wastes generated by wastewater treatment processes. PAHs were determined by an Agilent 1100 high performance liquid chromatograph with fluorescence and diode-array detection, separations being accomplished using an Envirosep PP column with a mixture of acetonitrile: water as mobile phase. This study revealed a low contamination of sewage sludge originating from Cluj Napoca wastewater treatment plant with PAHs (15.61 μg/kg dry weight for overall PAHs concentration) during a four-month monitoring period, with individual concentrations ranging from 0.06 to 11.50 μg/kg dry weight, the highest recorded values being for naphthalene (11.50 μg/kg dry weight), phenantrene (1.39 μg/kg dry weight) and benzo (g, h, i) perylene (0.63 μg/kg dry weight). As the recorded values during the study period were low, we can conclude that the environmental risks related with PAHs contamination is quite low; due to their hydrophobic character, groundwater pollution by levigation can be also excluded. However, seasonal variations of PAHs contamination are possible and for this reason this study will be extended for a full-year period.

The last part of this Chapter presents the results obtained studying the PAH's removal in a conventional active sludge wastewater treatment plant located in Cluj Napoca – Romania, in which wastewater with a predominantly organic character is treated using complex physical-chemical-biological processes. The collected samples were filtered to remove suspended matter, and then PAHs were extracted using liquid-liquid extraction with hexane and determined by high performance liquid chromatography using an Agilent 1100 system with both diode array and fluorescence detection. Separations were accomplished using an Envirosep PP column and a mixture of acetonitrile: water as mobile phase. Detection limits ranged from 0.05 μg/kg for naphthalene to 0.001 μg/kg for the other 13 of PAHs. The obtained results were expressed by the cumulative amount of 14 compounds which ranged from 0.116 μg/kg in the influent of the wastewater treatment plant to 0.0108 μg/kg in the effluent. The amount of carcinogenic PAHs (benzo [a] anthracene, benzo [a] pyrene, benzo [b] fluoranthene, benzo [k] fluoranthene, chrysene, dibenz [a, h] anthracene and indeno [1, 2, 3-c,d] pyrene) ranged from 0.0591 μg/ kg in the influent to 0.002 μg/ kg in the effluent.

Overall PAHs removal ranged from 9.31% to 60.55 %. Research showed that naphthalene, acenaphthene, fluorene, phenanthrene and anthracene are removed effectively during wastewater treatment, whereas for benzo (b) fluoranthene, benzo (k) fluoranthene, benzo (a) pyrene, benzo (g, h, i) perylene and dibenz (a, h) anthracene, indeno (1, 2, 3-cd) pyrene the recorded values were lower.

Chapter 5 summarized the main conclusions from this thesis as follows:

- ✓ The obtained data provided a general picture of PAHs sources for the sewerage system in Cluj urban area, indicating that PAHs in Cluj-Napoca wastewater originates predominantly from food preparation which involves combustion processes difficult to identify and quantify, and vehicle traffic which is one of the most frequent anthropogenic source of PAHs.
- ✓ Municipal wastewater characteristics vary from one location to another, depending on sources, effluents, land use, groundwater level and degree of separation between rainwater and sanitary waste.
- ✓ The objectives were achieved, namely sources of these pollutants were confirmed by the data.
- ✓ It is confirmed that this kind of pollutants are a complex function of the type and size conurbation (commercial, residential, mixed), type and density of traffic; airflow and precipitation allow transport of these PAHs away, dispersing them.
- ✓ Each PAH is associated with one of the following sources: transportation (Benzo(g,h,i) pyrene), household (pyrene), runoff roof (naphthalene), etc.
- ✓ Sources of PAHs from domestic use are more difficult to assess than those from industrial sources.
- ✓ Seasonal variations were observed for PAHs with higher levels in winter, when the domestic heating is working.
- ✓ HAPs are difficult to analyze in the environment, on the one hand due to the low concentrations in which they are present, on the other hand due to the effect of the matrix.
- ✓ For quantitative determinations required by the monitoring activity have solved these problems, recourse to traditional liquid-liquid extraction followed by analysis by liquid chromatography high performance fluorescence detection.

- ✓ The analytical method developed meets the sensitivity and selectivity required by determinations with very high recoveries (between 91-99%) and good reproducibility (CV between 3.22 and 4.99%) for measurements of wastewater.

POLYCYCLIC AROMATIC HYDROCARBONS IN WASTEWATER SEWERAGE SYSTEM FROM THE CLUJ-NAPOCA AREA

2.1. Introduction

Cluj-Napoca city is located on the Someşul Mic River valley, in the north-western part of Romania, at 23°35´E, 46 °47´N, being considered the unofficial capital of Transylvania. The Cluj-Napoca metropolitan area and the peri-urban area have a population of around 400,000 people. With a spectacular industrial development since the '50s when it became the main urban center in the Transylvanian Hollow, environmental pollution became a problem for county residents, with increasing number of people who imposed pressure by increasing demands of life, food and housing. As a result, PAHs contamination occurs, affecting the whole environment.

Being located under the Apuseni Mountains shelter, the Cluj-Napoca's climate is moderate continental, specific for the northwest hills' region, with some local differences due to landscape features which leads to substantial changes in the processes that characterize the general circulation of the atmosphere.

Wastewater is a complex matrix, which conveys amounts of PAHs (Gourlay-Francé et al., 2008) from domestic wastewater or mixture of domestic wastewater with industrial wastewater and/ or urban runoff (Council Directive, 1991; MO 324,2007). Urban wastewater is a poly-saprogenic water, strongly contaminated with organic substances and hence having a high deficit of dissolved oxygen (Popa et al., 2007). PAHs can originate from food preparation in households and food shops, from garages, vehicle washing, fuel stations, residential heating, roof runoff, wet and dry soil deposition (Boving and Neary, 2007; Draghici et al., 2009; Iain et al. 2001; Motelay-Massei et al., 2006; Oros et al., 2007; Thornton et al., 2001). PAHs are on the list of the main indicators of quality of wastewater discharged into the receptors included in the regulatory acts in terms of water management (MO 187, 2002).

Polycyclic aromatic hydrocarbons are organic pollutants (Levinson et al., 2005) which can affect the environment (Blanchard et al., 2004; Cao et al., 2005; Hwang and Foster, 2006) as well as public health; the consequences of PAHs contamination in urban wastewater were also reported (Gasperi et al., 2008). Worldwide, PAHs were studied in different

environmental matrices (Hwang and Foster, 2006; Li et al., 2010; Maliszewska-Kordybach et al., 2009; Tsakovski et al., 2010).

This study is based on the experimental data obtained from October 2010 until May 2011 on wastewater originating from Cluj Napoca's sewerage system, the main target objectives being to determine the concentrations of PAHs and to establish the different potential sources of PAHs in Cluj Napoca. Polynuclear aromatic hydrocarbons monitored in this research are: naphtalene, acenaphtene, fluorine, phenanthrene, anthracene, pyrene, benz (a) anthracene, chrysene, benzo (b) fluoranthene, benzo (k) fluoranthene, benzo (a) pyrene, dibenzo (a, h) anthracene, benzo (g, h, i) perylene, indeno (1,2,3-c, d) pyrene.

There are four main sewers in Cluj-Napoca: Cosbuc (which collects wastewaters from Manastur neighborhood), Floresti (which collects wastewaters from the west part of the city), Napoca (which collects wastewaters from Grigorescu neighborhood) and Someseni. Cosbuc and Napoca sewers drain Cluj-Napoca center and Someseni and Floresti sewers drain Cluj-Napoca suburbs. Manastur and Grigorescu neighborhood represent residential zones. One sampling site was established in a sewer that belongs to the industrial area; this extends from the railway station to the wastewater treatment plant, having a diameter of 2.65 m.

Sewerage system collects wastewaters and rainwater from all customers from Cluj-Napoca, Gilau, Floresti and Baciu and transports them to Someseni wastewater treatment plant. Many urban centers are drained by a unique sewer network in which wastewater is mixed with urban runoff water in wet weather (Passerat et al., 2010); in Cluj-Napoca, sewerage system is 80% unitary type and 20% divider type (separate network for rainwater/ domestic wastewater collection in Someşeni, Baciu, Aurel Vlaicu, Zorilor and Mănăştur areas), the wastewater flow rate being 2.170 L/s. Industrial wastewater are
pre-treated at industrial plant level, and then discharged into sewage system. Cluj County has a network of 326 km sewers, from which 312 km are in Cluj Napoca and the rest in the above mentioned villages. 86% from Cluj streets are drained. Sewerage pipes are made from different material – precompacted concrete, asbestos cement, PVC (especially those with diameter of 30-40 cm), ceramic, concrete, polyester reinforced with glass fiber.

Nowadays, the organic load of wastewater is increased with 30% comparing to that from 10 years ago by decreasing water flow consumed. Wastewater flows vary greatly in terms of time, with maximum in the morning and evening and with low seasonal variations, similar to drinking water.

PAHs analysis is difficult due to their very low concentration (Charalabaki et al., 2005), as well as the interferences that exists in urban wastewater; it is very important

to ensure a high sensitivity, robustness, selectivity and versatility of the analytical method (Busetti et al., 2006; Jäntschi, 2003; Sánchez- Avila et al. 2009). High performance liquid chromatography was used in the present study, as it fulfils all of these requirements.

2.2. Materials and methods

2.2.1. Chemicals and reagents

PAHs were purchased from Supelco (Bellefonte, PA, USA) as a TCL PAHs Mix at concentration of 20-1000 µg/mL in acetonitrile: methanol (90:10). Solvents used were all HPLC grade, being supplied by Merck (Darmstad, Germany). Calibration solutions were prepared daily by diluting the standard solution with acetonitrile. Ultrapure water was obtained from a WATEK IWA 20 water purification system.

2.2.2. Sampling sites

Measurements were carried out in 20.10.2010, 31.01.2011, 28.02.2011, 21.03.2011, 08.04.2011 and 13.05.2011, the geographic coordinates of sampling sites being those indicated in Table 1. The considered period of time was characterized by less precipitation in February and March and in early January it snowed. Floresti sewer is located at the N-E of the city, on a national road; Cosbuc sewer is near the Central Park; Napoca sewer is close to downtown, while Someseni sewer is located on the east of the city, near a industrial area (Fig. 1). All the sewers are placed under the street network.

Three samples were collected from roof runoff (two tile roofs and one zinc roof), in the city center and one sample originates from a roof runoff of a big gas station to test that this can be considered as a source of PAHs.

Table 1. Geographic coordinates of the sampling sites

Sampling sites	***Geographic coordinates***
Floresti sewer	46°44'53,13"N 23°30'25,85"E
Cosbuc sewer	46°46'01,88"N 23°34'31,39"E
Napoca sewer	46°46'16,30"N 23°34'39,05"E
Someseni sewer	46°46'52,80"N 23°41'19.67"E

Industrial area	46°47'31,04"N 23°39'32,79"E
Iuliu Maniu street- city center	46°77'08,87"N 23°59'30,4" E
Bd 21 Decembrie- city center	46°77'48,38"N 23°60'16,5" E
Garage from city center	46°77'08,12" N 23°59'69,86"E
Gas station	46°75'85,29" N 23°54'97,47"E

Sample collection was accomplished according the standard technique SR EN ISO 17993 (2004); one liter water samples was collected in brown glasses, which were previously cleaned with sulpho-chromic mixture, rinsed with distilled water, then dried at 80° C in an oven. Samplers were filled without air bubbles, then transported immediately to the laboratory being stored at 4 – 50C, until chemical analysis was performed.

2.2.3. Sample extraction and analysis

Determination of PAHs in liquid matrices often involves conventional extraction techniques such as liquid-liquid extraction (LLE), solid phase extraction (SPE), solid phase microextraction (SPME). Headspace solvent microextraction (HSME), dispersive liquid–liquid microextraction (DLLME), cloud point extraction (CPE), was developed to determine PAHs in water samples in recent years. Despite the LLE disadvantages, it proved to be a very useful technique (Xinna et al., 2009), this being the reason we selected it in our research.

Among different solvents used in literature (dichloromethane, cyclohexane, hexane, carbon tetrachloride), for liquid-liquid extraction of polynuclear aromatic hydrocarbons from wastewater, hexane proved to be the most appropriate for PAHs extraction. Currently, the European reference methods recommended liquid-liquid extraction with hexane, instead of dichloromethane, the solvent selected by EPA-US. (Gocan and Cobzac, 2006). Hexane has a low solubility in water (13 mg/L at 20°C), a density which differs much from that of water (0.6548 g/mL), is highly volatile and is easily removed, is compatible with the method of analysis, is selective in relation with PAH and has a high purity

The analytical methods for the detection and quantification of PAHs are generally based on gas chromatography or liquid chromatography (LC).Based on the physicochemical

properties of PAHs (less soluble in water and less volatile with increasing molecular weight), it is more suitable to use LC because it involves less sample preparation effort.

Hence, PAHs were extracted using liquid liquid extraction with hexane and determined by high performance liquid chromatograph with both diode array and fluorescence detection. Fluorescence detection enables very good sensitivity, while the diode-array detector helps confirming PAHs' identities.

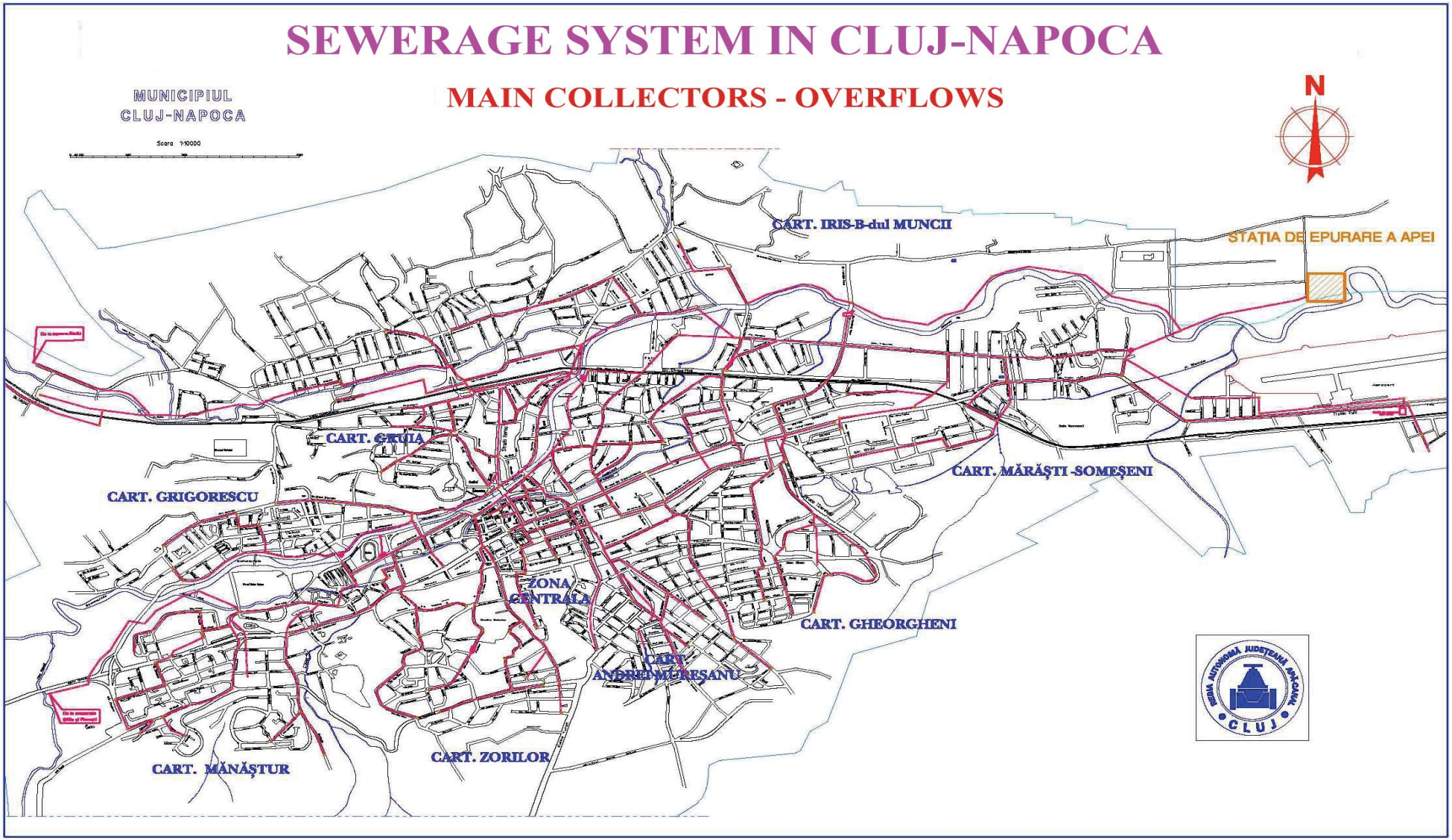

Fig. 1. The sewerage system in Cluj Napoca

2.3 Experimental

Suspended matter were initially removed by filtration on filter paper with size medium pore; 1 L filtrated wastewater samples were extracted with 30 mL hexane using a separation funnel, which was attached to a mechanical shaker, being agitated for 60 minutes. The hexane epiphase was dried with sodium sulfate then concentrated to dryness in a rotary evaporator. The resulted residue was redisolved in 1.5-2 mL acetonitrile.

As PAHs are light sensitive, the sample

extracts were stored in aluminum foil-wrapped bottles in order to minimize photolytic decomposition. All the analytical procedure takes around four hours. An Agilent 1100 high performance liquid chromatographic system was utilized, consisting in a solvent degasser, a quaternary pumping system, an autosampler, a column oven, a diode-array detector and a fluorescence detector; separations were accomplished using an Envirosep PP column (125mm×4.6mm I.D) using acetonitrile: water (45:55 v/v) as mobile phase.

Using a flow rate of 1.5 mL/min and an injection volume of 20 μL, the separation of 16 PAHs occurred in less than 30 minutes (Fig. 2).

Data processing was accomplished using Chemstation 08.03 Software. At initialization, the fluorescence detector wavelength settings were: for excitation - 224 nm, for emission - 500 nm. For peak identity confirmation, the DAD spectrum was compared with reference compounds spectrum in the spectrum library. Detection limits ranged from 0.05 ppb for naphthalene to 0.001 ppb for the other PAHs, while good linearities were achieved for all PAHs, with correlation coefficients higher than 0.998 (Fig.3).

Results were expressed by the cumulative amount of 5 compounds: benzo (a) pyrene, benzo (b) fluoranthene, benzo (k) fluoranthene, benzo (ghi) perylene and indeno (1,2,3-cd) pyrene and were also expressed by the cumulative amount of 14 compounds which includes, in addition to the previously mentioned PAHs, naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, pyrene, chrysene, benzo (a) anthracene and dibenzo (ah) anthracene.

Sample Info : PAH Mix 0.5

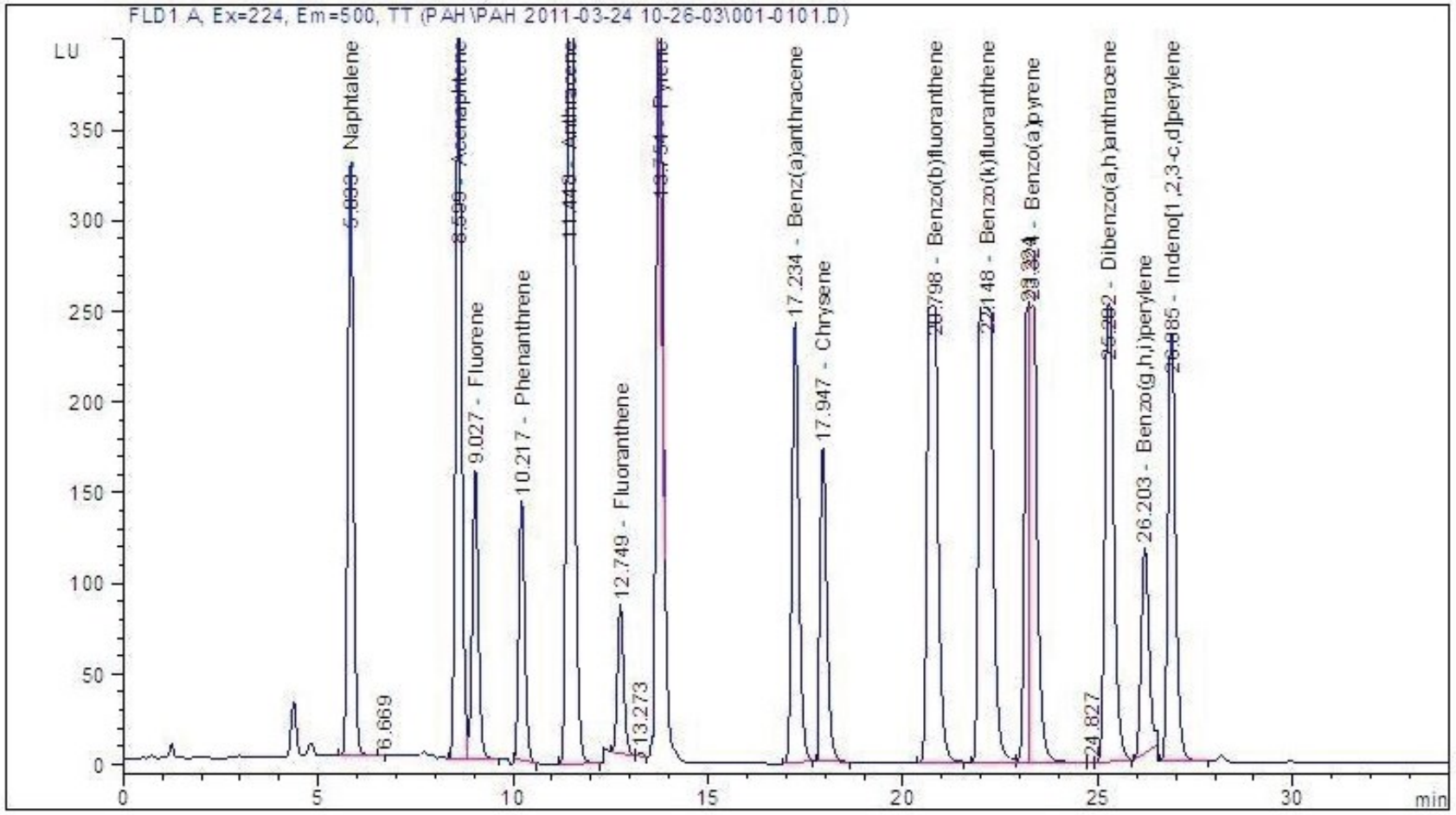

Fig. 2. PAHs chromatogram for reference mixture

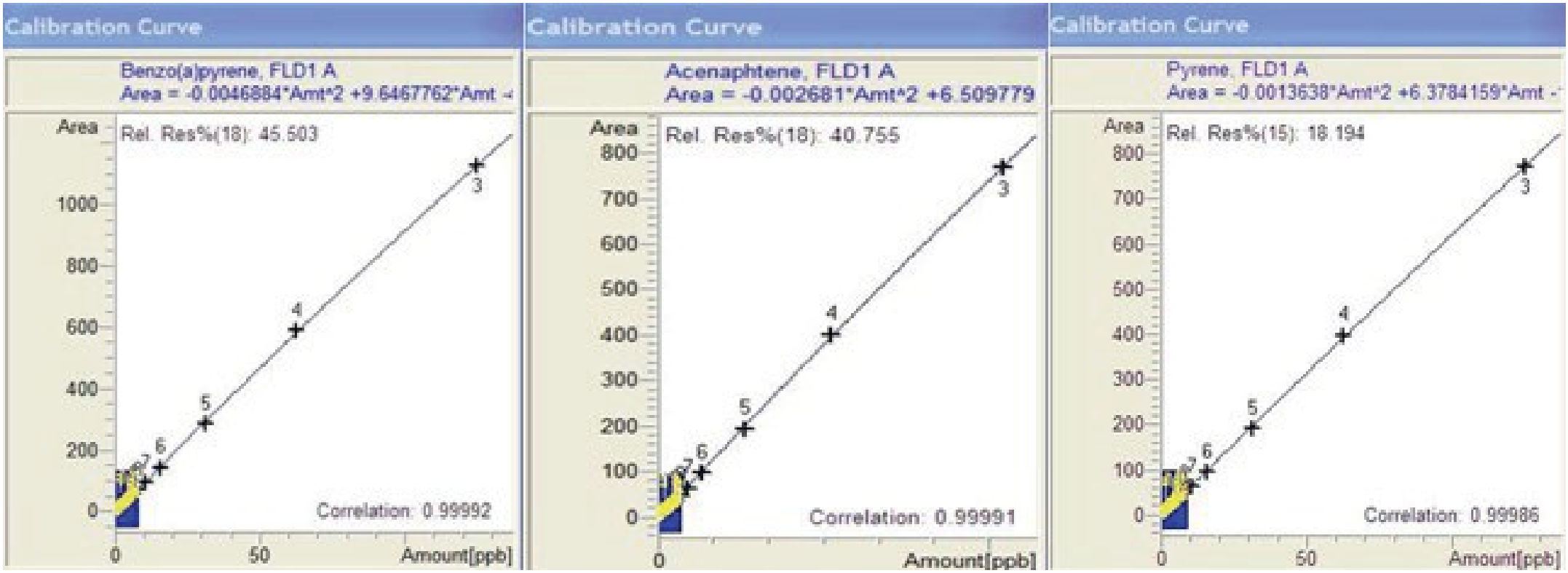

Fig. 3. Calibration curve of selected PAH compounds

2.4 Results and discussion

High concentrations of naphthalene, phenanthrene, pyrene, chrysene were detected in the sewer from industrial area. Table 2 presents the PAHs' concentration in the sewer from industrial area and Someseni sewer, which is closer to this area; it is obvious that almost all PAHs' concentrations in the industrial area are higher than those from the Someseni sewer.

Table 2. Σ14 PAHs in industrial area sewer and Someseni sewer (October 2010)

HAP	*Concentrations recorded in industrial area sewer (ppb)*	*Concentrations recorded in Someseni sewer (ppb)*
Naphtalene	0,0818	0,0272
Acenaphtene	0,0092	0,0064
Fluorene	0,0499	< LOD
Phenanthrene	0,1379	< LOD
Anthracene	0,0011	0,0016
Pyrene	0,0229	< LOD
Benz(a)anthracene	0,0009	0,0060
Chrysene	0,0155	0,0308
Benzo(b)fluoranthene	< LOD	0,0018
Benzo(k)fluoranthene	0,0006	0,0008
Benzo(a)pyrene	0,0002	< LOD
Dibenzo(a,h) anthracene	< LOD	0,0010
Benzo(g,h,i)perylene	< LOD	0,0017
Indeno(1,2,3-c,d)pyrene	0,0007	0,0005
Σ14	0,3207	0,0777
Σ16	0,0015	0,0048

Table 3 presents the PAHs concentration in roof runoff water in a cumulative manner, as the individual PAHs concentrations are much lower in these matrix.

Table 3. Σ14 PAHs concentration on roof runoff

Roof material	*Σ14 HAP (µg/l)*
Zinc (garage from city center)	0,1487
Tile (Bd 21 Decembrie- city center)	0,0569
Tile (Iuliu Maniu street- city center)	0,1087

Hence, roofs can be considered as a set of point source with PAHs concentration depending of roof type, location and age. The distance between the considered roofs is around 200 m; the buildings with tile roof belong to the historic center of Cluj-Napoca and the garage was built before around four years ago. As can be seen, the concentrations of PAH in roof runoff from zinc roof was found to be about three-fold higher than tile roof (21 December Bd) and PAHs concentration from tile roof from Iuliu Maniu is double of concentration from tile roof from Bd. 21 December.

In roof runoff, especially those PAHs with high molecular weight are present in high concentration. (Figs. 4 - 6). Naphtalene is on the tile roof and fluorine on the zinc roof.

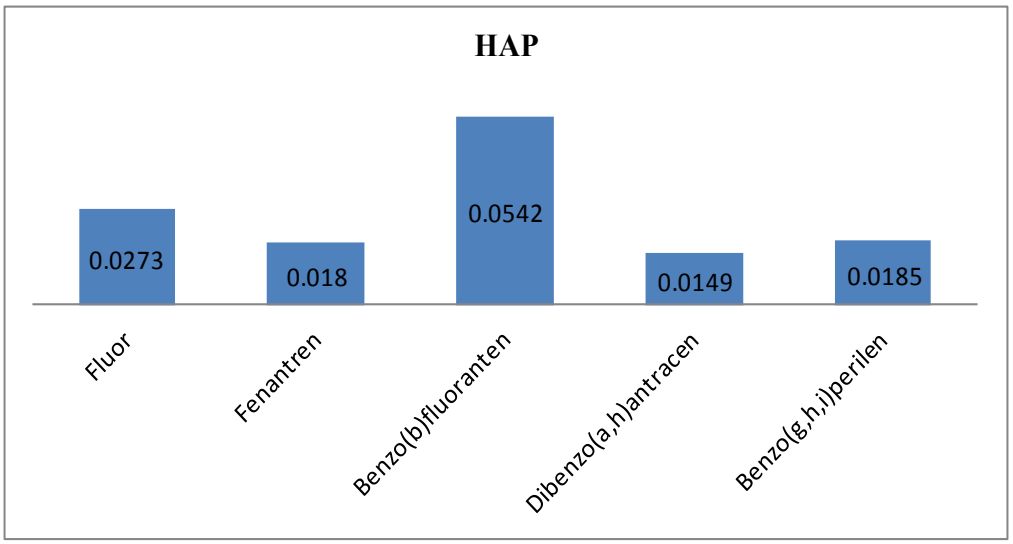

Fig. 4. PAHs concentrations on zinc roof

The highest PAHs concentrations were recorded in Cosbuc sewer - in October and February, in Floresti sewer - in February and March, in Napoca sewer - in October and March, in Someseni sewer – in February.

From households, PAHs can reach 50-60% of the total wastewater collecting system load for pyrene and phenanthrene (Cosbuc, Napoca). In Cosbuc sewer, pyrene concentration in October and February was high: 0.0429 ppb, respectively 0.0326; the phenanthrene concentration in October and January were of 0.1960 ppb and 0.0799 ppb. In Napoca sewer pyrene concentration in March was 0.0646 ppb, respectively for phenanthrene was high in October (0.1220 ppb).

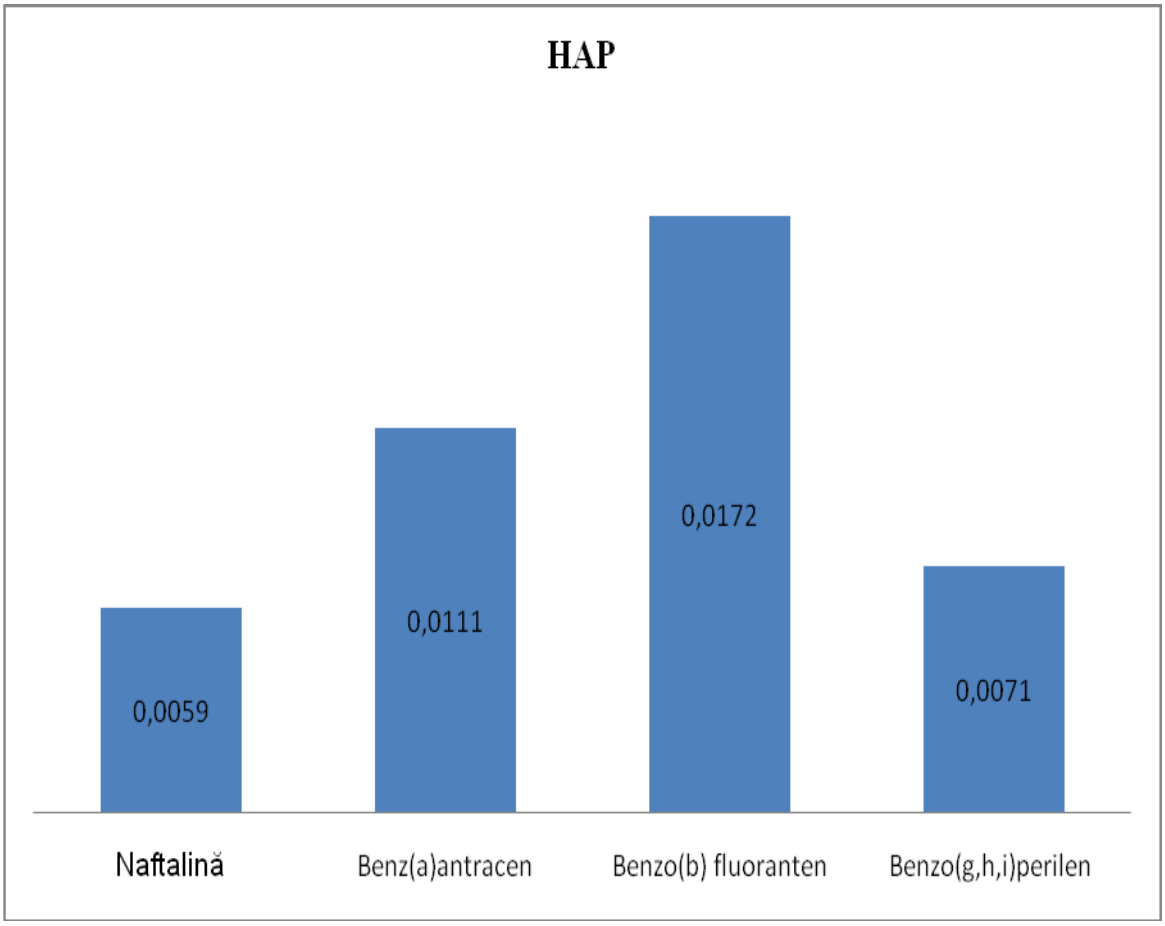

Fig. 5. PAHs concentrations on tile roof (Bd 21 December city center)

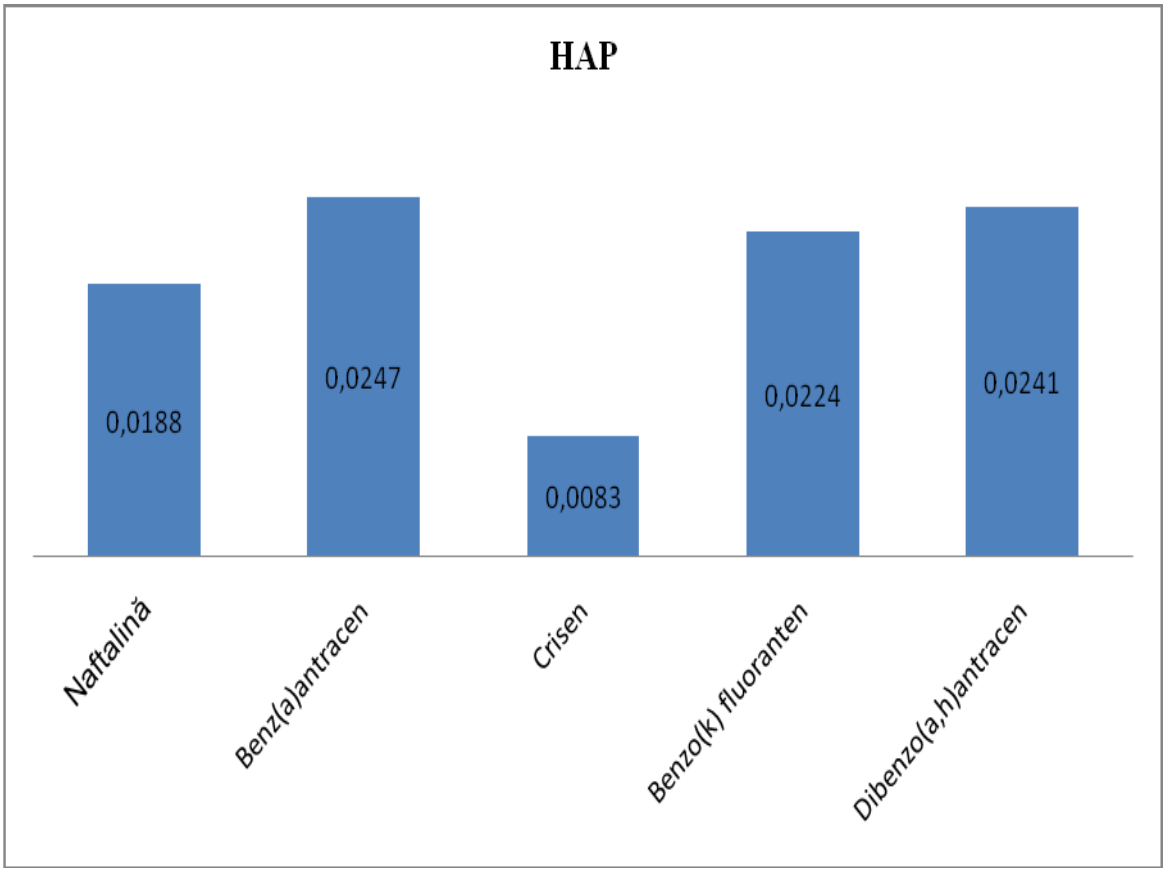

Fig. 6. PAHs concentrations on tile roof (Iuliu Maniu Str.,city center)

The screening accomplished on wastewaters included a gas station with washing facilities; here, the Σ14 PAHs was 0.3976 ppb, confirming the hypothesis that gas station can be considered as significative source of PAHs. The highest concentrations were recorded for naphtalene (0.1001 ppb), fluorine (0.1116 ppb) and pyrene (0.1054 ppb). Phenanthrene, chrysene and benzo(k)fluoranthene were under LOD. In all three monitored seasons (October-autumn; January, February - winter; March, April, May-spring) polynuclear aromatic hydrocarbon concentrations varied widely (Figs. 7 - 10).

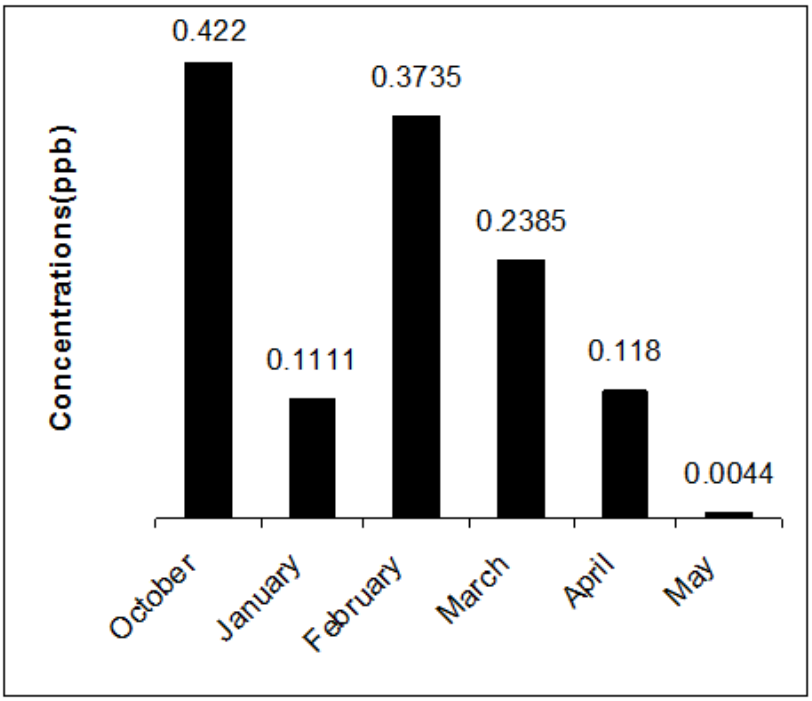

Fig. 7. Sum of 14 PAHs in Cosbuc sewer

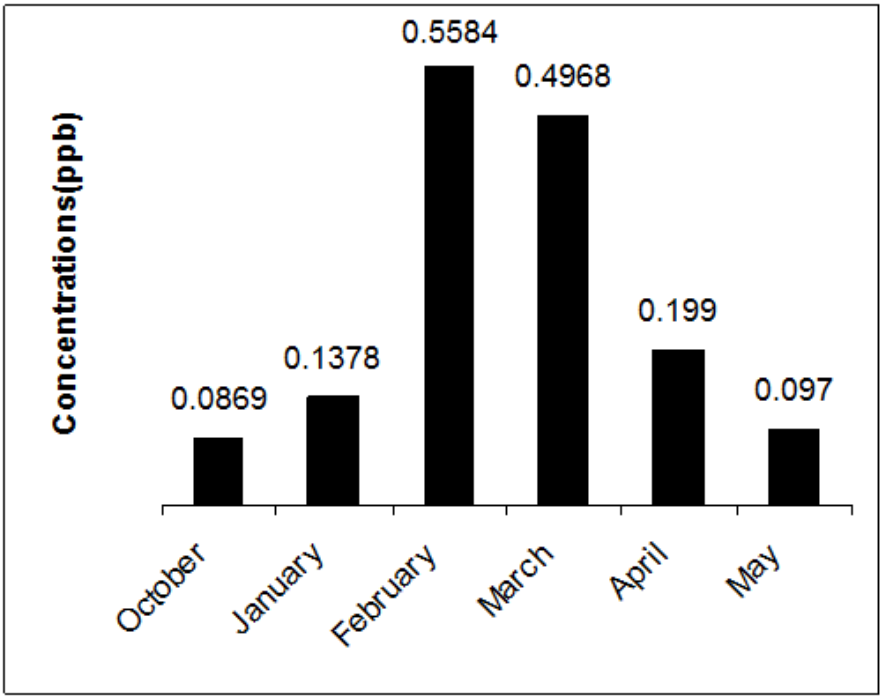

Fig. 8. Sum of 14 PAHs in Floresti sewer

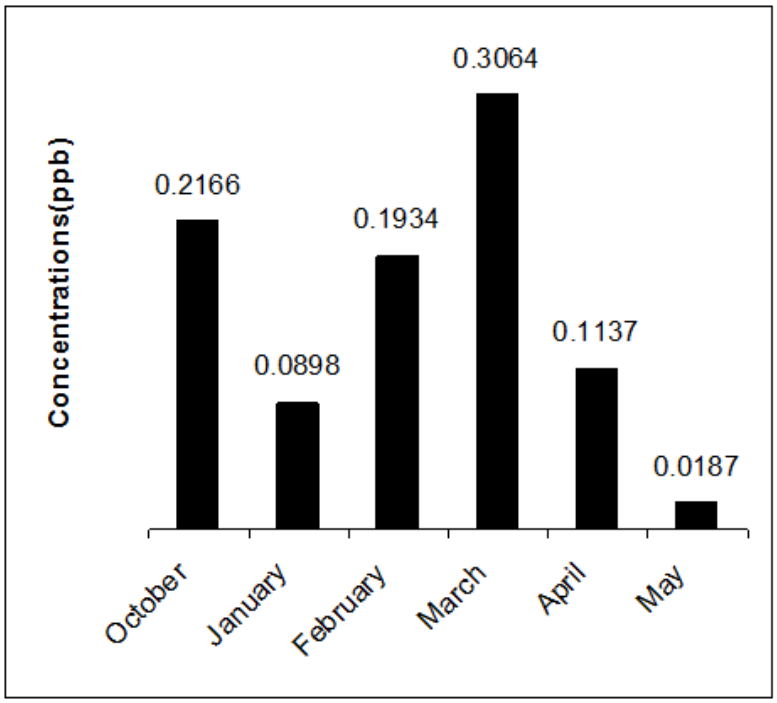

Fig. 9. Sum of 14 PAHs in Napoca sewer

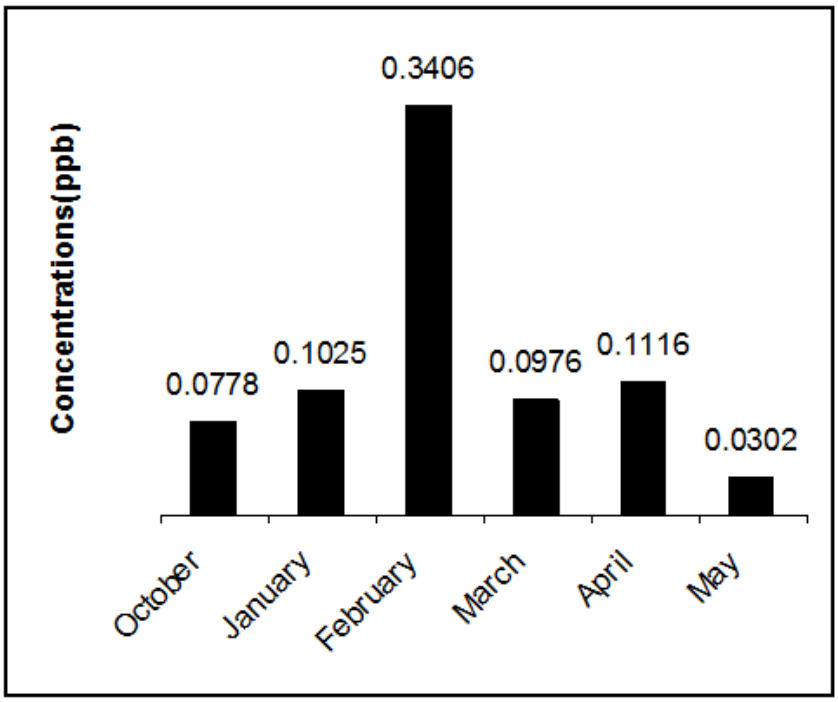

Fig. 10. Sum of 14 PAHs in Someseni sewer

Sample Info : Cosbuc 31.01.2011
V = 600 ml

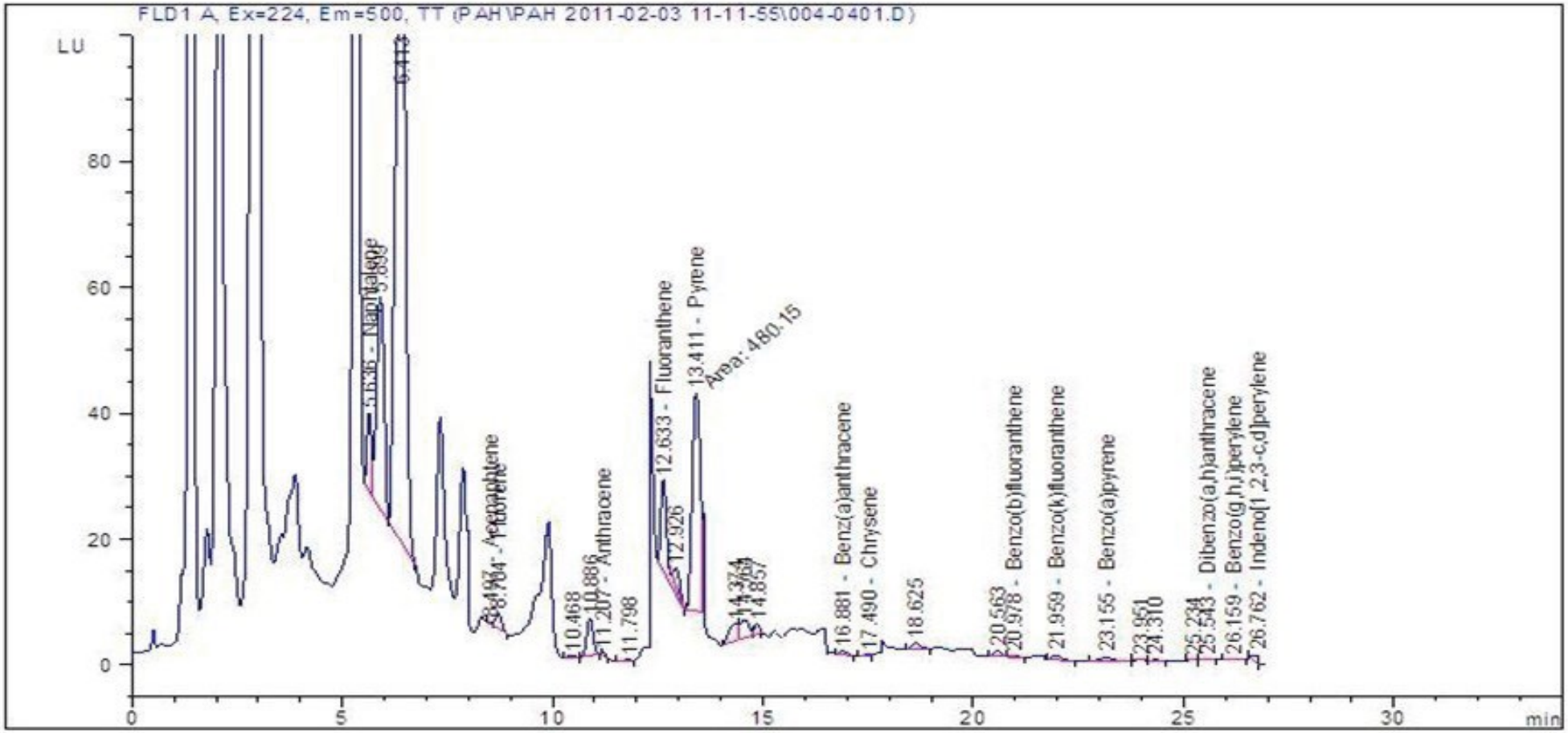

Fig. 11. A representative chromatogram of PAHs separated from urban wastewater collected from Cosbuc sewer

In February only benzo(k)fluoranthene was <LOD in Floresti sewer (Table 4). The Σ5 of PAHs represent around 3% from the Σ14 PAHs. High concentrations are in Cosbuc sewer which we cancorrelate them also with the heavy traffic.

Table 4. Concentration of PAHs from sewers in February

Sewer name	***Σ5 HAP (ppb)***
Coşbuc	0,0104
Floreşti	0,0136
Napoca	0,0036
Someşeni	0,0102

CONCLUSIONS

1. POLYCYCLIC AROMATIC HYDROCARBONS IN WASTEWATER SEWERAGE SYSTEM FROM THE CLUJ-NAPOCA AREA

Different PAH compounds are associated with each one of these sources: domestic usage, exhaust from automobiles and trucks, roof runoff. Important sources of PAHs include: industrial platforms in the airport area, CUG-platform discharges and some industrial units such as Armatura.

A significant proportion of PAHs in wastewater are derived from roof runoff and gas station with washing vehicle. Household sources of PAHs are likely to be more difficult to asses than commercial sources. Seasonal variations were observed for PAHs with higher levels in winter, when the domestic heating is working.

The obtained data provided a general picture of PAHs sources for the sewerage system in Cluj urban area, indicating that PAHs in Cluj-Napoca wastewater originates predominantly from food preparation which involves combustion processes difficult to identify and quantify, and vehicle traffic which is one of the most frequent anthropogenic source of PAHs.

Municipal wastewater characteristics vary from one location to another, depending on sources, effluents, land use, groundwater level and degree of separation between rainwater and sanitary waste. Some PAH's polluting sources still need to be identified, with special emphasis on the most important sources contributing to the system, especially diffuse sources.

2. POLYCYCLIC AROMATIC HYDROCARBONS IN SURFACE SOILS

This study proved that PAHs are part of the soil mixture, with total concentrations ranging from 0.09 to 81.40 μg/ kg, the highest recorded values being for chrysene (38.70 μg/ kg), pyrene (14.78 μg/ kg) and indeno(1,2,3-cd)pyrene (10.48 μg/ kg); the highest soil contamination was established for urban soil originating from Cluj Napoca's center (81.40 μg/ kg), while the lowest one proved to be in a rural agricultural area (Jucu - 0.09 μg/ kg).

3. POLYCYCLIC AROMATIC HYDROCARBONS IN SEWAGE SLUDGE FROM CLUJ-NAPOCA WASTEWATER TREATMENT PLANT

The obtained results show the need for several technological changes in the sludge management to reduce the concentration of these organic pollutants to levels that allow land application of sewage sludge according to the future European Directive. Due to its

hygienic instability and immaturity of PAHs, sludge should not be introduced into the soil environment directly. Composting is a preferred strategy of utilizing the sewage treatment byproduct.

4. URBAN SLUDGES UTILIZATION IN AGRICULTURE: POSSIBLE LIMITATIONS DUE TO THEIR CONTAMINATION WITH POLYCYCLIC AROMATIC HYDROCARBONS

This study revealed a low contamination of sewage sludge originating from Cluj Napoca wastewater treatment plant with PAHs (15.61 μg/ kg dry weight for overall PAHs concentration), with individual concentrations ranging from 0.06 to 11.50 μg/ kg dry weight, the highest recorded values being for naphthalene (11.50 μg/ kg dry weight), phenantrene (1.39 μg/ kg dry weight) and benzo (g, h, i) perylene (0.63 μg/ kg dry weight). As the recorded values during the study period were low, the environmental risks related with PAHs contamination is quite low in the studied case; due to their hydrophobic character, potential adverse effects such as groundwater pollution by levigation can be also excluded. However, seasonal variations of PAHs contamination are possible and for this reason this study will be extended for a full-year period.

5. HPLC ASSESSMENT OF POLYCYCLIC AROMATIC HYDROCARBONS' REMOVAL BY CLUJ NAPOCA'S ACTIVE SLUDGE WASTEWATER TREATMENT PLANT

The presence of PAHs in water bodies is a major concern at both locally and globally level due to the threat they pose to ecosystems. The HPLC method used within our study meets the required sensitivity and the selectivity, with high recoveries (between 91 - 99%) and good reproducibility (CV between 3.22 - 4.99%). Research showed that naphthalene, acenaphthene, fluorene, phenanthrene and anthracene are removed effectively during wastewater treatment, whereas for benzo (b) fluoranthene, benzo (k) fluoranthene, benzo (a)pyrene, benzo (g,h,i) perylene and dibenz (a,h) anthracene, indeno (1,2,3-cd) pyrene the recorded values were higher, these being resistant to the biological treatment.

6. FLUORIMETRIC DETECTION OF PAH'S FROM PYROGENIC SOURCES

Recorded spectra for a set of diluted PAH standard solutions of 0,01 μg/mL - 0,05 μg/mL shows constant and proportional maxima at 305,14 nm, 381,41 nm and 407,73 nm respectively. All maxima for investigated standards are between 400 and 470 nm.

Results shows that PAH's from pyrogenic sources extracted and concentrated in acetonitrile can be directly monitored by spectrofluorimetry. The technique has great potential as a rapid, inexpensive and non-destructive technique for field biomonitoring of PAH's exposure in environment.

As qualitative method spectrofluorimetry can be used succesfully, research on quantitative measurements using internal standardisation are in course. For future development of internal standard for pah measurements in environmental samples the spectrofluorimetric results will be correlated with future GC-MS analysis.

Final mentions

- Different environmental impacts for different PAHs.
- Reducing emissions from scratch is impractical because it requires cessation of several major industries: aluminum, burning fossil fuels, petroleum coke.

SELECTIVE BIBLIOGRAPHY

1. Abd-Elsalam H.E., E.E. Hafez, A.A. Hussain, A.G. Ali, A.A. El-Hanafy, 2009, Isolation and identification of three-rings polyaromatic hydrocarbons. American-Eurasian Journal of Agricultural & Environmental Sciences, 5 (1), 31 - 38.
2. Ahangar A.G., 2010, Sorption of PAHs in the Soil Environment with Emphasis on the Role of Soil Organic Matter: A Review. World Applied Sciences Journal, 11 (7), 759 – 765.
3. Alhafez L., N. Muntean, E. Muntean, T. Mihaiescu, R. Mihaiescu, D. Ristoiu, 2012a, Polycyclic aromatic hydrocarbons in wastewater sewerage system from the Cluj-Napoca area, Environmental Engineering & Management Journal, 11 (1), 5-12.
4. Alhafez L., E. Muntean, N. Muntean, 2012b, Assessment of urban pollution with PAHs' by snow analysis. Buletin USAMV Agriculture, 69 (2), 118-121. Cluj-Napoca, Romania, Print ISSN 1843-5246; Electronic ISSN 1843-5386.
5. Alhafez L., Muntean E., Muntean N., Dreve S., Ristoiu D., 2012c, Polycyclic aromatic hydrocarbons in urban surface soil from Cluj-Napoca (Romania). 37th International

Symposium on Environmental Analytical Chemistry, 22-25.05.1012, Antwerp, Belgium, Book of Abstracts, p.189.

6. Alhafez L., Muntean E., N. Muntean, Ristoiu D., 2012, Urban soil contamination with polycyclic aromatic hydrocarbons in Cluj-Napoca: a case study. Environmental Legislation, Safety Engineering and Disaster Management – ELSEDIMA-International Conference – UBB Cluj-Napoca, 25-27.10.2012, Romania, Book of Abstracts, p.2
7. Alhafez L., Muntean N., Muntean E., Ristoiu D., 2013a, Polycyclic aromatic hydrocarbons in sewage sludge from Cluj-Napoca wastewater treatment plant, Bulletin UASMV serie Agriculture 70(2), 387-389, Cluj-Napoca, Romania, Print ISSN 1843-5246; Electronic ISSN 1843-5386.
8. Alhafez L., N. Muntean, E. Muntean, M. Duda, 2013b, Urban sludges utilization in agriculture: possible limitations due to their contamination with polycyclic aromatic hydrocarbons, ProEnvironment, 6, 438-440, Romania, ISSN 1844-6698, eISSN 20661363
9. Alhafez L., N. Muntean, E. Muntean, D. Ristoiu, 2013c, HPLC assessment of polycyclic aromatic hydrocarbons' removal by Cluj-Napoca's active sludge wastewater treatment plant. ProEnvironment, 6 (16), 582-586, Cluj-Napoca, Romania, ISSN 1844-6698, eISSN 20661363
10. Blanchard M., Teil M.J., Ollivon D., Legenti L., Chevreuil M., (2004), Polycyclic aromatic hydrocarbons and polychlorobiphenyls in wastewaters and sewage sludges from the Paris area (France), Environmental Research, 95, 184–197.
11. Boving T.B., Neary K., (2007), Attenuation of polycyclic aromatic hydrocarbons from urban storm water runoff by wood filters, Journal of Contaminant Hydrology, 91, 43–57.
12. Busetti F., Heitz A., Cuomo M., Badoer S., Traverso P., (2006), Determination of sixteen polycyclic aromatic hydrocarbons in aqueous and solid samples from an Italian wastewater treatment plant, Journal of Chromatography A, 1102, 104–115.
13. Cao Z., Wang Y., Ma Y., Xu Z., Shi G., Zhuang Y., Zhu T., (2005), Occurrence and distribution of polycyclic aromatic hydrocarbons in reclaimed water and surface water of Tianjin, China, Journal of Hazardous Materials, A122, 51–59.
14. Charalabaki M., Psillakis E., Mantzavinos D., Kalogerakis N., (2005), Analysis of polycyclic aromatic hydrocarbons in wastewater treatment plant effluents using hollow fiber liquid-phase microextraction, Chemosphere, 60, 690-698.
15. Council Directive, (1991), Council Directive 91/271/EEC of 21 May 1991 concerning urban waste-water treatment, Official Journal of the European Communities, L 135, 40-52.

16. Draghici C., Dobrinas S., Chirila E., Stanciu G., (2009), Residues of polycyclic aromatic hydrocarbons from refinery spent catalysts, Environmental Engineering and Management Journal, 8, 935-938.

17. Gasperi J., Garnaud S., Rocher V., Moilleron R., (2008), Priority pollutants in wastewater and combined sewer overflow, Science of the Total Environment, 407, 263– 272.

18. Gocan S., Cobzac S., (2006), Modern Method of Organic Samples' Processing, Risoprint, Cluj-Napoca, Romania.

19. Gourlay-Francé C., Lorgeoux C., Tusseau-Vuillemin M.H., (2008), Polycyclic aromatic hydrocarbon sampling in wastewaters using semipermeable membrane devices: accuracy of time-weighted average concentration estimations of truly dissolved compounds, Chemosphere, 73, 1194–1200.

20. Hwang H.-M., Foster G.D., (2006), Characterization of polycyclic aromatic hydrocarbons in urban storm water runoff flowing into the tidal Anacostia River, Washington, DC, USA, Environmental Pollution, 140, 416-426.

21. Jäntschi L., (2003), Environment metrology and monitoring, Amici, Cluj-Napoca, On line at: http://lori.academicdirect.ro/works/?f=111.

22. Levinson J., Sluszny C., Yasman Y., Bulatov V., Schechter I., (2005), Detector for particulate polycyclic aromatic hydrocarbons in water, Analytical and Bioanalytical Chemistry, 381, 1584–1591.

23. Peng-hui Li P-h., Wang Y., Li Y-h., Wang Z-f., Zhang Hy., Xu P-j., Wang W-x., (2010), Characterization of polycyclic aromatic hydrocarbons deposition in PM2.5 and cloud/fog water at Mount Taishan (China), Atmospheric Environment, 44, 1996-2003.

24. Maliszewska-Kordybach B., Smreczak B., Klimkowicz-Pawlas A., (2009), Concentrations, sources, and spatial distribution of individual polycyclic aromatic hydrocarbons (PAHs) in agricultural soils in the Eastern part of the EU: Poland as a case study, Science of the Total Environment, 407, 3746–3753.

25. Motelay-Massei A., Garban B., Tiphagne-Larcher K., Chevreuil M., Ollivon D., (2006), Mass balance for polycyclic aromatic hydrocarbons in the urban watershed of Le Havre (France): Transport and fate of PAHs from the atmosphere to the outlet, Water Research, 40, 1995–2006.

26. Oros D.R., Ross J.R.M., Spies R.B., Mumley T., (2007), Polycyclic aromatic hydrocarbon (PAH) contamination in San Francisco Bay: A 10-year retrospective of monitoring in an urbanized estuary, Environmental Research, 105, 101–118.

27. Passerat J., Ouattara N.K., Mouchel J.M., Rocher V., Servais P., (2010), Impact of an intense combined sewer overflow event on the microbiological water quality of the Seine River, Water Research, 45, 893– 903.

28. Popa E., Zalaru C.M., Baciu I., (2007), Organic Pollutants in the Environment, (in Romanian), Bucharest University Publishing House, Bucharest.

29. Sánchez-Avila J., (2009), Determination and occurrence of phthalates, alkylphenols, bisphenol A, PBDEs, PCBs and PAHs in an industrial sewage grid discharging to a municipal wastewater treatment plant, Science of the Total Environment, 407, 4157–4167.

30. Thornton I., Butler, D., Docx P., Hession M., Makropoulos C., McMullen M, Nieuwenhuijsen M., Pitman A., Rautiu R., Sawyer R., Smith S., White D., Wilderer P., Paris S., Marani D., Braguglia C., Palerm J., (2001), Pollutants in urban wastewater and sewage sludge, Final report, ICON, I C Consultants Ltd, UK, London.

31. Tsakovski S., Tobiszewski M., Simeonov V., Polkowska Z., Namiesnik Tsakovski J., (2010), Chemical composition of water from roofs in Gdansk, Poland, Environmental Pollution, 158, 84–91.

32. Xinna Z., Lingyan F., Jia H., Jianwang L., Huili W., Changjiang H., Xuedong W. (2009), Analysis of PAHs in water and fruit juice samples by DLLME combined with LC-fluorescence detection, Chromatographia, 69, 1385-1389.

33. Hotărârea de Guvern privind stabilirea limitelor de încărcare cu poluanţi a apelor uzate industriale si orasenesti la evacuarea in receptorii naturali, NTPA-001/2002. Publicat in Monitorul Oficial, Partea I nr. 187 din 20 martie 2002.

34. Ordinul de Ministru nr. 88 / 2007 pentru aprobarea Regulamentului-cadru al serviciului de alimentare cu apă şi de canalizare. Monitorul Oficial al României, nr. 324 / 15 mai 2007

35. SR EN ISO 17993, (2004), Water quality - Determination of 15 polycyclic aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection after liquid-liquid extraction, International Organization for Standardization, On line at: http://www.iso.org/iso/iso_catalogue/catalogue_tc/catalogue_detail.htm?csnumber=31666 .

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