



## Evaluation of organic pollution from leaching water of industrial wasteland: A Case Study for Kenadsa region (Algerian South West)

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### Abstract

Cessation of coal mining from the Kenadsa Coalfield (Algeria) resulted on the appearance of large contaminated surfaces left in a wasteland. Persistent Organic Pollutants (POPs) mainly characterized by priority Polycyclic Aromatic Hydrocarbons (PAHs) have never been addressed for Saharan soil. The objective of this study is to clearly identify and quantify the site pollutants; to better inform and envisage cleaning approaches that reduce potential adverse risks and impacts on the environment as part of a planned urbanization project. The organic matter of the contaminated soil of Kenadsa is characterized by gas chromatography coupled with mass spectrometry and  $\mu$ FTIR spectroscopy. The aromatic fraction is marked by a preponderance (85.1%) of aromatic hydrocarbons of low molecular weight (2-3 cycles). In addition, compounds containing more than four benzene units are hardly observed in the waters of the leaching. Among the lighter compounds, we identified a proportion of 13.7% oxygenated especially alkyl compounds dibenzofurans and 1.2% of aliphatic hydrocarbons. By spectrophotometry ( $\mu$ FTIR), saturated hydrocarbons are characterized by a smaller proportion of light n-alkanes. Polar compounds from waters of the leaching are dominated by oxygenated aromatic compounds. Overall, the results show that the Kenadsa site is much polluted with these aromatic hydrocarbons, essentially the PAHs.

**Keywords:** Contaminated soil, Leaching water, Organic pollution, Polycyclic Aromatic Hydrocarbons (PAHs), Environmental risk.

### 1. Introduction

Kenadsa coalfield is located in Algerian Southwestern. (Figure1)



**Figure 1:** Geographical situation Kenadsa (Algeria)

It is in 1918 that the mining operations commenced with the production of coal and metallurgical coke [1] whose volatile content accounted for 24%. A ferro-manganese industry arose near this industrial area. Over the subsequent years the soil has been increasingly contaminated with Polycyclic Aromatic Hydrocarbons (PAHs), the PAHs oxidation derivatives, heterocyclic, phenol, BTEX, aliphatic and polar hydrocarbons [2] and metals. Due to the volatility and toxicity of these pollutants, it is essential to foresee their future [3,4] to measure the risk of transportation to vulnerable targets such as water resources, ecosystems – leading to adverse impacts on human health.

The objective of this study is to present a detailed structural characterization of organic contamination of soil samples from the former coking plant Kenadsa (Saharan Algeria) with the aim to envisage a cleaning. In fact, several techniques are described, among them, the use of sewage sludges [5], or oxidative degradation [6] or by washing with a surfactant [7], for decreasing the risks and the possible impacts of this environmental pollution. One of the main difficulties in the study of organic contaminants is found in the wide variety of sources that generate them and their complexities. Moreover, the additional contribution of natural sources involves a composite residual organic mixture whose chemistry is difficult to decipher. When released into the environment, organic pollutants evolve according to their state (solid, liquid or gas) and speciation. While they undergo during their migration in the different compartments (air, water and soil) degradation processes [8] and operation [9-14]. They can be quickly assimilated by living organisms, partially degraded or, for stronger/resilient contaminants, accumulated in the soil.

The example of polycyclic aromatic hydrocarbons reflects the problems caused by organic contaminants:

- (1) They first have harmful properties of living organisms,
- (2) Sources are very diverse as they may be natural or anthropogenic.

The United States Environmental Protection Agency (U.S. EPA) conducted to the PAHs classification in the list of priority pollutants because of the persistent nature (POPs) and toxic to some of them (US-EPA 1985) [15] which can cause cell dysfunction [16] by binding to their metabolites in basic biological molecules such as proteins, RNA, DNA.

However, the "natural samples" used levied directly on site of the former coking plant Kenadsa (Algerian Sahara).

The goal of this study, characterization of these materials in contrast to studies targeting model systems (usually simplified and well characterized) requires performing fine characterizations in order to obtain the best possible knowledge of selected targets.

To investigate the very complex chemistry of organic matter, different characterization techniques were used to obtain a thorough knowledge of the environment. Chromatographic analyzes [17] were used for the molecular characterization of extractable organic fractions with coupled gas chromatography-mass spectrometry (GC-MS) [18] for the analysis of polycyclic aromatic hydrocarbons (PAHs) and spectroscopic techniques such as microscopy Fourier Transform Infrared ( $\mu$ FTIR) [19,20] for a characterization of the functional groups present in the extractable organic compounds.

## 2. Materials and methods

A sample of 5 kg of soil was collected from the Kenadsa site (Southern Algeria). The soil was dried by ventilation at 20°C, sieved to 30 mm and stored in the refrigerator. Sieving of a portion (3 kg  $\pm$  3%) of less than 30 mm fraction shows that it contains 30% (mass) of particles greater than 2 mm diameter, 20% of particles with diameters between 63 microns and 2 mm, and 50% of fine particles of diameter less than 63 microns. The determination of total organic carbon fraction shows that the soil contains 13% (by weight) of organic carbon. However, the sieve fraction, the determination of organic carbon gave a value of 1630 mg / kg.

### 2.1. Analytical

#### 2.1.1. Gas Chromatography (GC)

Aliphatic and aromatic hydrocarbons as well as polar compounds are analyzed by gas chromatography HP 5890 Serie II GC coupled to a HP 5972 mass spectrometer, using a splitless injector, a 60 m DB-5 J&W, 0.25 mm i.d, 0.1  $\mu$ m film fused silica column. The temperature program was 60 to 300°C at 3°C/min followed by an isothermal stage at 300°C for 15 min (constant helium flow of 1 ml/min).

Because of the presence of carboxylic acids in the polar fractions, silylation using BSTFA + TMCS (99/1) was carried out in order to improve the chromatographic resolution [21]. A small aliquot of sample (7 mg) is dissolved with the derivative solution at a 5 mg/ml concentration and treated during 15 minutes at 50°C. Then, 1  $\mu$ l of the solution is directly injected in the gas chromatograph.

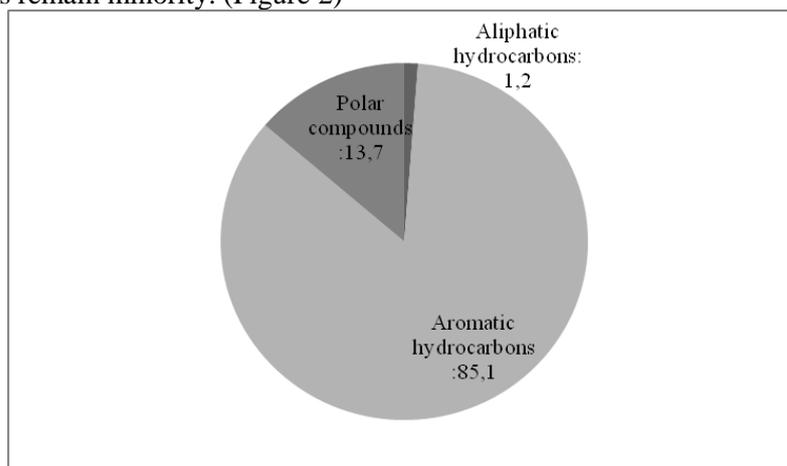
#### 2.1.2. Fourier Transform Infrared Microspectroscopy ( $\mu$ FTIR)

Aromatic hydrocarbons and polar compounds are analyzed by using a special sample preparation technique [22,23] avoiding drawbacks usually encountered when using bulk infrared on KBr pellets such as contamination by water adsorbed on the highly hygroscopic KBr [24]. Polar aliquots (m < 0.5 mg) are placed between the two diamond windows (2 mm diameter, 1 mm thickness) of a compression cell (7.5 cm X 5.1 cm, Spectra-Tech int.). After compression of the sample by screwing, the top window was removed. The visible light X 10 objective gives an enlarged image of the sample and allows the selection of the area to be analyzed. The micro-FTIR analysis was performed on a Bruker IFS-88 equinox

spectrometer coupled with a Bruker multipurpose infrared microscope which was fitted with a 250  $\mu\text{m}$  narrow band MCT detector cooled to 77K. The standard analytical conditions were X 15 infrared objective, 40-60  $\mu\text{m}$  diameter infrared spot, 60 scans (30 seconds), and spectral resolution of  $4\text{cm}^{-1}$ . Spectra are rationed to the background collected on a clean diamond window in the same analytical conditions. The assignments of the main I.R. bands are determined by reference to previous works [25, 26].

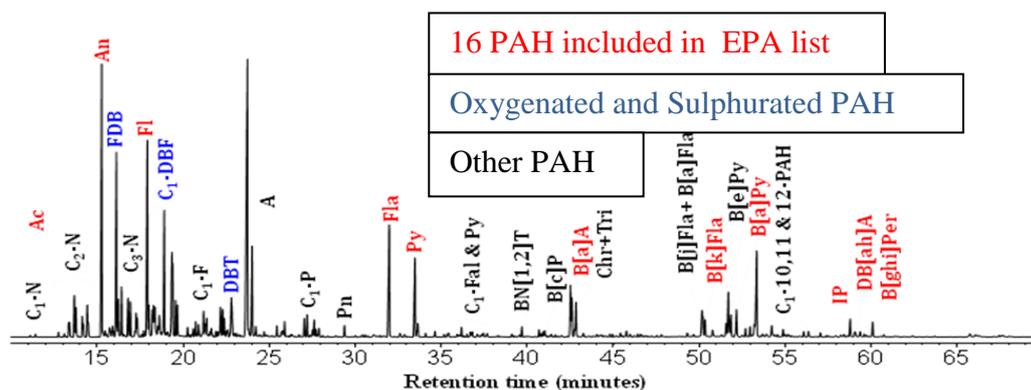
### 3. Results and discussion

The percentage of organic extract in the soil is about for 18%. The organic extract of the soil sample has a percentage of polar compounds raised (13.7%). and a higher proportion of aromatic hydrocarbons (85.1%). The aliphatic hydrocarbons remain minority. (Figure 2)



**Figure 2:** Different organic fractions extracted from crude polluted soil

The quantification by HPLC of the 16 PAHs pertaining to list of EPA present in organic extract of the soil show that the mass concentration of the 16 PAHs is of  $1220\text{ mg. kg}^{-1}$ . The content of benzene PAH with two cycles (figure 4) is weak as well for the soil samples. This characteristic is probably due to the loss evaporation of these light compounds at the time of the stages of re-concentration. The molecular distribution of the aromatic hydrocarbon polluted soil clearly shows that the presence of low molecular weight compounds is dominant (figure 3).



**Figure 3:** Chromatograms of the aromatic hydrocarbons (fullscan) from the gross polluted soil

It is among the latter a large proportion of aromatic hydrocarbons substituted. All time, the proportion of compounds of higher molecular weight is important.

The molecular distribution of aromatic hydrocarbons from Kenadsa polluted soil (figure 4) shows that the low molecular weight of PAHs (2 and 3 cycles) is much more abundant (11 priority PAHs). (Table1).

It is necessary to know that the molecules of weak molecular weight present a pointed toxicity whereas the molecules of high molecular weight show carcinogenic and bioaccumulation effects. [27].

There are no Algerian guidelines for organic pollution of soils. For objectives of cleanup in developed countries, Dutch repository is often used [28]. For the PAHs, three values are proposed in the Dutch guidelines of contaminated sites :

A =  $1\text{mg.kg}^{-1}$  is reference value

B = 20mg.kg<sup>-1</sup> is a high concentration which requires further investigation to determine the cause and importance of the pollution.

C = 200mg.kg<sup>-1</sup> represents an unacceptable contamination beyond which a risk to the ecosystem or human health is possible.

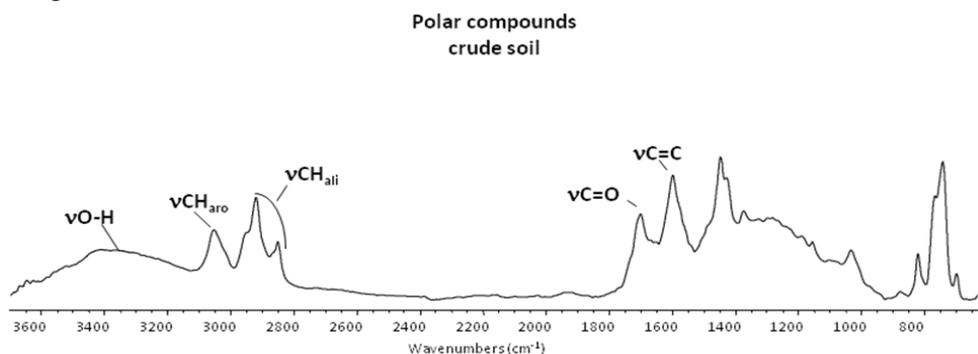
**Table 1:** Identification of the aromatic hydrocarbon chromatograms of figure 3.

Code*	Aromatic unit number	Compounds
N	2	Naphthalene
C <sub>i</sub> -N	2	Alkyl-naphthalene (i = substitution degree)
Can	2	Acenaphthylene
Ace	2	Acenaphthene
Fle	2	Fluorene
C <sub>1</sub> -Fl	2	Methyl-fluorene
DBF	2	Dibenzofuran
C <sub>1</sub> -DBF	2	Methyl-dibenzofuran
DBT	2	Dibenzothiophene
BN[1,2]T	3	Benzo(b)naphto(1,2-d)thiophene ?
Phe	3	Phenanthrene
Ant	3	Anthracene
C <sub>1</sub> -P	3	Methyl-phenanthrènes
CpP	3	Cyclopenta(def)phenanthrene
Pn	3	Naphthalene, 2-phenyl
Fla	4	Fluoranthene
Pyr	4	Pyrene
C1-5U-PAH	5	Methyl-5 aromatic unit PAH
IPY	6	Indeno[1,2,3-cd]pyrene

Code\*: abbreviation compounds

The PAHs content obtained is 1220mg. It represents 6 times the extreme value of the Dutch standards. Consequently, the site of the old Kenadsa cokeworks is strongly polluted. It can present a risk for the human health if this is not to clean up before build a future urban space.

There is, furthermore, also, an amount of least significant light aromatic and oxygenated hydrocarbons as nitrogen (in particular alkyl dibenzofurans). HAPs parent also shows a considerable ratio of toxic Ben[a]Pyrene. (Figure 4)



**Figure 4:** Polar compounds Infrared spectrum of the crude polluted soil

By Microspectrophotometry Infrared Fourier Transform analysis of aromatic hydrocarbons, it clearly appears from stretching bands associated with aliphatic C-H bonds ( $\nu_{C-H\text{ ali}}$ : 2920-2800 cm<sup>-1</sup> and  $\delta_{C-H\text{ ali}}$ : 1470-1440 cm<sup>-1</sup>) while those associated with aromatic C-H bonds are present in  $\nu_{C-H}$  (3100 - 3000 cm<sup>-1</sup>). We also note the band stretching vibration  $\nu_{C=C}$  (1650-1550 cm<sup>-1</sup>) and bands associated with oxygen function ( $\nu_{OH}$ : 3400 cm<sup>-1</sup> and  $\nu_{C=O}$  1690 cm<sup>-1</sup>). The high intensity of oxygen function ( $\nu_{C=O}$  and OH) shows the predominant presence of oxygenated aromatics. The spectrum is characterized by deformation vibrations  $\gamma_{C-H\text{ aro}}$  associated with two out of the plane and adjacent 2-3H and 4-5H suggest that the presence of polar compounds somewhat condensed, to 800 cm<sup>-1</sup>. (Figures 4 and 5).

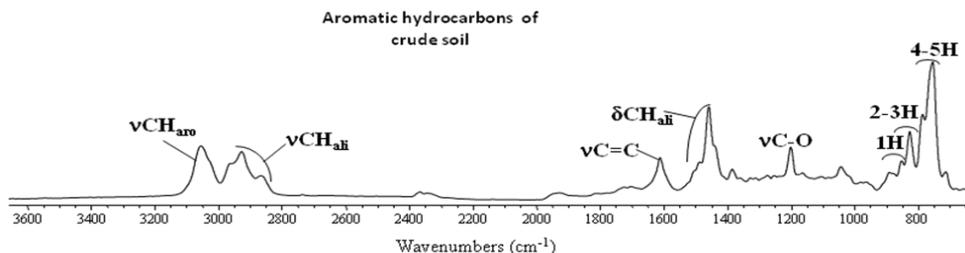


Figure 5 : Aromatic hydrocarbons Infrared spectrum of the crude polluted soil

## Conclusion

1. The molecular signature and spectroscopic results indicate that the organic geochemical raw soil shows dominance of PAHs but limited molecular weight (2 to 3 benzene rings mainly) and polar HAPs with the presence however of a more limited quantity of compounds of higher molecular weight. This preponderance of compounds of low molecular weight was also observed in the distribution of saturated hydrocarbons.
2. The predominance of low molecular weight compounds in polluted soil and the presence in the smaller proportion of compounds of higher molecular weight suggest that this signature is inherited; (i) by the presence of coal tar in soil (source compounds high molecular weight) and (ii) by the accumulation of the leaching of compounds from coal tar located outside the sampling region (source of low molecular weight compounds). It is important to remind toxicity of the molecules with weak molecular weight and carcinogenic and bioaccumulation effects of the molecules of high molecular weight.
3. Finally, the excessive quantity of the analyzed priority PAHs show that the site of the old Kenadsa cokeworks is strongly polluted according to the Dutch standards. The cleanup is essential before building a future urban space.

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