Study on the Content of Polycyclic Aromatic Hydrocarbons in the Water from the Industrial Area

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This study has been performed to identify the degree of pollution with polycyclic aromatic hydrocarbons in the soil and water of the highly industrialized town, Targoviste, and its surroundings. This research represents the first stage of a larger project aiming at monitoring the PAHs during the entire food chain meant to obtain meat products starting with the feeding of the animals and ending with the obtaining of the finished products. The measurements will be realized using a modern methodology which will permit the establishing of low levels of PAS in the analyzed products. Many of them - the benzo [a] anthracene, the chrysene, the benzo [b] fluoranthene, the benzo [a] pyrene and the benzo [ghi] perylene- are known to be potentially carcinogenic for humans. Therefore, they have been included in the list of priorities of the Water Framework Directive 2000/60/EC and, also, sixteen of them have been established by EPSA U.S. as major pollutants. Their distribution in the environment and the potential risks to human health, have attracted the public attention. There have been dosed 14 PAHs. The determinations have been made using a modern methodology that will allow the detection of the lowest levels of contaminants. For this purpose PAHs have been separated by a high-performance liquid chromatography (HPLC) of water samples collected from areas surrounding the town.

Keywords: polycyclic aromatic hydrocarbons, HPLC, water, pollution, traceability

Pollution is a complex phenomenon most frequently involved in disturbing the balance of environmental compounds that affect health biocenosis. The industrial area of Targoviste (metallurgical industry), of Fieni (cement industry), of Doicesti (thermal industry) are specific sources of pollutants of great diversity. [1]. The identifying of the causes of pollution and of contamination levels with chemical factors is the main concern of research in order to prevent the toxic effects induced by pollution [2]**.** Based on the principles mentioned in Article 175 (3) Directive 2004/107/EC of the European Parliament and Council, the Sixth Community Environment Action, adopted by Decision no. 1600/2002/EC of the European Parliament and Council, establishes the need to decrease pollution to levels that minimize adverse impacts on human health, paying particular attention to sensitive population and the environment as a whole [3]. A list of the most hazardous PAHs is presented in Decision 2455/2001/EC of the European Parliament and the Council, amending Directive 2000/60/EC. The polycyclic aromatic hydrocarbons (PAHs) are a group of compounds consisting of two or more aromatic rings. The effects of polycyclic aromatic hydrocarbons (PAH) on human health, including the environmental and food chain as a whole, are felt through the ambient air concentrations and depositions; therefore, the accumulation of these substances in soil and groundwater protection must be taken into account [4-7]. The polycyclic aromatic hydrocarbons are a group of organic compounds, very stable, consisting of at least 2 fused aromatic nuclei, having in their constitution only carbon and hydrogen atoms [8, 9]. They can enter the food during technological processes of production. Some of them are considered potentially carcinogenic for humans, in particular the benzo[a]anthracene, the chrysene, the benzo[b]fluoranthene, the benzo[a]pyrene and the benzo[ghi]perylene [10, 11]. At a temperature of 18-20 deg. C the PAHs are solid, colourless, white or slightly yellow-green, with high melting points and boiling. The PAHs are used as intermediates in the processes of obtaining plastic materials, dyes and paints, pesticides. They reach the environment due to incomplete combustion of organic fuels during industrial processes or due to other human activities [12]. Not all the polycyclic aromatic hydrocarbons are considered genotoxically carcinogenetic fact that depends on their molecular structure [13, 14].

Thus, the PAHs are classified into: low molecular weight PAHs (those containing 2 or 3 aromatic rings) and high molecular weight PAHs (those containing 4 or more aromatic rings). The latter are the most carcinogenic and teratogenic [15, 16]. People can become contaminated with PAHs by ingestion of food, water and air in the rooms and the environment. Food can be contaminated from the environment through air, water, soil, or during its processing and culinary preparation. The smoke resulting from burning cigarettes has a high content of polycyclic aromatic hydrocarbons [16, 17]. Numerous research papers on PAHs in environmental samples, air [18], sediments from lakes [19 - 21], tea and coffee [22, 23], fruit and vegetables [24], food of animal origin [25] have been published.

Experimental part

Determined compounds

In this study 14 PAHs recognized as high priority pollutants by the U.S. Environmental Protection Agency (U. S. EPA, 1993) have been analyzed. These compounds have been selected because of their highest toxicity potential, and also to their mobility and transmission to the human beings.

The following polycyclic aromatic hydrocarbons have been determined: the naphthalene, the phenantrene, the fluoranthene, the fluorene, the anthracene, the acenaphthene, chrysene, the benzo [a]anthracene, the benzo [e] pyrene, the benzo[g,h,i] perylene, the benzo [k] fluroanthene, the benzo [b] fluroanthene, the indeno [1,2,3] cd pyrene, the pyrene.

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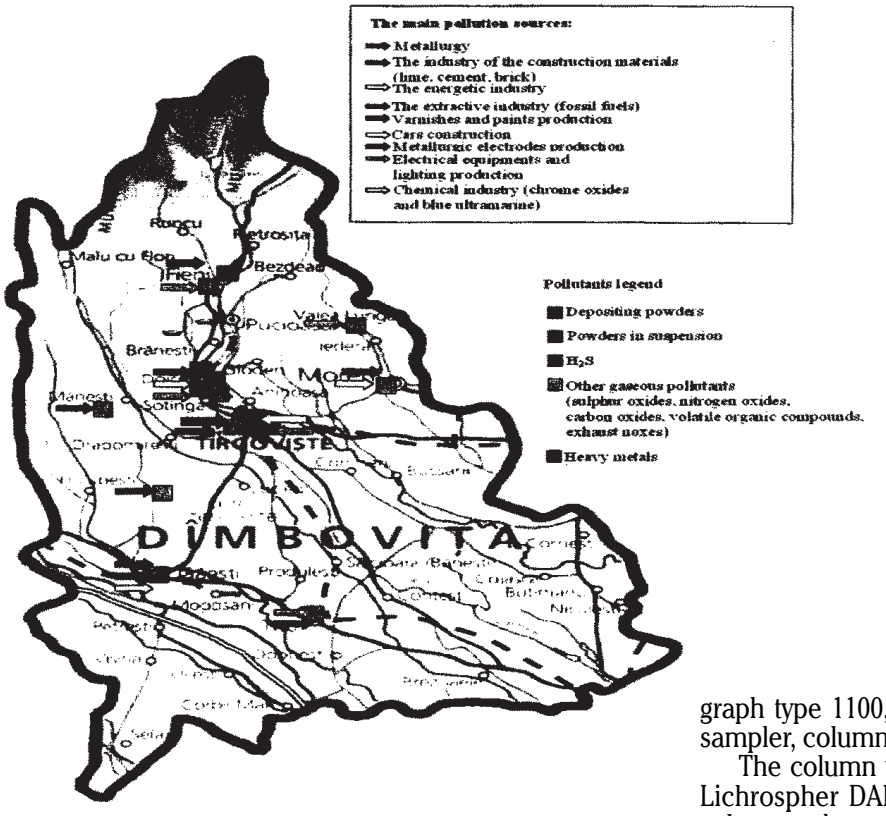

Fig.1. The pollution sources in Targoviste city and surrounding area

Samples

The water samples have been taken from four different sources in the town of Targoviste and its surrounding areas. (fig.1.)

The following notations have been used:

WA-the water entrapped from the deep source of surrounding areas;

WAT-the water entrapped from the deep source of Targoviste;

WS-the water entrapped from a surface source of surrounding areas;

WP-the water from the public network of the Targoviste

The volume- the water samples held 1 l and have been placed in glass recipients after the samples'collecting .

Method and reagents

The principle of determining the polycyclic aromatic hydrocarbons in water was based on the liquid chromatography technique, according to SR EN ISO17993: 2004. The high performance liquid chromatography (HPLC) is an evolution of a more ancient method, namely the classical column chromatography, which used to serve primarily to the preparative isolation of natural compounds. By placing pumps and consequently, working at higher pressures (200atm), the development of some efficient stationary phases, of ever smaller size (recently consisting of stationary phases spherical granules with diameters of 2-5μm), in ever shorter columns (3-10cm) resulted in the initial improvement of the method.

The method is based on the liquid-liquid extraction (with hexane) of PAHs from water followed by the HPLC separation and the fluorescence detection, using the external standard method. The extraction is continued with hexane; after that the purification of the organic extract is performed by passing the sorbent SPE cartridge especially for PAH. Finally, the extract concentration is performed using the Rota evaporator and the chromatographic analysis.

The determinations of PAH compounds have been performed with an Agilent Technologies HPLC chromatograph type 1100, equipped with quaternary pump, auto sampler, column thermostat and fluorescent detector.

The column used for the separation of the PAHs was Lichrospher DAP 250x3cm RP C 18. 5 μm, with guard column and precolumn. The used mobile phase: acetonitrile - water gradient from 60:40 to 100% acetonitrile.

Scheme of work for a HPLC: solvent pump→ injector → column → detector → recorder.

Results and discussions

The recommendation (2005/108/EC) issued by the European Commission stipulates that all Member States must do monitoring for PAHs in foodstuff. It aims to provide information concerning the sources of environmental food contamination by PAHs.

The U.S. Environmental Protection Agency (EPA) has established a Maximum Contaminant Level (MCL) for benzo(a)pyrene of 0.2 μg/L. The reference values, in Romania, with normal and the alert limits for the chemical elements from water are mentioned in Law no. 458/2002 of 07.08.2002, modified and completed by Law no. 311 28/06/2004. In the case of the WP sample all the hydrocarbons studied were below the detection limit, and in the case of WA, WS, WAT samples there were detected some of the 14 PAHs.

Pollution in this region is caused by processing coal, oil, natural gas, iron production, steel, power and heating in residences, fire. Soils, surface waters and precipitation may be contaminated with PAHs in the atmosphere, due to oil spills and emissions from cars in traffic. Animal feed may be contaminated by depositing particles in the air or by developing them in a contaminated soil.

The normal values for PAHs in water should not exceed 0.1 μg/L. Figure 2 presents the resulting chromatograms following the analysis of water sample collected from the source area of Targoviste town's surrounding. Note that the values of naphthalene (0.014 μg/L), phenantrene (0.005μg/L) and benzo (a) anthracene (0.006 μg/L) were higher than those from deep sources. Other polycyclic hydrocarbons were monitored in the detection limits. The amount of benzo [e] pyrene (<0.001 μg/L), which presents an increased risk for cancer, was below the limit allowed by Law no. 311 of 28/06/2004 (0.01 μg/L) in all samples. The total PAHs normal content should not exceed 0.1 μg/L [26, 27].

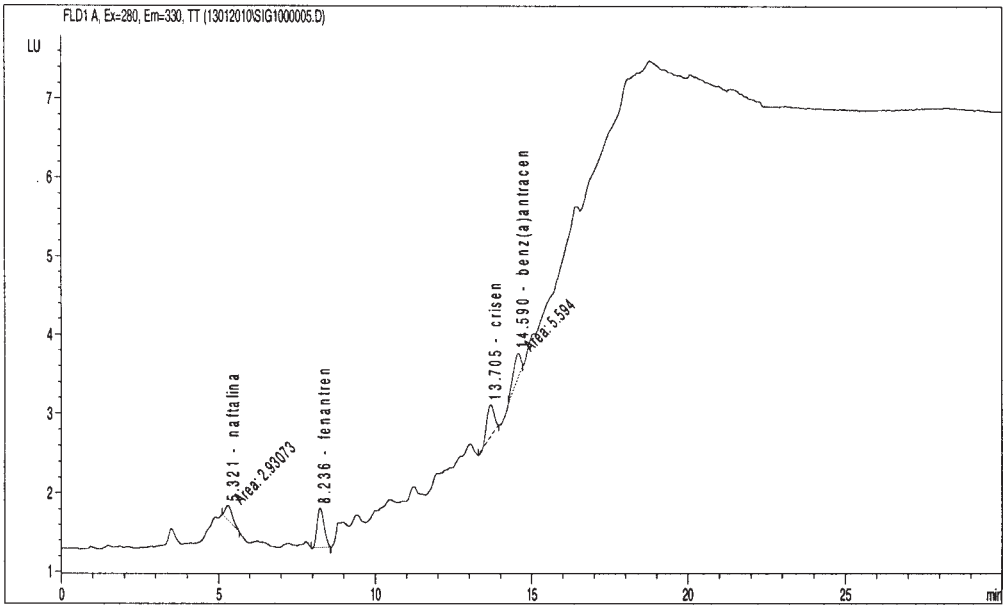

Fig. 2. The HPLC chromatogram obtained for the sample WS

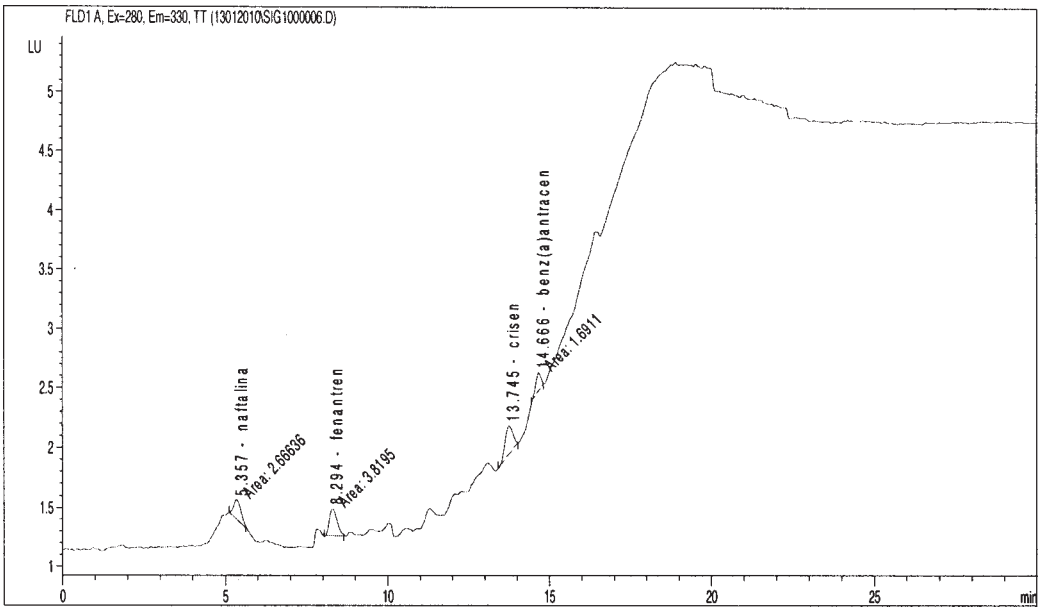

Fig. 3. The HPLC chromatogram obtained for the sample WAT

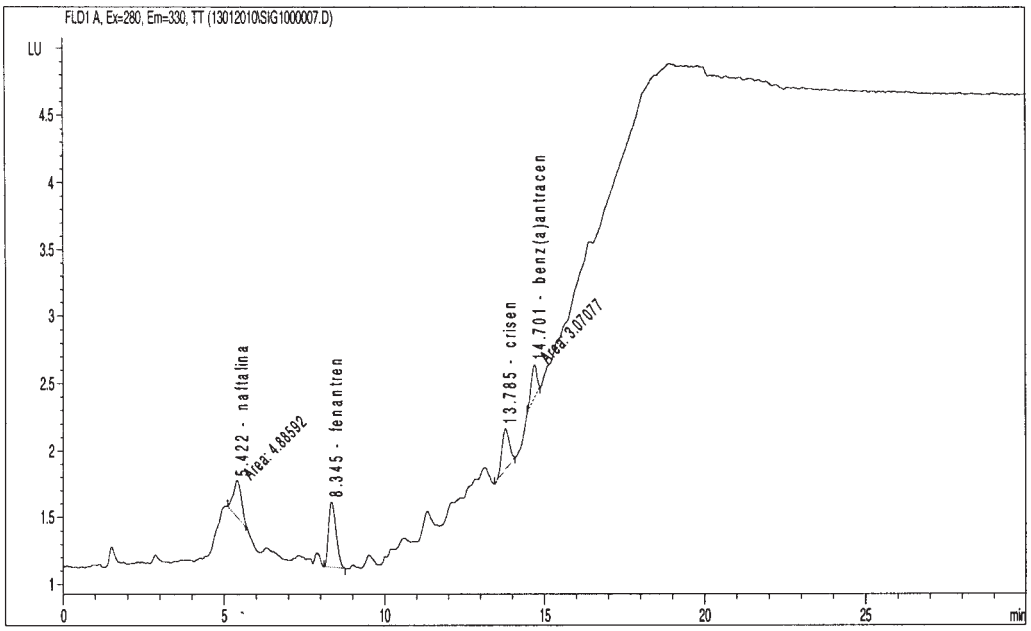

Fig. 4. The HPLC chromatogram obtained for the sample WA

In figures 3 and 4 there are presented the chromatograms of samples taken from deep sources: WA and WAT. In these samples there were determined 0.011 μg/L naphthalene, 0.004 μg/L phenantrene, 0.002 μg/L benzo (a) anthracene and 0.002 μg/L chrysene.

In the surface waters there is a larger amount of naphthalene by 21.4% compared with water depth, with 20% phenantrene and 66.6% chrysene.

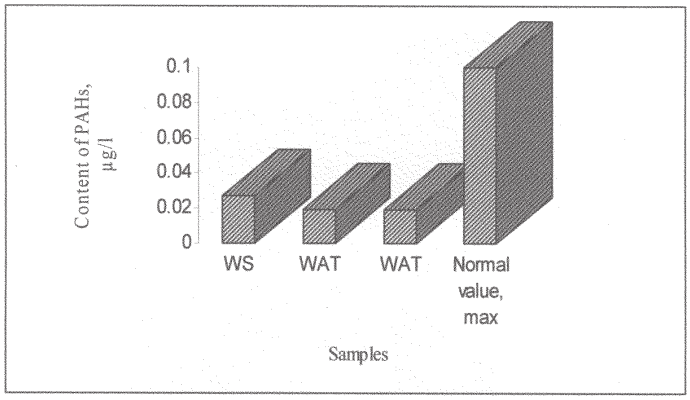

Fig. 5 The PAHs content of the analyzed samples in comparison with the normal values

The total content of PAHs in the analyzed samples was different. (fig. 5) The water samples taken from surface sources of the area surrounding the town of Targoviste had a contamination of 27% of the maximum value and water samples taken from the deep source of PAH content was 19% of the maximum.

The recommendation (2005/108/EC) issued by the European Commission stipulates that all Member States must do monitoring for PAHs in foodstuff. It aims to provide information on sources of environmental contamination of the food products with PAHs.

Conclusions

The presence of polycyclic aromatic hydrocarbons in the analyzed samples highlights their reduced degree of pollution. What is important is the fact that the benzo (a) pyrene has not been detected in none of the analyzed samples. The water from the analyzed surface sources had a higher content of PAH (0.027 µg/L) and that from the source depth was 0.019 µg/L, PAHs.

Even if a more obvious contamination in surface waters can be noticed, this does not raise problems in terms of toxicity, because the values are below the alert threshold provided by the European standards. Consequently, the waters from the town of Targoviste and its surrounding areas can be used both for the population and animal consumption.

Since the contaminated water may be a source of PAHs transmission to animals and implicitly to the food chain providing milk and meat for direct consumption or meat products, the level of pollutants in the monitored area should be lowered down.

Acknowledgements: This study was supported in part by Grant 5D43 TW00641 from the Fogarty International Center , National Institutes of Health , USA to Michigan State University, "The monitorising of the polycyclic aromatic hydrocarbons level in the food chain of meat products with a view to health risk assessment by the benchmark dose concept"Research has been done in collaboration with National Research and Development for Industrial Ecology – Bucharest (ECOIND).

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Manuscript received: 19.03.2010