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Residue Analysis of Some PAHs in Some Algerian Soil: A Preliminary Environmental Impact Assessment

Djellouli Hadja Mebarka (a) *, Safia Taleb (a), Abderazzek Benghalem (a), Pietro Tundo(b) Mohamed Tawfic Ahmed (c) ,), Mourad Arabi(d)

(a)*Laboratory of Materials and Catalysis, Faculty of Sciences, D. Liabès university , Site 1, BP 89, 22000 Sidi Bel-Abbès, Algeria.*
(b Dipartimento Scienze Ambientali, University Ca' Foscari, Venezia, Italy
(c) *Faculty of Agriculture, Suez Canal University, Ismailia, 41522, Egypt.*
(d) *National Institute of* Forest *Research*, BP 193, Ain-Dheb, Médéa, Algeria.

Abstract

Polycyclic Aromatic Hydrocarbons are among the most persistent pollutants in various environmental matrices including soil. Because of their considerable toxicity even at low concentrations, it is essential to detect them at such very low levels (about ng/Kg) and to quantify them with precision and reliability.

The objective of the present work is to determine residues of some PAHs in samples of superficial soil collected from a number of sites including the vicinity of an industrial park of a cement factory, rural soil, surrounding this industrial park, cereal grown soil close to the industrial park and also from urban ground in the north west of Algeria. A high resolution gas liquid chromatorgraph, coupled with high resolution mass spectroscopy (HRGC / HRMS) was used to measure PAH residues and their distribution in the soil.

Results show that all investigated soil samples are highly contaminated with PAH. The concentration of the PAHs varies between 24, 62704.10^4 and 1072, 45064. 10^4 ng/kg. Residues of the potentially carcinogenic PAH benzo [a] pyrene, were also detected in some of the soil samples.

Residues detected in the present study vary between 2,189.10^3 ng/kg and 506, 4848.10^3 whereas the value of Hazardous Substances Data Bank (HSDB) is approximately 2.10^3 ng/Kg.

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The present results indicated that soil samples examined in the present study are highly contaminated with PAHs compounds, posing potential toxicological risk, considering their carcinogenic and/or mutagenic properties.

Keywords: PAH; HRGC / HRMS; contaminated soil; North West Algerian Area.

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1. Introduction

Soil pollution presents a fundamental problems to human and environmental health. Sources of soil pollution are numerous and would include motor vehicles exhaust, particles emitted from the smokestacks, incinerators and open burning of solid waste. Polycyclic aromatic hydrocarbons are among the most hazardous contaminats of soil for their genotoxic [1], mutagen and carcinogenic toxicity [2, 3]. In addition, certain pollutants in the ground can penetrate to rach subterranean water, ending up in rivers and other surface waters bodies. Moreover, crops, including edible vegetables can absorb the contaminants from contaminated soil [4] hence, introducing these deleterious chemical contaminats to food chain, directly affecting consumers health [5].

The polycyclic aromatic hydrocarbons are organic compounds made up of several aromatic cycles (2 to 10) condensed. Among these polycyclic aromatic hydrocarbons, the American Environmental Agency (US-EPA) listed 16 molecules like "priority" pollutants presenting major environmental problems because of their toxicity such as: phenanthrene, anthracene, fluoranthene, pyrene, benzo(a) anthracene, chrysene, benzo(a)pyrene, benzo(ghi)perylene, indeno(1,2,3-cd)pyrene [6].

Except naphthalene, PAHs are not very volatile and are presented at the pure state in the form of solid or of more or less viscous liquid. The common characteristics of these compounds are boiling and raised melting points, a low solubility in water. The latter decreases when the molecular weight increases. These compounds are lipophilic and soluble in many organic solvents. Thus, they are potentially bio-cumulated and concentrated in the sediments and the soils. The persistence of PAHs increases with the number of cycles of the molecule. The principal risk that presents the polycyclic hydrocarbons aromatic on health, is their capacity to induce the development of cancer in the exposed living organisms like at the man. Indeed, benzopyrene is potentially carcinogenic [7, 8].

2. Objective of study

The objective of our study is to determine the concentration of PAHs in various samples of surface soil collected from near an industrial park of cement factory, a rural area, surrounding this industrial park, from cereal grown field distant from this industrial park and finally from soil of an urban area. Considering that the industrial park is the main source of emitting PaH, the soil sample collection sites were selected in order to find out the extent to which emitted PAHs would reach, along with their distribution in soil.

Analytical Method

The physicochemical methods of analysis used in our study are described by the Agency for Environment American [9]. It is based on an analysis by high-resolution Gaz Chromatography coupling high-resolution Mass Spectrometry and, in isotopic dilution after purification using various adsorbents. This technique provides a very high sensitivity,

± 0, 2 ng/kg.

3.1. Sampling

The samples of soils were taken in the bottles preserved at refrigerating temperature (lower to 5°C), safe from the light. These samples come from surface soils in the vicinity direct of the industrial park of cement factory, on the surface of a rural soil, surrounding this industrial park, and cereal agricultural soil distant from this industrial park and finally from an urban soil in north west of Algeria (Fig 1).

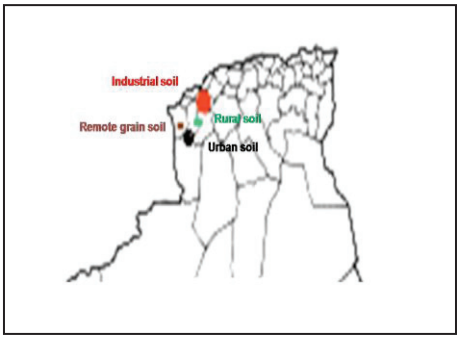

Fig. 1: Soil Sampling Sites, North West Algeria

3.2. Values of the white

The white of analysis was measured for the entirety of the phases of the method of analysis, of which the extraction, purification and the quantification.

3.3. Reagents and solvents used

The solvents (hexane, dichloromethane, toluene, nonane) used are of (picograde) purity grade. The anhydrous sodium sulfate Na_2SO_4 and neutral silica (200 - 400mesh) was used for the purification. Chemical standards were used in the analyzes in CG/FID and CG/SM. They contain 16 HAP standards and deutered like Acenaphtilene-D8, Benzo[e]pyrene-D12 with respective concentrations varying between 1 ng/µl^{-1} to 10 ng/µl^{-1}.

3.4. Soxhlet extraction

Soil sample were allowed to dry by passing through a drying oven for one hour at temperature of 70°C in order to eliminate water. Extraction is done in a Soxhlet, under heating and atmospheric pressure. The tube extractor of the Soxhlet apparatus was rinsed with solvent. For this purpose, 100 ml of toluene are carried to boiling, during one hour. Then, a mixture of 10 gr. of the sample and 04 gr. of the hydromatrix were placed in a thick paper cartridge to which one adds 10 µl standard interns (Intern Standard PAH:

50ng). The samples of the soil to be analyzed are extracted with 300 ml of toluene. The extract is then concentrated to be purified.

3.5. Clean up

A glass column packed with 06 gr. of neutral silica and 03 gr. of sodium sulfate was used for clean up. The concentrated extract with 1 ml is transferred in the column. The first elution is carried out with 25 ml of hexane. This fraction does not contain PAHs. The one second elution is carried out with 25 ml of mixture of 12, 5ml of hexane and 12,5ml of CH_2Cl_2 which underwent evaporation under nitrogen. To final, 10 µl of standard recovery PAH (1 ng) and 10 µl of nonane are added.

3.6. Analysis

The analysis was carried out by High-resolution Gas Chromatography coupled with High-resolution Mass Spectroscopy (HRCG/HRSM - Type HP 6890) in mode IE with 35 eV and with a resolution of 10,000 (5% valley). The carrier gas was helium (1.0 ml/min). The quantitative determination was performed by an isotope dilution method using the relative response factors previously obtained from three standard solution injections. All measurements were carried out in an accredited laboratory (Laboratorio Microinquinanti Organici – LECCE-Italy)

3. Results and discussion

The concentrations of HAPs obtained in various samples of the ground are shown in the Fig 2 and table1. Results indicated that the concentrations of PAHs vary between $24, 62704.10^4$ and $1072, 45064.10^4$ ng/kg. This shows that all investigated soil samples are strongly contaminated by PAHs, posing potential toxicological risk even to low concentrations, considering their carcinogenic and/or mutagen properties.

In fact, PAHs are not very biodegradable, which makes them persistent in the environment. Moreover, their hydrophobic character involving their bioconcentration in the food chain. However, the most studied molecule Polycyclic Aromatic Hydrocarbons is benzo[a]pyrene owing to the fact that it is potentially carcinogenic. In fact, recent studies publish a value of ubiquitaric concentration of 2.10^3ng/Kg [10, 11].

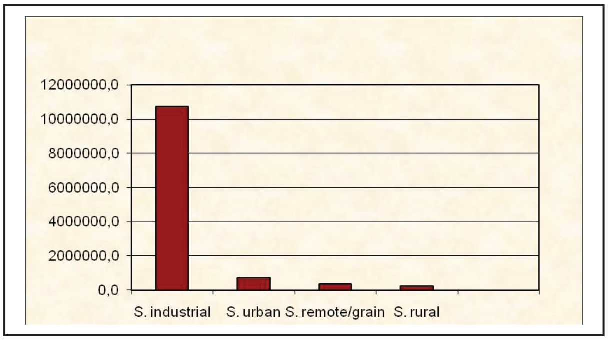

Fig. 2: Residues of PAHs (ng/Kg) in Algerian Soil Samples

However, concentration of residues detected have varied between $2,189.10^3$ and $506, 4848.10^3$ ng/kg, this show that the various samples of the soil analyzed are also contaminated by the benzo[a]pyrene. The concentrations of the benzo[a]pyrene are summarized in the Fig. 3 and table 1.

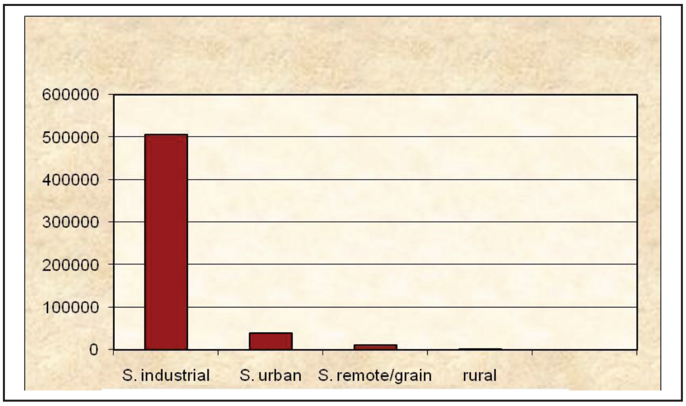

Fig. 3: Residues of Benzo[a]Pyrene (ng/Kg) in Algerian Soil Samples

In addition, we observed that the soil near the industrial park is very contaminated by these pollutants. This confirms that industry is one of the independent sources of PAHs.

Table1. Concentrations of total PAHs (ng/Kg) Detected in Samples of Algerian Soil

	Industrial soil	Urban soil	Cereal grown soil	Rural soil
Naphtalene	83.6	41.8	358.4	141.2
Acenaphthalene	133366.6	1619.3	732.1	<19.3
Acenaphtene	2252.4	<19.1	<19.1	1071.9
Fluorene	3634.6	750.5	1201.1	1623.0
Phenanthrene	399088.0	50721.3	40013.4	36726.7
Anthracene	251370.8	7533.3	3135.9	1493.5
Fluoranthene	2513462.4	139817.8	62424.2	33025.5
Pyrene	2342651.8	172504.5	132557.1	142276.8
Benzo[a]anthracene	1920015.6	110668.8	24556.1	5109.0
Chrysene	482928.0	49593.5	13833.2	4432.4
Benzo[b]fluoranthene	720570.2	50389.3	18713.5	3216.6
Benzo[k]fluoranthene	421556.4	32092.1	12408.2	1859.2
Benzo[a]pyrene	**506484.8**	**39921.1**	**11763.2**	**2189.0**
Indeno[1,2,3,cd]pyrene	345669.6	23848.5	19005.9	2827.0
Dibenzo[a,h]antracene	81331.8	5915.4	3693.9	1204.8
Benzo[g,h,i]perylene	280340.2	22637.4	17448.9	2550.0
Dibenzo[a,e]pyrene	195749.8	15678.1	12409.9	3385.9
Dibenzo[a,h]pyrene	91355.4	8988.2	8164.3	3137.9
Dibenzo[a,i]pyrene	19152.0	4996.9	3203.2	<192.9
Dibenzo[a,l]pyrene	13442.4	3884.2	<190.8	<192.9
ΣPAHs	**10724506.4**	**741602.1**	**385622.5**	**246270.4**

Recently, some studies showed that the soils constituted the principal environmental break point of PAHs. IWild and Jones [12] estimate that 90% of the PAH emitted in the environment are stored in the soils, this situation not taking into account the sites contaminated following industrial activities like the oil refineries. Indeed, these cement works are not far from one oil refinement. It is likely that the emission of sediments of the cement works is the privileged support of these PAHs. More problematic still, the agricultural cereal soil present an important concentration of PAH and benzopyrène with regard to the urban ground. Indeed, this cereal soil is also near a municipal discharge of household waste. This presents a risk for the contagion of grains. However because of their toxic character, it is necessary to supervise and limit this persistent pollution.

Conclusion

This study shows that the various samples of the soils analyzed are contaminated by Polycyclic Aromatic Hydrocarbons. In front of the importance of the risks met, it is necessary to lay down reduction objectives of the emissions of these pollutants in the interest of a sustainable environment.

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