

POLLUTION OF AGRICULTURAL LAND BY NAPHTHALENE OF ROADSIDE ORIGIN

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Abstract: The aim of this work is to study the mobility of polycyclic aromatic hydrocarbons, mainly naphthalene, in an agricultural soil in road environment. The recorded naphthalene concentrations in soil's surface horizons ($19.37 \pm 0.32 \text{ mg}\cdot\text{g}^{-1}$), allowed to highlight that the traffic and road's infrastructures are an important toxic source of naphthalene to the environment. This pollutant can disperse and fall dry or wet on the edges of the pavement, carried by storm water runoff into the ground. This naphthalene accumulation is influenced by the physical and chemical parameters of the soil (*pH*, cation exchange capacity, clays rate). High levels of naphthalene in soil were observed at low *pH* ($r = -0.25^{**}$), in contrast, soil cation exchange capacity (CEC) and the clays rate are positively correlated with these levels ($r = 0.20^*$ and $r = 0.17^{**}$).

Keywords: *Algeria, environment, naphthalene, PAHs, soil pollution, road traffic*

INTRODUCTION

Soil plays a vital role in the environment because it is at the interface with other media: atmosphere, biosphere, surface water and groundwater, basement.

The soil is used to overcome poverty and enhance food security. For this, a sustainable agriculture must be mainly linked to a better management of natural resources, especially agricultural soils. Thus, the different soil contaminations may pose to living beings not only a direct threat by ingestion, but also indirect hazards. Indeed, some chemicals in the soil are leached into groundwater and streams by runoff water. In addition, certain plants absorb contaminants from the soil hence entering the food chain [1].

Many researchers emphasize soil pollution by polycyclic aromatic hydrocarbons (PAHs) with their widespread distribution and biological effects, representing an important class of pollutants. According to Menzie *et al.* [2], PAHs are organic compounds whose ring structure has at least two aromatic rings. Sixteen PAHs are commonly analyzed in the different components of the environment, as recommended by the U.S. Environmental Agency (US EPA). Naphthalene is the lightest PAH; solid quite volatile, it is used as a moth repellent and present in high concentrations in creosote; it is well absorbed through the respiratory tract, skin and digestive system, its oxidation produces hydroxylated and dihydroxylated metabolites [3].

According to Bisson [4], approximately 89 % of naphthalene in the environment comes from incomplete combustion (pyrolysis), mainly from residential wood heating and from naphthalene sublimation used as mite repellent. About 10% of releases to the environment are due to coal production and distillation, while losses in the production of naphthalene represent less than 1 %. Tobacco smoke also releases small amounts of naphthalene. Almost all of the freed naphthalene disperses into the air.

Gasoline engines, diesel engines, slow cure asphalt, consumer products, and industrial sources are estimated to contribute 44, 9, 13, 15, and 19 % of the statewide total naphthalene emissions, respectively [5]. Gasoline is comprised of over 200 chemicals. Many of these are hazardous substances regulated in USA, such as: $\frac{3}{4}$ benzene (up to 5 %), $\frac{3}{4}$ toluene (up to 20 %), $\frac{3}{4}$ naphthalene (up to 2 %), $\frac{3}{4}$ trimethylbenzene (up to 5 %) and others [6]. The addition of 500 g of naphthalene per 10 liters of gasoline increases the fuel octane number by 3-4 units: 92th gasoline "turns" in the 95th. Once in benzene, naphthalene leaves a significant amount of carbon, increases the number of harmful exhaust gases. In addition, it crystallizes, clogs the fuel system, from fuel pump, hoses, and ending with injectors. Thus, there is significant uncertainty associated with naphthalene emission factors of gasoline and diesel vehicles. Emissions tend to vary with season due to changes in temperature and relative humidity, fuel composition, and vehicle fleet composition [7].

This study aims to determine whether there is a polycyclic aromatic hydrocarbons pollution of agricultural soils linked to road traffic in the region of Tiaret (Algeria).

MATERIAL AND METHODS

Selection of sampling sites

The study was conducted in Tiaret with the following geographical coordinates: 35°23'17" North, 1°19'22" East and a min. 970 m - max. 1,143 m - an area of 111.45 km², which is located in the northwest of Algeria between the Tell chain in the north and the Atlassian chain in the South, at an altitude of 980 m on average (Figure 1). The climate is semi-arid Mediterranean with an average annual rainfall of 400 mm/year. Prevailing winds are from the west and northwest, their average speeds range from 3 to 4 m·s⁻¹. Tiaret city has over 200 km urban road network.

In 2015, Tiaret's car park comprised 14,984 vehicles of all types including 49 % working on gasoline and 51 % on diesel oil. Indeed, this park is heterogeneous because of the variety of vehicles that constitute it (particular or utility vehicle, petrol or diesel, recent or old, etc).

Sampling

Twenty one samples were harvested from four different sites. The choice of the site was based on the nature of the site that is, an agricultural soil in the vicinity of either a national road NR 14 (near two different zones) or wilaya road W7 and the national road NR23 which was sampled from each site; five samples are at the edge of the road and a single sample away from the road to the W7 (to the witness), as shown in Figure 1.

The sampling was done randomly from the surface of the studied sites. It is important to note that the daily traffic recorded on Road No. 14 and No. 23 is, respectively, 600 and 800 vehicles per day [8].



Figure 1. Location of sampling points in the study area



Samples treatment

In the laboratory, samples were dried overnight in an oven (Memmert Model) at 40 °C, sieved (< 2 mm) and then ground. Some physico-chemical soil parameters, including pH, cation exchange capacity and particle size were determined by the usual methods. Samples must be collected in brown glass bottles and kept at 4 °C.

Extraction and purification

The analysis of the PAHs consists of filling the Soxhlet cartridge with 20 g of a mixture / sodium sulfate sample, in equal proportion, placing a glass wool plug on the sample and extracting it with a 50 / 50 mixtures of hexane and acetone (110 mL) for 8 hours.

The samples are then concentrated by a rotary evaporator (GFL Model) every day at 40 °C. The purification column is filled with 2.5 g of deactivated alumina by lightly tapping it and then by 1/2 cm³ of anhydrous sodium sulphate. This column is rinsed with about 5 mL of hexane. The meniscus of the solvent from the surface of the sodium sulfate will be mixed with 20 mL of hexane. After purification, the volume obtained is again mixed with about 12.5 mL of acetonitrile to be concentrated until the hexane disappears. The final volume is 5 ± 0.5 mL.

Then, it was transferred to a caliber of adequate volume (1 - 25 mL) and the tube was rinsed with a small amount of acetonitrile. A small amount of sample was placed in the 1.5 mL vial [9].

Analysis was performed by high performance liquid chromatography (HPLC) using C18 silica column chromatography. The conditions for dosing naphthalene are:

- temperature: 32 °C;
- flow rate: 1 mL·min⁻¹;
- injection: 10 µL;
- mobile phase: acetone and hexane / water;
- naphthalene retention time: 6.5 min.;
- fluorescence: excitation / emission: 213/329 nm;
- UV: 219 nm.

All reagents used were analytically pure and purchased from PHYWE Company (Germany).

RESULTS AND DISCUSSION

Naphthalene content in soil

Results presented in Table 1 summarize the naphthalene levels in soil bordering the pavement of three roads covered by this study. The sum of 16 PAHs in U.S. EPA (Σ16 HAP6) of an agricultural uncontaminated soil are generally between 1.6 and 76 ppm [10]. PAHs are produced by incomplete combustion of organic matter, recent or fossil. Their formation is mainly due to industrial activities [11] found in soils of brownfields in France a high dose of naphthalene from 23 to 46 mg·kg⁻¹ and concentrations of other PHAs varied between 16.1 and 10350 mg·kg⁻¹ PAHs. On the other hand, approximately 89 % of naphthalene in the environment comes from incomplete combustion (pyrolysis), mainly from residential wood heating and sublimation of naphthalene used

as a moths repellent, which explains the low dose of naphthalene in agricultural soils related to road traffic. Table 1 reveals a soil contamination by PAH ($19.6 \pm 0.74 \text{ mg}\cdot\text{g}^{-1}$) with a remarkable variability between sampling points, hence the recorded values of PAH greatly exceed the control value ($15.8 \text{ mg}\cdot\text{g}^{-1}$).

The low availability of PAHs is caused by sensitivity to light and degradation by different ways: abiotic pathways (volatilization, oxidation), biotic pathways (bacterial and fungal enzymatic degradation); for example, strains of *Pseudomonas*, *Sphingomonas*, *Alcaligenes*, *Comamonas* and *Rhodococcus* able of degrading naphthalene were isolated [12].

Table 1. Descriptive statistics of PAH concentrations ($\mu\text{g}\cdot\text{g}^{-1}$) in soil

	N	Mean \pm SD	Min	Max
PAH (naphthalene)	20	19.37 \pm 0.32	18.50	20
Control	1	15.80	-	-
Standard	1	1.60	-	-

Effect of physical and chemical factors of soil on naphthalene accumulation in soil

The size and structure of microbial communities in soil vary substantially depending on the physico-chemical characteristics of the soil itself. Biodegradation processes are complex phenomena resulting from interactions between the different components that directly influence the availability of PAHs. The impact of all these environmental factors ultimately results in the gradual dissipation of a fraction of the initial mixture of pollutants, the remaining fraction containing the most recalcitrant compounds to degradation [13]. In order to study these effects, we conducted a correlation analysis with an analysis of variance of these parameters. The accumulation of PAHs therefore depends on the clay content, resulting soil CEC, but also on the pH.

Effect of soil pH

The correlation is shown in Figure 2, on which a negative relation is observed ($r = -0.25^{**}$). On the other hand, analysis of variance indicates a significant effect ($p < 0,001$) of the pH on soil PAH.

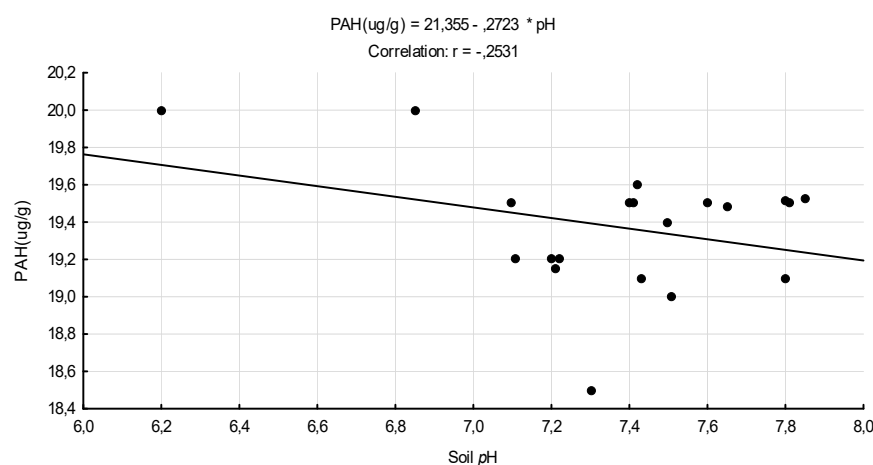


Figure 2. Correlation analysis between soil pH and naphthalene accumulation in soil

We observe that at low pH , different interpretations have been suggested to explain the influence of soil pH on the accumulation of PAHs. The majority of soil microorganisms can live in pH values ranging from 6.0 to 8.0. Biodegradation processes usually take place in pH range from 5.0 to 8.0, the optimum being considered between pH 6.5 and 8.5 [14]. Particularly for PAHs biodegradation, the optimum pH values were set between 7.0 and 7.8 [14, 15].

Knowledge of soil pH may also provide additional guidance on the bioavailability of inorganic nutrients. A decrease in pH in the rhizosphere, by the release of HCO_3^- or H^+ by the roots, promotes the absorption of phosphorus. The solubility of this element is maximal at a pH of 6.5, an alkalization of the environment which may cause the precipitation of calcium phosphate salts. In contrast, soil acidification causes the dissolution of iron and aluminum oxide that may precipitate later in the form of phosphate salts [16].

Finally, soil acidification alters the sorption forces between hydrophobic compounds such as PAHs and soil organic matter. When the pH decreases, the humic material undergoes protonation (H^+), causing a decrease in polarity. This results in a higher affinity for hydrophobic compounds such as PAHs [17]. The adsorption mechanism constituting a major decrease in the availability of PAHs in soil, therefore it tends to increase [18].

Effect of cation exchange capacity

Soil cation exchange capacity (CEC) is positively correlated with PAHs concentrations in soil ($r = 0.20^*$) as shown in Figure 3. Analysis of variance revealed a lightweight significant effect of this parameter for a significant threshold 10 % ($p < 0.086$).

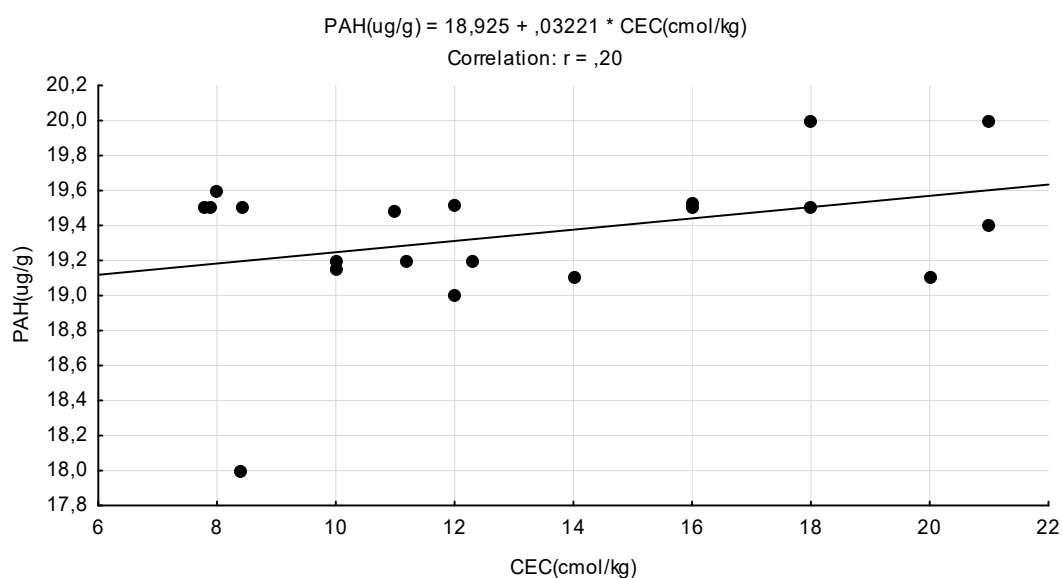


Figure 3. Correlation analysis between cation exchange capacity (CEC) and naphthalene accumulation in the soil

The cation exchange capacity is interdependent and largely determines the quantities of retained pollutants, including adsorption of pollutants that can be represented by the

CEC, which is the maximum amount of cations that the soil can hold by physico-chemical adsorption. The persistence of PAHs in soil depends on their ability to adsorb and desorb to the surfaces or interfaces of soil at the level of organic matter (OM). The latter is the main sorbent for PAHs in soil because of the many hydrophobic links that constitute it [19]. Studies on the sorption of PAHs in soils consider that it follows a linear model except in the case of OM-rich soils. The non-linearity could increase with the density of the OM. It seems that this deviation from the linearity is correlated with the atomic O / C ratio of soil OM. The linear sharing model considers the soil OM as a gel phase and amorphous and there is no limit to the number of sites available for sorption when the solute concentration increases [20]. The availability of PAHs also depends on their attachment to humic substances: a high molecular weight reduces the availability of pollutant by stabilization and formation of bound residues while a low molecular weight increases PAHs mobility. PAHs are found in small quantities available in the soil solution by their adsorption on surfaces and the formation of non-aqueous phases [21]. The presence of surfactants in the environment (from microorganisms or plants) facilitates the transport of PAHs from the solid phase to the aqueous phase [22]. In the long term, PAHs sequestered in soil particles evolve. Part of PAHs then are recalcitrant to biodegradation: PAHs are fixed on fine grained fractions of soil [23] inaccessible to microorganisms, thus limiting their desorption [24].

Clay's effect

Clays are characterized by a non-neutral electric surface, which determines their ion exchange capacity. These minerals have two types of charge.

The first, a negative sign, is structural and cannot be changed. It is linked to substitutions of Al^{3+} Si^{4+} or Mg^{2+} , Fe^{2+} , Al^{3+} in the clay sheets. The second, related to the chemical reactions that occur on the surface of minerals, is a surface charge variable depending on the medium pH. For a low pH, the H^+ ions bind to the majority of clay more than the OH^- ones. This result in an overall positive charge and clay is characterized by an anion exchange capacity. For high pH, OH^- dominant ions lead to opposite phenomenon, and clay develops a cation exchange capacity.

A positive relationship between the accumulation of PAHs in the soil and the rate of clays was observed; the more is this rate important, the more the CEC is also important, the more the soil has a high accumulating power. Figure 4 shows this relationship ($r = 0.17^{**}$).

Analysis of variance shows a highly significant effect on the correlation ($p < 0.001$). Indeed, the higher the clays are, the higher the CEC is and the higher soil accumulates PAHs.

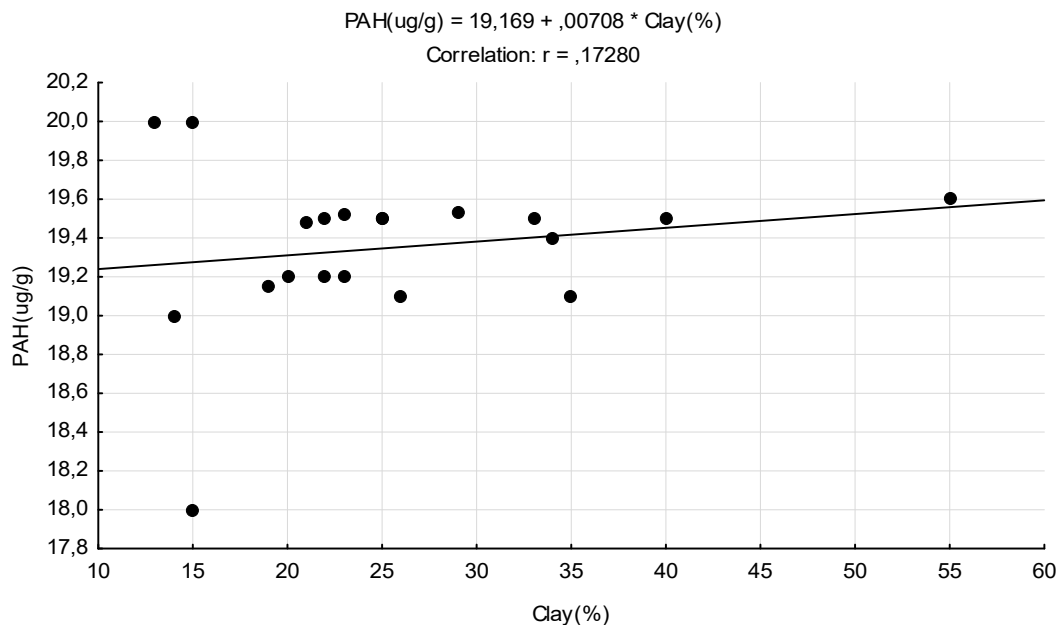


Figure 4. Correlation analysis between clays rate (%) and naphthalene accumulation in soil

Clay soils have an adsorption surface to PAHs greater than loamy or sandy soils, which can lead to bioavailability and reduced mineralization of contaminants. Most PAHs gradually migrate within microaggregated silts or clays whose size may be less than 20 microns [25]. The pore size of the fine soil particles is often less than the bacteria themselves that can not directly access the PAHs. Therefore, the degradation of pollutants depends on their distribution. The number of degrading bacteria may fluctuate with the water content of the soil, affecting the bioavailability of PAHs by salvation [15].

CONCLUSION

The main goal of this work is the study of the content and mobility of PAHs, mainly naphthalene, based on physico-chemical parameters of agricultural soil located near a road with high traffic pressure, contaminated with naphthalene. The experimental protocol consisted in the determination of PAHs concentrations in 21 soil samples. The results show that agricultural soils are contaminated with naphthalene and exceed the control levels. The accumulation of naphthalene in soil is influenced by physico-chemical parameters of the soil, such as soil pH, CEC and clays rate. At low pH, naphthalene ($r = -0.25^{**}$) is available, on the contrary, the soil CEC and the clays rate are positively correlated with the concentration of naphthalene in the soil ($r = 0.20^*$ and $r = 0.17^{**}$, respectively). Soils are not a final trap for this pollutant. During physico-chemical conditions change of the environment, naphthalene can be remobilized by various mechanisms, leading to contamination of groundwater or surface water.

Naphthalene present in runoff waters can migrate into the soil during the infiltration of the water and contributes to the degradation of soil quality; it may therefore reach the underground water and affect water resources.

Finally, this preliminary study shows that the different soil samples analyzed were contaminated with naphthalene. Given the importance of the risks encountered, it is necessary to set targets for reducing emissions of these pollutants in the interest of environmental sustainability.

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