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Investigation of polycyclic aromatic hydrocarbons in soils around Elbasan industrial area, in Albania

Jonida Tahiraj[1*], Elda Marku[1], Georg Raber[2]

[1]*Chemistry Department, Faculty of Natural Sciences, University of Tirana, Albania*
[2]*Institute of Chemistry-Analytical Chemistry, University of Graz, Graz, Austria*
[*]*jonida.tahiraj@fshn.edu.al*

Abstract

Polycyclic aromatic hydrocarbons (PAHs) have been recognized to cause serious health and environmental problems due to their carcinogenic, mutagenic and teratogenic properties. For the first time, a comprehensive study was conducted in Elbasan district in order to know the current situation concerning PAH levels in this area which is under the influence of the metallurgical activity since 1976, currently operated by a Turkish company. 36 surface soil samples were collected in total in urban, agricultural and industrial areas, in March 2017. The samples were ultra-sonicated with dichloromethane, and the extracts were analyzed using an Agilent 7890A gas chromatograph equipped with a quadrupole Mass Spectrometer 5975C. High levels of contamination were observed at station 7 (Coke Plant) and station 10 (Refractory Brick and Carbon Mass Plant), where the mean concentration of 14 PAHs was in range 17235 µg/kg and 1635 µg/kg (dry weight), respectively. PAH pattern was dominated by four- and five- ring PAHs, contributing to 37%, 41 % and 42% of the total PAHs content at the industrial, urban and agricultural areas respectively. The sum of the 14 PAHs in the industrial area were considerably higher than those in urban and agricultural areas. The diagnostic molecular ratios revealed that the sources of PAHs were of mixed origin. The highest sum of the 7 carcinogenic PAHs was found in the industrial area. In general, the PAH concentrations in this study were below the maximum PAH concentrations allowed by the Canadian legislation for soils.

Keywords: PAH, Soil pollution, GC-MS, Industrial, Ultrasonic extraction

1. Introduction

Polycyclic aromatic hydrocarbons are ubiquitous compounds of different structures, physical and chemical properties entering onto environment from natural and anthropogenic sources. The United States Environmental Protection Agency have identified 16 PAHs (naphthalene, acenaphthene, acenaphthylene, anthracene, benzo[a]anthracene, benzo[b]fluoranthene, fluorene, chrysene, phenanthrene, pyrene, benzo[a]pyrene, benzo[g,h,i]perylene, benzo[k]fluoranthene, dibenzo[a,h]anthracene, indeno[1,2,3,-c,d]pyrene and fluoranthene) as priority pollutants due to their wide distribution into environment and potential human health risk (Bojes and Pope, 2007). Several PAHs are increasing attentions due to their carcinogenic and mutagenic properties (Kim et al., 2007); O'Hara and Rice, 1996). Among them, seven PAHs are probably carcinogenic for humans, such as: benzo(a)anthracene, chrysene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, dibenzo(a,h)anthracene, and indeno(1,2,3-cd)pyrene (Jiang et al., 2009). Soils present an important sink for these compounds, because of high hydrophobicity and their stable chemical structure (Wang X-T., 2013) (Agarwal T.,

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2009). Soil contamination partly originates from PAH emissions to the atmosphere via dry and wet deposition. PAHs in soil can be dispersed by surface runoff and air dust production. These compounds are strongly related with soil organic matter where they are likely to be retained for many years. Sources of PAHs are commonly categorized into pyrogenic and petrogenic sources (Albanese et al., 2014; Jiang et al., 2009). To identify the sources of PAHs, the ratio between low and high molecular weight (LMW; HMW PAHs) and also the ratio between isomeric PAHs have been used from several authors (Li et al., 2010; Pérez-Fernandez et al., 2015; Yunker et al., 2002). In recent years, public concern over possible adverse health effects for the population living near this industrial area has increased. Consequently, the main objective of this study was to investigate the presence of these contaminants in the area of the largest metallurgical combine located in Elbasani town, in Albania, and hence to identify their sources using diagnostic molecular ratio. Elbasan is one of the most industrial cities, located between 41˚6'45" North latitude and 20˚4'56" East longitude, with surface area of 872.03 km^2. The metallurgical combine is located in the vicinity of Bradashesh village and 5 km west from Elbasani town. The industrial activity started in the late 1960's initially with a cement factory and gradually expanded with different units of the metallurgical combine. This area consists of different plants such as iron and steel, ferro-chromium smelter, refractory bricks, coke plant, and other metallurgical units that canbe an important source of PAHs. These compounds can thermally desorb during the steel–iron production processes, or can be formed during incomplete combustion of scrap organic material and additives like coal. Some of these plants had worked till 1992 and nowadays there are only abandoned buildings.

2. Materials and methods

Thirty-six surface soil samples were randomly collected for the determination of PAHs, in March 2017 according to a guideline presented by International Atomic Energy Agency IAEA (2004). The distribution of sampling sites was as following: 21 surface soil samples were collected inside the metallurgical combine, 6 in garden park of the town and 9 in the agricultural area (Vidhas and Bradashesh village) near metallurgical combine, as shown in Figure 1. Soil samples of approximately 0.5–1 kg, were placed into glass jar covered with aluminum foil, stored with ice in freeze box at 4 ˚C until arrival at the laboratory. Further analysis was carried at the Analytical Chemistry Laboratory in Graz University. Samples were dried at 35 ˚C, and milled at 90 μm for further analysis using Ball Mill, Retsch, 200 MM).

2.1. Analytical procedure

For PAHs analysis, approximately 0.5 gram of dried soil from each sample was spiked with 1,000 ng (50μl of 20 mg L^{-1}) deuterated internal standards such as naphthalene-D8; acenaphthene-D10; phenanthrene-D10 and chrysene-D12 to control the quality of the sample preparation steps and calibration. Elemental sulfur was removed by adding activated copper granules to the collection flasks. Thereafter, samples were ultrasonically extracted with dichloromethane for 30 minutes in room temperature. After centrifugation, the organic phase was taken and evaporated at 60˚C. The final extract was re-dissolved in 1 ml dichloromethane. Extracts were analyzed using gas chromatography with mass spectrometry detection (an Agilent 7890A gas chromatograph - Mass Spectrometer 5975C), using helium as a carrier gas and a DB-5ms fused silica capillary column. The detection was achieved with a mass selective detector using electron ionization (EI) in the single ion monitoring mode (SIM). Splitless injection of 1 µl was made with an autosampler. The carrier gas flow was 1.5 ml/min. For the analysis of the 16 PAHs the injector temperature was 280 °C and the interface temperature was 300 °C. The oven temperature was programed as follows: 50 °C for 2 min, increase at a rate of 25 °C/min until 200 °C for 0 min then at 15 °C/min until 300 °C for 20 min. Chromatograms and mass spectra were evaluated using Agilent Mass Hunter Software.

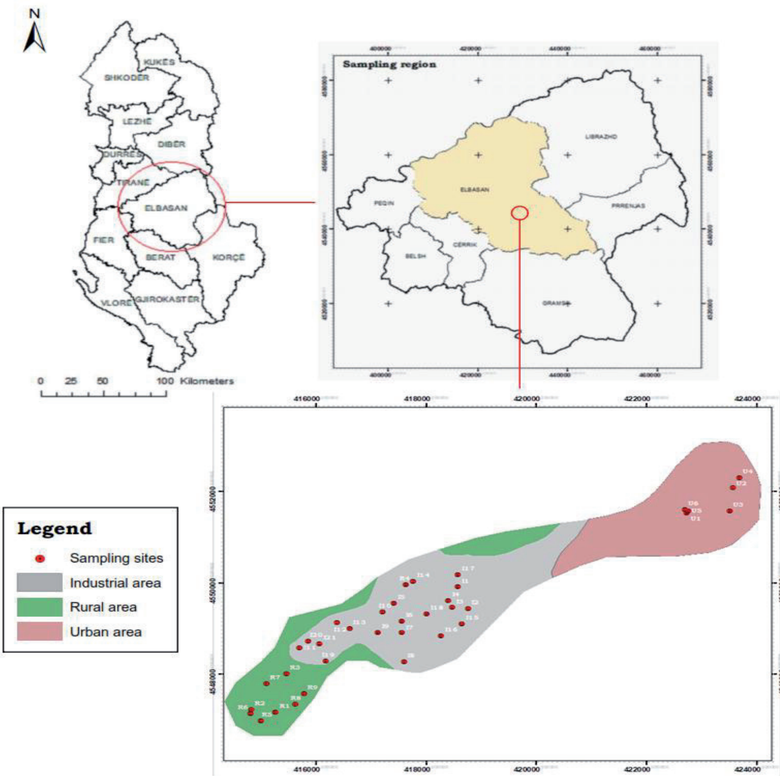

Fig. 1. Location map of sampling sites in Elbasani town, Albania

3. Results and discussion

3.1. PAHs content in surface soil

Fourteen PAHs compounds (ACY: acenapthylene; ACE: acenapthene; FLU: fluorene; PHE: phenanthrene; FLT: fluoranthene; PYR: pyrene; BaA: benz(a)anthracene; CHR: chrysene; B(b)F: benzo(b)fluoranthrene; B(k)F: benzo(k)fluoranthrene; BaP: benzo(a)pyrene; IND: indeno(1,2,3-cd)pyrene; DBA: dibenzo(a,h)anthracene; BghiP: benzo(g,h,i)perylene were analyzed in 36 surface soil samples. The frequency detection of PAHs in industrial soil samples varied from 52- 100%, in urban area varied from 34-100% and in rural area varied from 37-100%. The total PAHs concentrations for industrial, urban and agricultural areas ranged from 202.2-241,291.3 µg kg^{-1} (mean: 14,730.0 µg kg^{-1} median: 864.2 µg kg^{-1}); 89.8-2013.7 µg kg^{-1}(mean: 623.2 µg kg^{-1}; median: 253.01 µg kg^{-1}); 118.6-2005.08 µg kg^{-1} (mean:560.9 µg kg^{-1}; median: 202.1 µg kg^{-1}). According to the sum of the 14 PAHs the highest value was found in the industrial area, in station I7 (coke plant) followed by station I10 (refractory bricks and carbon mass plant). The lowest concentration was measured in station I5 (scrap storage site). For urban and agricultural area, the stations U3 and R9 were more polluted with PAHs than other stations. Comparing the PAHs levels with the target value set by Dutch government for unpolluted soils (20 -50 µg kg $^{-1}$) (Van Brummelen et al., 1996), the soils in our study are highly polluted. A wide range of PAHs concentrations was observed in all samples collected from three areas, where industrial area showed generally the highest concentrations compared with urban and rural ones.

The average concentration ofΣ14 PAHs in the industrial area was fourteen times higher than values in urban and rural sites, respectively. The carcinogenic PAHs (Σ7 carcinogenic PAHs)in the industrial, urban and ruralareascontribute with 57%, 47%, 44% of Σ14 PAHs.Benzo(a)pyrene, one of the most potent carcinogenic PAHs showed a median value of 9.27 µg kg^{-1}; 3.99 µg kg^{-1}; 52.9 µg $kg^{-1}$for urban, rural and industrial areas, respectively. Median concentrations of the individual PAHs in three areas are presented in Figure 2. The bar diagramsshow that the FLT and PYR were the most abundantcompounds in allthree areas. These 4- ring PAHsare reported as markers for coal combustion (Wang et al. 2011). In industrial, urban and rural soil samples, PAHs were dominated by PYR>FLT>BbF>CHY>PHE>IND. The same profile indicates similar sources of PAHs in these areas. Rural area showed a little difference in the PAH trend where 3- ring PAHs were more abundant compared with industrial and urban areas. This can be related with the fact that LMW PAHs have the tendency to be transported in long distances in atmosphere (Agarwal et al., 2009). On the other hand, HMW PAHs are mainly associated with rapid deposition and tend to accumulate close to the source origin. The composition profile of PAHs was characterized from high molecular weight PAHs that are known to be carcinogenic and are considered as products derived from combustion (Khalili et al. 1995). In agreement to the Bakker et al. 2000, who reported that HMW PAHs were deposited closer to strong point sources, in our study the highest levels were found near the coke plant area.

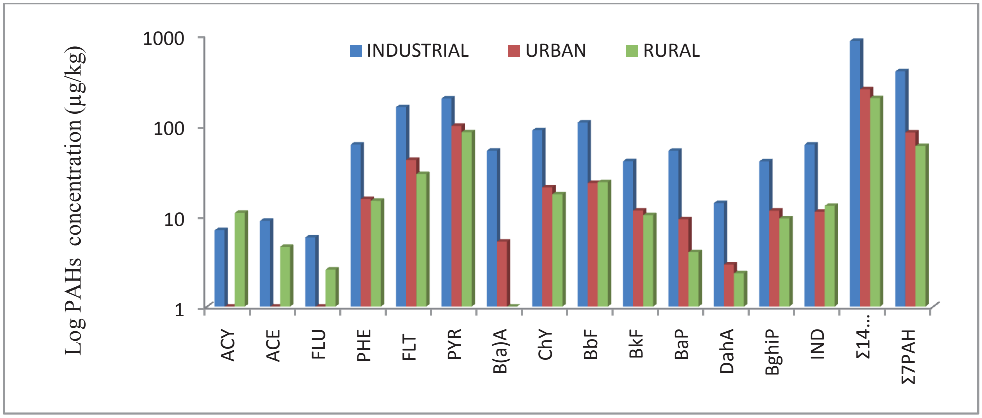

Fig. 2. Individual PAHs pattern in soils. Median content of individual PAHs (µg kg^{-1}) in industrial, urban and rural areas

3.2 Molecular diagnostic ratio

Molecular diagnostic ratio of selected PAH concentrations is widely used to distinguish PAHs emission from petrogenic and pyrogenic origins (Bucheli et al., 2004; Yunker et al., 2002). In order to identify the PAHs sources, the isomer ratios of IND/(IND+BghiP), BaP/BghiP and FLT/(FLT+PYR) were calculated. Yunker et al. (2002), suggested that a FLT/(FLT+PYR) ratio less than 0.4 indicates petroleum input, ratio between 0.4 to 0.5 liquid fossil fuel combustion and ratio > 0.5 indicate coal, grass or wood combustion, IND/(IND + BghiP) ratio of > 0.5 indicates grass, coal, wood combustion sources and the ratio of BaP/BghiP > 0.6 indicates traffic sources. An evaluation of our data is presented in Figure 3. The IND/(IND + BghiP) and BaP/BghiP ratio collectively indicated the traffic emission and coal/biomass combustion as the main? sources of PAHs in Elbasani surface soil samples. Figure 3A-3B shows that the representative diagnostic ratios were FLT/(FLT+PYR) varied from 0.22-0.55; 0.09-0.51; 0.13-0.49 for industrial, urban and rural areas, respectively. IND/(IND + BghiP) varied from 0.42-0.71 (industrial); 0.52-0.57 (urban); 0.36-0.68 (rural) and BaP/BghiP varied from 0.23-1.56 (industrial); 0.93-1.42 (urban); 0.16-2.06 (rural). The ratios showed that 86%, 56%, and 50% of the industrial, rural and urban samples, suggest that the emission from coal/biomass combustion appeared to be the predominant source of PAHs. The results indicate that the PAHs in the studied areas were predominantly pyrogenic, coal/wood/grass/vehicular combustion mixed sources. Therefore, PAHs in surface soil samples are dominated by pyrogenic inputs.

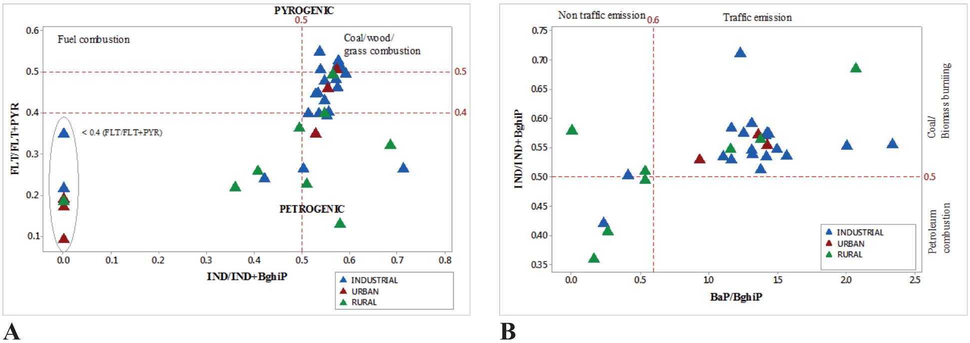

Fig. 3. Cross plot for the isomeric ratio: **A**: IND/IND+BghiP versus FLT/FLT+PYR, and **B**: BaP/BghiP versus IND/IND+BghiP

3.3 Comparison with other studies

The PAHs concentrations in soil samples from different areas around the world remarkably varied, due to many factors, such as: i) the type of pollution source, ii) emission density, and iii) soil properties. All these properties contribute to the fate and distribution of PAHs into soils (Duan, 2014). The levels of PAHs in soils are not yet regulated by law in Albania. Therefore, we compared the concentrations of PAHs with those reported in other studies. The mean concentration of 14 PAHs with a value of 623 µgkg^{-1} observed in our study were found in the same level with urban soils from Tokushima of Japan (610.6 µgkg^{-1}), (Yang et al., 2002) and lower than mean concentration observed in 12 PAHs in Estonian soils 2200 µgkg^{-1} (Mielke et al., 2001), and urban soil samples in New Orleans as reported by Trapido 1999 with a median value of 3731 µgkg^{-1}. Numerous investigations have assessed the environmental contamination by PAHs in several industrial sites. The mean concentration of ∑ 14 PAHs in our industrial area, with a value of 14,730 µg kg^{-1},was higher compared with industrial soils from Kohtla-Jarve (Estonia) with a value of 12,390±9810 and lower than industrial soils of Serbia and Belgium reported by (Bakker et al., 2000) (Skrbic B. & Miljevic N., 2002). Bakker et al. (2000) found a total PAHs concentration of 300,000 µgkg^{-1}in soil samples collected at 50 m from an oil refinery of Zelzate (Belgium), and concentrations ranged from 3000 to 14,000 µgkg^{-1}in sites situated at 1.3 and 4.2 km from the oil refinery. Skrbic and Miljevic (2002) determined PAH pollution in soils of the vicinity of an oil refinery in Novi Sad, after the Kosovo war and reported a value of 47,900 µgkg^{-1}. Agricultural area showed lower value of ∑14 PAHs (560 µgkg^{-1}) compared with agricultural soils from Poland (616 µgkg^{-1}), and higher value than Delhi, India agricultural soils with a value of 158 µgkg^{-1} (Maliszewska-Kordybach et al., 2008; Agarwal et al., 2009). PAHs contamination of this study area can be explained with direct influence of numerous industrial activities including steel-iron plant, ferro-chromium plant and some other units of metallurgical combine, such as coke plant which operated until 1992. Additionally, this town has a climate with sunshine and rain fall every year, which made soil PAHs levels decrease by evaporation and run off.

4. Results

The results obtained from this study showed that the median concentrations of Σ14 PAH were 252.3 µgkg^{-1}, 202.2 µg kg^{-1}, 864.2 µgkg^{-1} in urban, rural and industrial areas, respectively. Among the three areas, the higher levels of PAHs were found in the industrial soil samples. The composition of PAHs wascharacterized by high molecular PAHs. The 4-ring PAHs such as FLU and PYR were the most abundant onesin the surface soil samples of Elbasani town, indicating extensive combustion of different fuels. The different isomeric ratio indicated that the PAHs mainly comefrom pyrogenic input. The sources of PAHs may be mostly ascribed to the processes of the metallurgical industries during handling and transportation of the raw materials and products, and also to the emissions from road traffic, wood/grass and coal combustion.

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