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## PAHs in drinking water and contamination source of it

### ABSTRACT

*Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the environment and are part of numerous organic contaminants that are persistent in the environment. This study was undertaken to assess the identification and concentration of 15 PAHs in drinking water in different geographic regions of Albania. Another purpose is to explain the exposure of them to human health. There are thousands of PAH compounds in the environment but in practice PAH analysis is restricted to a few compounds as: Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, etc listed by US EPA as potentially toxic. This article describes a reproducible method according to EN ISO 17993:2003 for sample preparation and HPLC analysis of PAHs in water, fluorescence detection mode after liquid-liquid extraction for the determination of 15 selected PAH in drinking and ground water. All the results of the water samples are negative, it is not possible to detect these compounds.*

**Keywords:** *contamination, polycyclic aromatic hydrocarbons, drinking water, human health.*

### 1. INTRODUCTION

Polycyclic aromatic hydrocarbons are organic compounds that are mostly colorless, white, or pale yellow solids. PAHs, consist of hundreds of separate chemicals that occur together as mixtures. PAHs are naturally occurring and are concentrated by the burning of fossil fuels and the incomplete burning of carbon-containing materials (such as wood, tobacco, and coal). PAHs enter the environment through various routes and are usually found as a mixture containing two or more of these compounds whose sources include tire particles, leaking motor oil, vehicle exhaust, crumbling asphalt, atmospheric deposition, coal gasification, and parking lot sealants, as well as sources inside the home (such as tobacco smoke, wood fire smoke, grilling or charring meat) [1-7]. PAHs have complex chemical structures, so they do not break down easily and are persistent in the environment. PAHs are also commonly found in particulate matter of air pollution. PAHs tend to adhere to surfaces, attaching readily to sediment particles and leading to elevated concentrations in sediments [2].

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Some PAHs are known to be toxic to aquatic animals and humans. Generally, higher molecular weight PAHs tend to be more stable, persist in the environment longer, are less water soluble, and are more toxic. Exposure to UV light can increase toxicity of PAH compounds and increase toxicity to some aquatic species.

### 2. SCIENTIFIC STUDIES HAVE DOCUMENTED DETRIMENTAL IMPACTS FROM PAHs ON AQUATIC ORGANISMS

PAHs generally have a low degree of acute toxicity to humans, meaning harmful effects through a single or short-term exposure are minimal. Mammals absorb PAHs through inhalation, contact with skin, and ingestion [2,3]. The International Agency for Research on Cancer (IARC) classifies two PAHs as probable human carcinogens and three as possible human carcinogens. The US EPA classifies seven PAHs as probable human carcinogens. The IARC and EPA both classify benzo(a)pyrene and benz(a)anthracene as probable human carcinogens. Benzo(a)pyrene is often used as an environmental indicator for PAHs.

PAHs in streams and lakes are thought to rarely pose a human health risk via drinking water because of their tendency to attach to particles rather than dissolve in water. US EPA has a

maximum contaminant level (MCL) for PAH in drinking water of 0.2 ppb. Human health risks from consuming fish are thought to be low because PAHs do not readily bioaccumulate within vertebrates. Bivalve mollusks readily accumulate PAHs in their tissues, however[5]. PAHs enter water bodies through atmospheric deposition and direct releases of substances through petroleum spills and use, municipal wastewater treatment plants, industrial stormwater runoff, landfill leachate, and surface runoff. Many studies have been conducted recently regarding run off sources of PAHs. Rainfall runs off parking lot and road surfaces, transporting PAHs that originate from tire particles, leaking motor oil, vehicle exhaust,

crumbling asphalt, atmospheric deposition, coal gasification, and parking lot sealants. PAHs attach readily to sediment particles, leading to high concentrations in bottom sediments of water bodies. A literature review on tire wear particles in the environment indicates that the high aromatic (HA) oils generally used in tires contain PAHs. Zinc, PAHs, and a suite of other organic compounds (including phthalates, benzothiazole derivatives, phenolic derivatives, and fatty acids) found in tires are noted to likely cause toxicity in aquatic organisms. Because of this toxicity, the European Union has banned sales of tires that contain HA oils. This is estimated to reduce future PAH emissions from tires by 98 percent [4,1].

Table 1. Physico-chemical characteristics of PAHs

Tabela 1. Fizičko-hemijske karakteristike PAH

Component	Color	Melting point(°C)	Boiling point(°C)	Vapor pressure at (Pa ne 25°C)	Density	n-octanol: waterpartition coefficient (log K <sub>ow</sub> )	Water solubility at 25°C(ug/l)	Henry's low constant at 25°C(kpa)
Naphtalene	white	81	217.9	10.4	1.154	3.4	3.17X10 <sup>4</sup>	4.89x10 <sup>-2</sup>
Acenaphthylene		92-93		0.89	0.899	4.07		1.14x10 <sup>-3</sup>
Acenaphthene	white	95	279	0.29	1.024	3.92	3.93x10 <sup>3</sup>	1.48x10 <sup>-2</sup>
Fluorene	white	115-116	295	8.0x10 <sup>-2</sup>	1.203	4.18	1.98x10 <sup>3</sup>	1.01x10 <sup>-2</sup>
Anthracene	colorless	216.4	342	8.0x10 <sup>-4</sup>	1.283	4.5	73	7.3x10 <sup>-2</sup>
Fluoranthene	light yellow	108.8	375	1.2x10 <sup>-3</sup>	1.252	5.22	260	6.5x10 <sup>-4</sup>
Phenanthrene	colorless	100.5	340	1.6x10 <sup>-2</sup>	0.98	4.6	1.29x10 <sup>3</sup>	3.98x10 <sup>-3</sup>
Pyrene	colorless	150.4	393	6.0x10 <sup>-4</sup>	1.271	5.18	135	1.1x10 <sup>-3</sup>
Benzo a anthracene	colorless	160.7	400	2.8x10 <sup>-5</sup>	1.226	5.6	14	
Crysene	blue fluorescence	253.8	448	8.4x10 <sup>-5</sup>	1.274	5.91	2	
Benzo b Fluoranthene	colorless	168.3	481	6.7x10 <sup>-5</sup>		6.12	1.2	5.1x10 <sup>-5</sup>
Benzo k Fluoranthene	light yellow	215.7	480	1.3x10 <sup>-8</sup>	6.84	0.76	4.4x10 <sup>-5</sup>	
Benzo a pyrene	yellow	178.1	496	7.3x10 <sup>-7</sup>	1.351	6.5	3.8	3.4x10 <sup>-5</sup>
Benzo (ghi) perylene	light yellow-green	278.2	545	1.4x10 <sup>-8</sup>	1.329	7.1	0.26	2.7x10 <sup>-5</sup>
Indeno 123cd pyrene	yellow	163.6	536	1.3x10 <sup>-8</sup>		6.58	62	2.9x10 <sup>-5</sup>
Dibenzo ah anthracene	colorless	266.6	524	1.3x10 <sup>-8</sup>	1.282	6.5	0.5	7x10 <sup>-6</sup>

The general characteristics of PAHs are high melting and boiling points, low vapor pressure, and

very low aqueous solubility. The latter two characteristics tend to decrease with increasing

molecular weight, on the contrary, resistance to oxidation and reduction increases. Aqueous solubility of PAHs decreases for each additional ring. Meanwhile, PAHs are very soluble in organic solvents because they are highly lipophilic. PAHs also manifest various functions such as light sensitivity, heat resistance, conductivity; emit ability, corrosion resistance, and physiological action.

However, the general uses of some PAHs are:

- *Acenaphthene*: manufacture of pigments, dyes, plastics, pesticides and pharmaceuticals.
- *Anthracene*: diluent for wood preservatives and manufacture of dyes and pigments.
- *Fluoranthene*: manufacture of agrochemicals, dyes and pharmaceuticals.
- *Fluorene*: manufacture of pharmaceuticals, pigments, dyes, pesticides and thermoset plastic.
- *Phenanthrene*: manufacture of resins and pesticides.
- *Pyrene*: manufacture of pigments.

Other PAHs may be contained in asphalt used for the construction of roads, in addition to roofing tar. Furthermore, specific refined products, of precise PAHs, are used also in the field of electronics, functional plastics, and liquid crystals [7].

### 3. ANALYTICAL METHOD

A preconcentration step for sample enrichment may be necessary for the analysis of PAH levels in uncontaminated aqueous samples. It is very important the procedure of sampling different samples. The main steps of analyzing PAH compounds are: extraction, drying of the extract, enrichment, clean-up of the extract if it is necessary. After liquid/liquid extraction procedures (e.g. with dichloromethane) Detection is carried out by high-performance liquid chromatography with a fluorescence detector [7].

#### Reagents:

- *Extraction solvents*: Hexane, dichloromethane or other volatile solvents may be used as well, if it is proved that there is equivalent or better recovery.
- *Extraction clean-up solvents*: Hexane, dichloromethane, acetone, etc.
- *HPLC solvents if it is used this instrument*: acetonitrile, methanol, water, all of them HPLC grade.

#### Enrichment

Evaporate the dried dichloromethane extract with a rotary evaporator, bath temperature 40°C. Do not evaporate the extract to dryness, as losses of the 2-3 ring compounds may occur. Dilute the extract to a known volume with the same solvent that has been used for the preparation of the reference solutions. Transfer the enriched test sample, if necessary after filtration through a microfilter into a glass sample vial. Keep the extract in a cool and dark place until the analysis is carried out [7].

#### Calculation

Calculation of the concentration expressed in micrograms / l of the analyte  $\rho_i$  in the water sample:

$$\rho_i = \frac{(y_i - b_i) \cdot V_e}{a_i \cdot V_s} \quad (1)$$

$y_i$  - measured value of the analyte  $i$ , expressed as peak area

$a_i$  - is the slope of the calibration function of the analyte, for example expressed as peak area,

$b_i$  - intercepted calibration factor with ordinate, expressed as peak surface.

$V_e$  - The volume in ml of the extractant from which injection was made.

$V_s$  - volume in ml of the test sample.

#### Chromatographic operation

Parameter	Shimadzu Nexera X2
Solvents:	A:H <sub>2</sub> O, B: Acetonitrile
Column :	Inertsil ODS PAH, 4.6 × 250 mm, 5µm
Gradient:	0 min - 20 % B; 2min -25min - 100 % B, gradient ;25 min -30 min 20% B
Solvent flow :	1.2 mL/min
Injection volume:	5 µL
FLD:	programmed Ex/Em

### 4. RESULTS

In this study 15 samples of drinking water from different regions of Albania were analyzed. The samples are collected randomly. All the results of the water samples are negative, it is not possible to detect these compounds. Lack of PAHs in water samples may be due to low water solubility and their tendency to be absorbed in sediment, soil and air.

The main source of contamination of PAHs in drinking water is not usually the source of drinking water, but the layer of drinking water distribution pipes. At least in the past, the Coal Coat was a common coating material for water pipes used to provide effective corrosion protection.

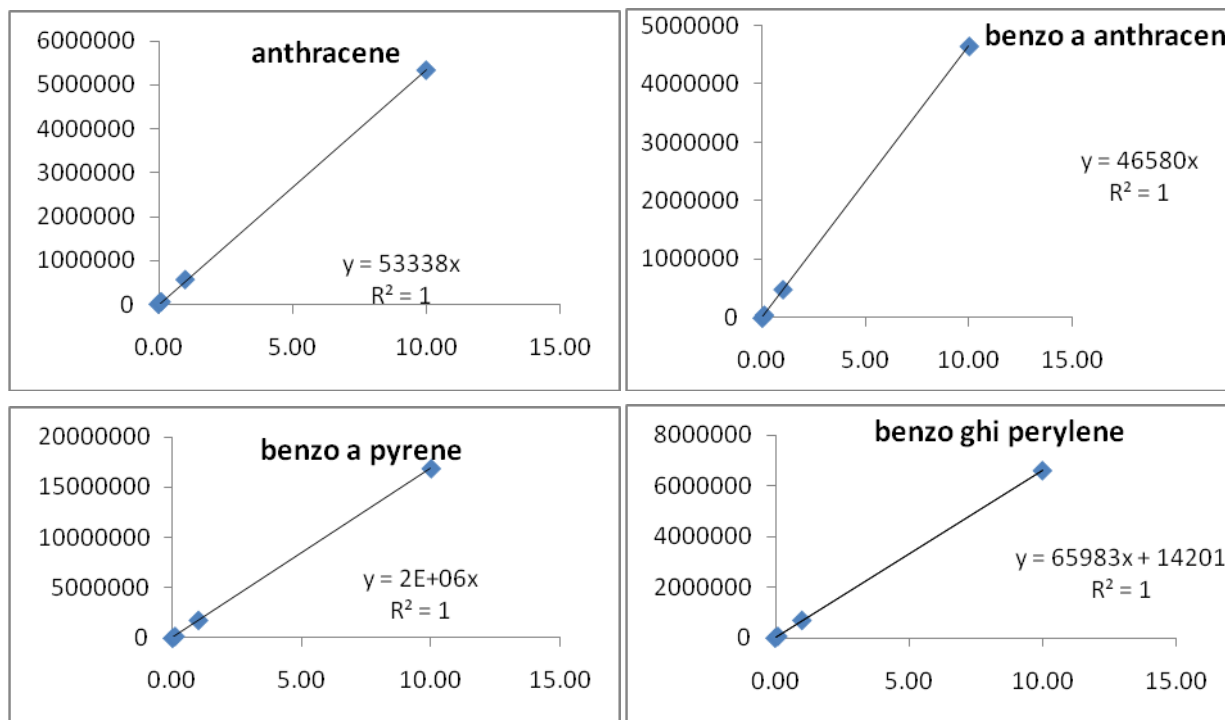


Figure 1. The calibration curve of some PAHs

Slika 1. Kalibraciona kriva nekih PAHs

Table 2. Retention time and concentration of PAH

Tabela 2. Vreme zadržavanja i koncentracija PAH

Component	Retention time	Concentration
Naphtalene	4.201	N.D
Acenaphthene	4.662	N.D
Fluorene	4.804	N.D
Anthracene	5.12	N.D
Fluoranthene	5.429	N.D
Phenanthrene	5.837	N.D
Pyrene	6.413	N.D
Benzo a anthracene	7.383	N.D
Crysene	7.921	N.D
Benzo b Fluoranthene	9.969	N.D
Benzo k Fluoranthene	11.238	N.D
Benzo a pyrene	12.896	N.D
Benzo (ghi) perylene	14.395	N.D
Dibenzo (a,h) anthracene	17.97	N.D
Indeno 123cd pyrene	19.179	N.D

5. CONCLUSIONS

PAHs are an important class of environmental contaminants because of their potentially adverse health effects. The main sources of exposure to

PAHs are from breathing contaminated air, eating contaminated food and drinking contaminated water. Water can become contaminated with PAHs from runoff in urban areas, waste water from certain industries and petroleum spills. [8] One of the main sources of PAHs contamination in drinking-water is the coating of the drinking-water distribution pipes. After the passage of drinking-water through those pipes or after repair work, significantly increased PAHs levels have been detected in the water.

In this study, all drinking water samples had a level of contamination of non-detectable PAHs by the methods used for their analysis.

It should be emphasized that the areas where the samples are taken are clean areas of industrial pollution, waste disposal, roads, etc.

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## IZVOD

### PAH U PIJAĆOJ VODI I IZVORI KONTAMINACIJE

*Polciklični aromatični ugljovodonici (PAHs) su prisutni u okruženju i deo su brojnih organskih zagađivača koji su uporni u životnoj sredini. Ova studija je preduzeta da bi se procenila identifikacija i koncentracija 15 PAH u pitkoj vodi u različitim geografskim regionima Albanije. Druga svrha studije je da se objasni njihov uticaj na ljudsko zdravlje. Postoje hiljade PAH jedinjenja u okruženju, ali u praksi PAH analiza je ograničena na nekoliko jedinjenja: Naftalen, Acenaphthilene, Acenaphene, Fluoren, Fenantren, Antracen, Fluoranten itd., koji su navedeni u US EPA kao potencijalno toksični. Ovaj članak opisuje ponovljivu metodu prema EN ISO 17993: 2003 za pripremu uzorka i HPLC analizu PAH u vodi, detekciju fluorescencije nakon ekstrakcije tečnosti i tečnosti za određivanje 15 odabranih PAH u pitkoj i podzemnoj vodi. Svi rezultati uzoraka vode su negativni, nije moguće otkriti ova jedinjenja.*

**Ključne reči:** kontaminacija, polciklični aromatični ugljovodonici, voda za piće, zdravlje ljudi.

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