Evidence of Organic Contamination in Urban Soils of Cotonou Town (Benin)

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Research Article

ABSTRACT

In Cotonou (Benin), growth of the population leads to an excessive use of natural resources, inducing organic contaminations. Surface soils collected in the town, were extracted and fractionated by liquid chromatography in three families: aliphatic, aromatic hydrocarbons and polar fractions. Each fraction was characterized by gas chromatography-mass spectrometry. All the results show that an anthropogenic input exists (waste oils). Indeed, aliphatic hydrocarbons have specific markers emphasizing the presence of petrogenic products: UCM (unresolved complex mixture), specific distribution of pentacyclic triterpane. However, specific molecular biomarkers reveal also natural input. Nevertheless, samples from similar origins do not always have the same pattern. This fact underlines that organic sources are numerous in theses soils and imply a mixture of fingerprints. Moreover, modifications of the organic matter fingerprints with time (alteration, lixiviation…) complicate correlation between organic sources and contaminated soils.

Keywords: Soils; aliphatic hydrocarbons; polar fractions; biomarkers.

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1. INTRODUCTION

In Cotonou, the largest and most developed city of Benin, the population growth during the last decade (from 500.000 in 1992 to 1.400.000 in 2007), has induced the increase in urban activities especially transportation and industries (INSAE, 2008). These activities lead particularly to an increase in old second hand car (more than 240.000) and motorcycles (more than 90.000) numbers (Tractebel, 2000). As a consequence, the illegal marketing of petroleum products imported from Nigeria has significantly increased. This fuel is in general of poor quality as it is the result of different mixtures done by the dealers. Moreover, unofficial gasoline stations frequently exists along the streets of the town, leading to frequent leakages from tanks or tanker trucks and dump of waste petroleum by-products on soils. Despite the existence of regulations concerning liquid waste, they are disposed directly on soil. It is common for discharge on public streets and sidewalks surrounding oils drain, or oil from the repair of inoperative engines on site. This behavior contributes actively to soil and groundwater pollution in the study area. Soclo et al. (2000) have shown sediment contaminations in the harbour of Cotonou and its lagoon by hydrocarbon by-products (petroleum trade along the lagoon and road and waste oils dumped from mechanics shops).

Several authors have also documented the effect of such contaminations on the environment: human, aquatic life, crop and soils (Xin-ming et al., 2002; Shailaja and D'Silva, 2003; Gasca et al., 2005). In case of the Nokoué Lake, located in the north of Cotonou, Tossou (2000) had showed that the halieutic products contain rather important hydrocarbons total contents, inherited from direct discharge of the petroleum by-products in the lake.

In Cotonou, very few works describe the level of organic contamination of soil. However the knowledge of soil pollution in the town is very important. Soils are essentially in sandy material with little organic matter and this material is widely used in south of Benin for filling wetlands. Using this type of soil allows us to track contamination by organic products. We used the approach of organic geochemistry (molecular characterization: Faure (1999); Faure et al., (2000); Faure et al., (2004); Jeanneau, et al., (2007); Bloundi et al., (2008) to assess the degree of contamination of soils and also to specify the sources of contamination in the town. A molecular characterisation is performed specially for n-alkanes and pentacyclic tripertanes. Such molecular families were already used to track by-product petroleum contamination in lake and river sediments (Faure et al., 2000).

2. MATERIALS AND METHODS

2.1 Sampling

The sampling area (the town of Cotonou) is 67.50 km^2. The soils in the city of Cotonou are not the ones from the local ground. These are banking soils taken from the multiple yellow sand pits which can be found almost everywhere in the coastal area of Benin. In the surface (0–5 cm) yellow sand, the water pH was 4.5. The inorganic fraction of the yellow sand contained a very low proportion of silt (2.6%) compared to the sand proportion (97.4%). Mean carbon and nitrogen contents were of 8.0 mg C g^{-1} soil and 0.8 mg N g^{-1} soil, respectively. Three types of sites were selected for samples collecting. The yellow sands career was selected as a reference sites (soil regarded as a non-contaminated soil). These reference sites are free of building sites and are sometimes covered with vegetation. The second type of sites is located along roadside (named "road soils"). These soils are generally subject to a variety of activities: traffic, the sale of goods of all kinds including

foods. The third is specific to anthropogenic activities sites (named "specific soils") such as mechanics, carpentry workshops and petroleum products handling facilities. Twenty three (23) surface soils sample (0-5 cm depth) were collected throughout the town in December 2005 (Fig. 1). Theirs descriptions were summarized in Table1. Soil samples were kept in polyethylene plastic bag at 4ºC and then freezed before analysis. For each sample, the total organic carbon (TOC) was carried out by dry combustion in an induction furnace at a temperature of 1200ºC (analyzer LECO CS 125).
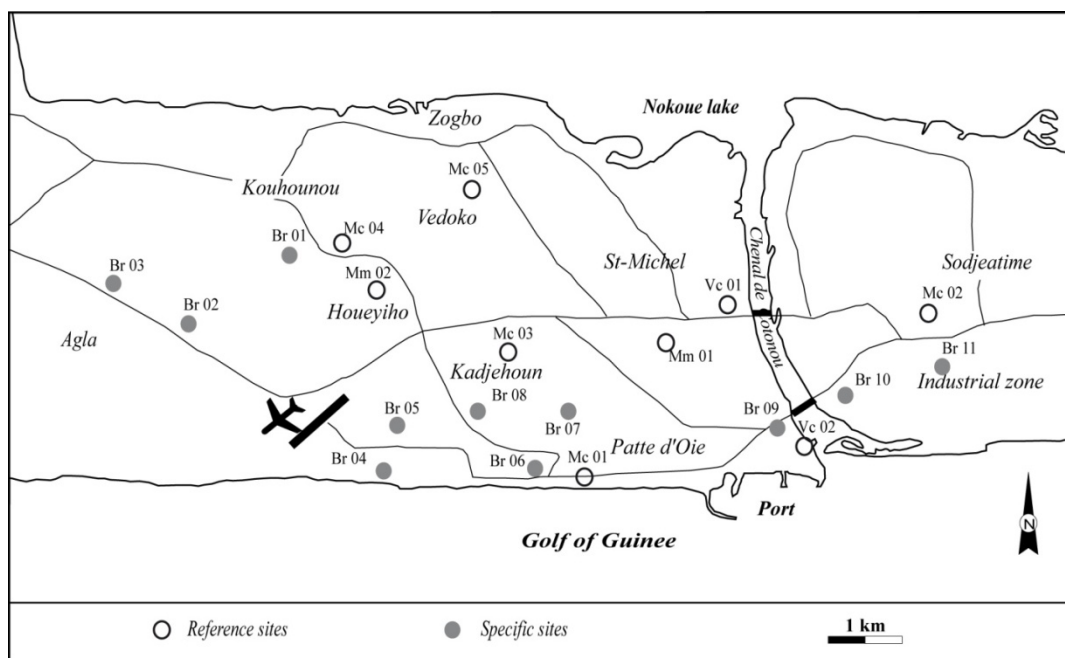

Fig. 1. Samples sites collation in Cotonou
(reference sites are located outside the town)

2.2 Extraction of Organic Fractions

The extractable organic matter (EOM) was isolated from soils with an accelerated solvent extractor (ASE 200 Dionex) using dichloromethane, by reference to the method of Jardé, (2002), modified. The conditions of extraction by ASE were 100ºC, 130 bars, 5-mn heat-up time, two cycles of 5-mn static time, 150% flush, 100 seconds purge with nitrogen. The EOM was then concentrated and evaporated to dryness under nitrogen in order to determine the EOM amount. A liquid chromatography on alumina and silica column was carried out so as to isolate aliphatic hydrocarbons from the EOM (Behar et al., 1992, Faure et al., 2000). At first, the EOM was diluted with dichloromethane and then transferred to the top of the micro-column of activated alumina; elution of hydrocarbon fraction (aliphatic + aromatic) and low polar compound were carried out using dichloromethane. High molecular weight and polar compound were covered with a mixture of dichloromethane and methanol (1/1). Then aliphatic, aromatic and polar fractions were isolated by liquid chromatography on an activated silica column with successive elution by *n*-pentane, a mixture of *n*-pentane and dichloromethane (2/1), and a mixture of methanol and dichloromethane (1/1), respectively.

Table 1. Sample description

Samples	Site location	Colour of samples	Level of traffic
Reference soils			
Ref 01	Yellow sand pit + vegetation	Light beige	-
Ref 02	Yellow sand pit	Light beige	-
Ref 03	Yellow sand pit	Ochre	-
Road soils			
Br 01	Round point	Light beige	dense
Br 02	Round point	Light brown	middle
Br 03	Residential	Light brown	middle
Br 04	Residential	Light beige	middle to dense
Br 05	Residential	Light beige	middle
Br 06	Administrative zone	Light beige	middle
Br 07	Administrative zone	Light beige	dense in a week
Br 08	Administrative zone	Light beige	dense in a week
Br 09	Residential zone	Light beige	dense
Br 10	Administrative zone	Light beige	dense in a week
Br 011	Industrial zone	Light beige	middle in a week
Specific soils			
Vc 01	Near petroleum products sellers	Black	Dense
Vc 02	Near petroleum products sellers	Black	Dense
Mm 01	Joinery	Light beige	Dense
Mm 02	Joinery	Light beige	Dense
Mc 01	Mechanics workshop	Black	Dense
Mc 02	Mechanics workshop	Black	Dense
Mc 03	Mechanics workshop	Black	Dense
Mc 04	Mechanics workshop	Black	Dense
Mc 05	Mechanics workshop	Dark beige	Dense

2.3 Gas Chromatography-mass Spectrometry (GC-MS)

Aliphatic hydrocarbons and polar compound were analysed by gas chromatography-mass spectrometry (HP 5890 series II GC coupled to HP 5972 mass spectrometer) with 60 m DB-5 J&W, 0,25 mm i.d; 0,1µm film, fused silica column. The even temperature program was the following: from 70ºC to 130ºC at 15ºCmin^{-1}, then from 130ºC to 315ºC at 3ºCmin^{-1} and then a 15 min hold at 315ºC. The carrier gas used was helium at 1.4 mL.min^{-1} constant flow. For polar compound analysis, a preliminary silylation was done using BSTFA [N,O-bis (trimethylsilyl) trifluoroacetamude], (Wenclawiak et al., 1993) before injection in the chromatograph.

2.4 Quality Control and Assurance

Extraction: In order to evaluate the possible artificial contamination and loss during the pretreatment including extraction, separation and purification, solvent blanks are carried out at the same time with similar methods as soil samples.

Chromatography: Prior to molecular analyses and regularly (every ten injections), an *n*-alkane standard solution (C_{10}–C_{40}, Multistate hydrocarbon from Accu Standard) was injected

in the GC-MS in order to control the quality of the chromatographic analysis (separation quality, retention time repeatability, low molecular over heavy molecular abundance ratio). Biomarkers (n-alkanes and pentacyclic triterpanes) were identified by examination of their mass spectra and their respective distributions and by comparison with published data (Philp, 1985; Peters and Moldowan, 1993).

3. RESULTS AND DISCUSSION

3.1 TOC, EOM, Aliphatic Hydrocarbons and Polar Compound Quantification

The total organic carbon (TOC) of the 23 soils varies from 0.08 to 7.89% (Table 2). As suspected, reference soils exhibits low TOC value, accepted Ref 01. Indeed, this sample was collected in a high vegetation zone, explaining an elevated TOC (high content of root).

Table 2. Total organic carbon (% of dry soil), OEM (mg/g of dry soil) and aliphatic hydrocarbon proportion (% of OEM)

Samples	TOC (% of dry soil)	EOM (mg/g of dry soil)	Aliphatic hydrocarbons (% of EOM)
Reference soils			
Ref 01	0.57	0.27	8.51
Ref 02	0.08	0.03	21.70
Ref 03	0.09	0.06	17.93
Road soils			
Br 01	0.37	1.83	51.72
Br 02	0.67	8.40	32.90
Br 03	0.50	1.81	51.21
Br 04	0.38	0.33	45.53
Br 05	0.35	1.01	37.71
Br 06	0.62	0.64	44.34
Br 07	0.35	0.83	46.54
Br 08	0.27	1.01	46.91
Br 09	0.37	0.58	47.70
Br 10	0.52	0.87	50.67
Br 11	0.34	1.74	51.80
Specific soils			
Vc 01	0.87	40.44	53.31
Vc 02	2.44	0.42	31.56
Mm 01	2.31	0.16	21.81
Mm 02	2.34	23.08	52.82
Mc 01	7.89	12.43	20.56
Mc 02	2.28	29.18	21.85
Mc 03	0.56	19.47	50.43
Mc 04	2.44	23.08	47.72
Mc 05	0.38	1.41	48.41

Reference soils have very low TOC compared to road soils, which have from 0.27 to 0.67% of TOC. The highest values were obtained for the specific anthropogenic activity samples. Compare to other samples: example of Nador lagoon sediment in Morocco (Bloundi et al., 2008), yellow sand samples are very poor in TOC content. This low level of TOC, justify both their use as reference soils and the analytical method used.

The extractable organic matter (EOM) values vary from 0.03 mg/g at 40.44 mg/g of soil (Table 2). Reference samples are characterized by very low EOM values. Road soils show slightly higher values than the previous ones. In this group, Br 02 is noted for its EOM value particularly high (8.40 mg/g of soil). Specific activities sites soils show the highest EOM contents. Only Vc 02, Mm 01 and Mc 05 seem atypical, since their EOM values are much lower, respectively 0.42, 0.16 and 0.14 mg/g of soil.

For most of samples collected at roadside and those of specific activities sites, the rate of aliphatic hydrocarbons represents an average of 50% of EOM. Reference soils have the lowest rates. Among specific activities sites samples with the same origin, a difference appears sometimes in the rate of aliphatic fraction. For example samples taken at the level of mechanics workshops, samples Mc 01 and Mc 02 show rates lower than 22% compared with others who have an average of 50%. Vc 02 and Vc 01, shows respectively 31.56 and 53.31% of aliphatic hydrocarbons. Mm 02 shows a rate (52.82%), which is more than double of that of Mm 01 (21.81%).

3.2 Characterisation of Aliphatic Hydrocarbons

Two families of biomarker were considered within the framework of this work: *n*-alkanes and pentacyclic triterpanes. *n*-Alkanes are synthesized by living organisms but also result from anthropogenic contribution (industrial discharge, wastewaters, oil product). The analysis of their distribution allows distinguishing the various sources of organic matter (Faure, 1999; Faure et al., 2000; Jeanneau et al., 2006; Bloundi et al., 2008).

The aliphatic hydrocarbons of the different soils have been analyzed at the molecular level. The Fig. 2 shows different representative distributions of aliphatic hydrocarbons of soils (reference soils, road soils and specific soils). Aliphatic hydrocarbons of reference soils contain n-alkane only. Specific soils and road soils are characterized by the predominance of *n*-alkanes, pentacyclic triterpane and a high molecular weight unresolved complex mixture (UCM). Moreover, some of soils present another unresolved complex mixture within low molecular weight (Br 08, Br 017).

The chromatographic patterns based on *n*-alkane distributions in the C_{16}-C_{34} range in road soils and specific soils showed four groups (Fig. 3). The first one (Br 08) is characterized by the predominance of low molecular weight *n*-alkanes, The second chromatogram (Br 06) shows the predominance of intermediate molecular weight *n*-alkanes. The third (Vc 02) does not show a particular tendency. The fourth tendency (Mc 05) shows the predominance of high molecular weight *n*-alkanes. These tendencies can be inherited by a progressive evolution of the biodegradation level of n-alkanes in soil taken in the town of Cotonou.

Reference soils chromatograms are without UCM and characterized by the predominance of odd over even *n*-alkanes of high molecular weight (Ref 01) and even over odd *n*-alkanes of low molecular weight (Ref 03). The UCM correspond to a mixture of iso-and cyclo-alkanes which cannot be resolved with traditional chromatographic columns (Gough and Rowland, 1990); they are generally associated with distillated petroleum product (lubricant, road asphalts) (Jarde, 2002).
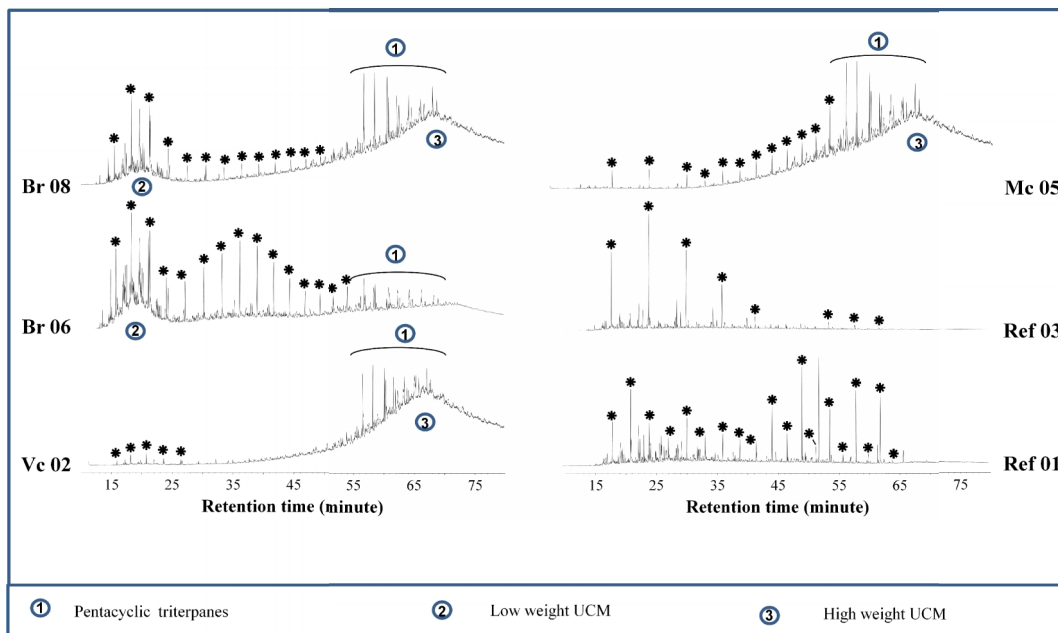

Fig. 2. Molecular distribution of aliphatic hydrocarbons (full scan).
Case of Br 08, Br 06, (road soils); Vc 02, Mc 05 (specific soils); Ref 03 and Ref 01 (Reference soils)

3.3 Pentacyclic Triterpanes

Pentacyclic triterpanes (m/z=191) are biomarkers frequently used by petroleum geochemists to evaluate the thermal maturity of sedimentary organic matter and carry out oil – source rock correlation (Ourisson et al., 1982; Volkman et al., 1997). Within the framework of this study and except of reference soil (reference soil with vegetation), the distribution of the pentacyclic triterpanes (Fig. 4) is similar for all the samples and is marked by the predominance of thermal isomers in $\alpha\beta$ conformation. Such distribution is characteristic of the contribution of thermal mature organic matter: it reveals a contamination by petroleum products: crude oils and especially petroleum by-products (Durand et al., 2004; Volkman et al., 1997).

3.4 Sources Identification by Molecular Indices

Based on the distribution of *n*-alkanes and pentacyclic triterpanes, some indices generally used in organic geochemistry were calculated. Table 3 shows the result for each sample. The carbon preference index (CPI) calculated on *n*-alkanes has been studied in order to establish the difference between natural and petrogenic aliphatic hydrocarbons (Faure et al., 2000). It is considered as a scale between petrogenic input, values close to 1 and natural

inputs, values higher than 4 (Giger et al., 1974). The odd-even predominance (OEP) underlines the occurrence of odd *n*-alkane over even *n*-alkane in the C_{16}-C_{20} range (Scalan et al. and Smith, 1970). The ratio of the peak areas of pentacyclic triterpanes/*n*-alkanes, draws the occurrence of pentacyclic triterpanes (hopane) compared to the resolved n-alkanes and the ratio of the peak areas of low molecular weight UCM / high molecular weight UCM (LMW UCM / HMW UCM), underline the occurrence of low molecular weight UCM compared to high molecular weight UCM. These ratios are used to appreciate the aliphatic fraction of the three groups of samples (reference soils, road soils and specific activities soils) and to draw the anthropogenic impact.
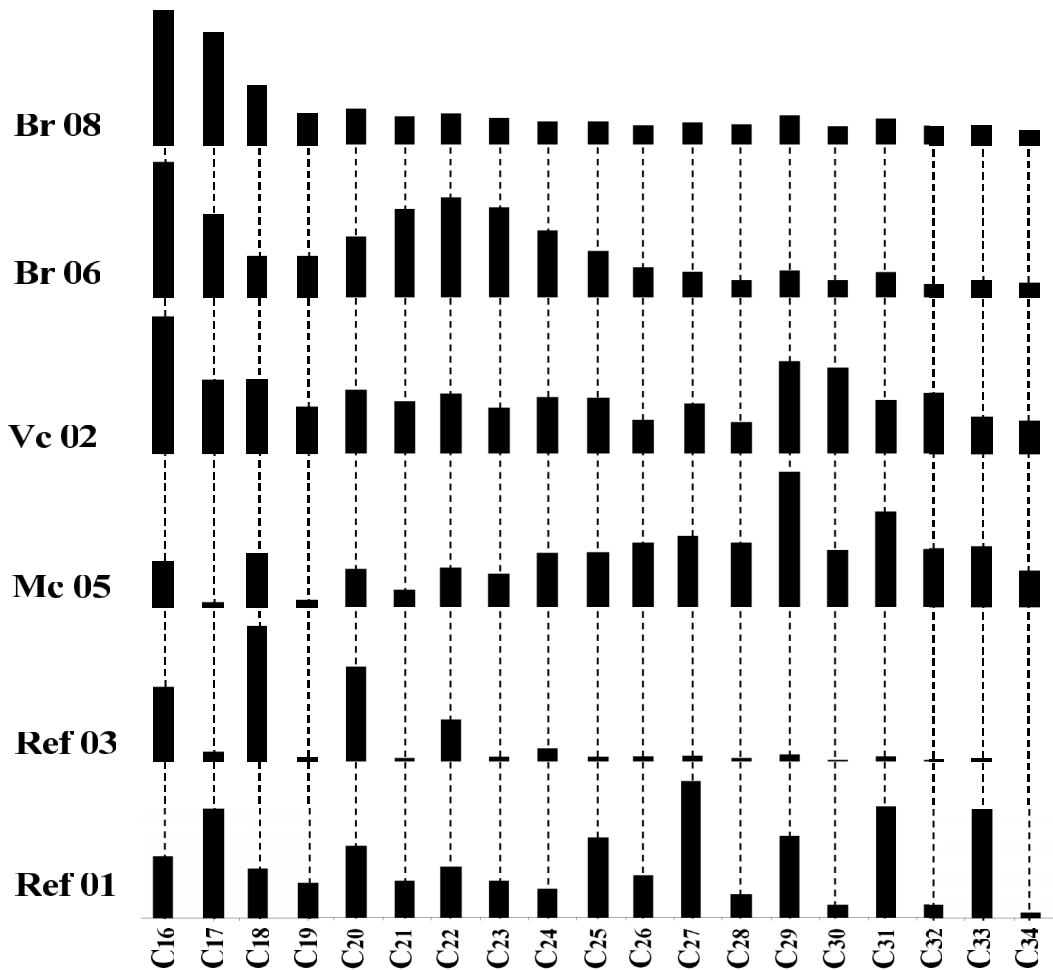

Fig. 3. *n*-Alkane distribution.
Case of Br 08, Br 06 (road soils); Vc 02, Mc 05 (spécific soils); Ref 03 and Ref 01 (reference soils)

Different indices calculated reveal some particularities for reference soils and Mc 05 samples. Samples Ref 02, Ref 03 and Mc 05 show high OEP (16), between 10 and 32 and a low ratio of pentacyclic tripertanes/n-alkanes. The preponderance of even n-alkanes in the C_{16}-C_{20} range is relatively unusual in sediments. Wang et al. (2010) had observed the same *n*-alkanes distribution in lacustrine sediment in Linxia basin. This even preponderance of *n*-alkanes in the C_{16}-C_{20} range can be due to (i) special redox conditions (reduction of alkanoic

acids with initial even carbon number the aliphatic chain either to preservation of initial n-alkanes with even carbon number), or (ii) to an interaction with mineral phases (in carbonated sediment, alkanoic acids is converted to n-alkanes with conservation of the initial chain length). However, whatever their origin, n-alkanes with even carbon number in the C_{16}-C_{20} range is characteristic of the sand used to fill sites in Cotonou, this explains the signature of Mc 05 sample. The sample Ref 01 is characterized by the highest CPI (4.94). This value is generally inherited from the important contribution of higher plants, especially in epicuticular waxes (Tissot and Welte, 1984; Zhu et al., 2005). During the soil sampling, reference sample Ref 01, was taken from the top of soil horizon under the vegetation. The typical signature "higher plants" seems therefore consistent with the sample. In addition, the even carbon predominance in n-alkanes in the range C_{16} - C_{20} is probably hidden in the Ref 01 sample by the intense bacterial activity, leading to (i) a preferential production of odd *n*-alkanes in the range C_{15}-C_{23} and (ii) a consummation of initial n-alkanes. However, the predominance of the odd carbon numbers in the range of C_{27}–C_{35}, with a maximum value at C_{29}, in the sample MC 05 is typical of terrestrial plant waxes (Elias et al., 1997; Wang et al., 2010, de Souza et al., 2011). However, the occurrence of UCM in the sample Mc 05 proves that the sample was also contaminated with petroleum products from motorcycle engine repair (unique activity performed on this site).
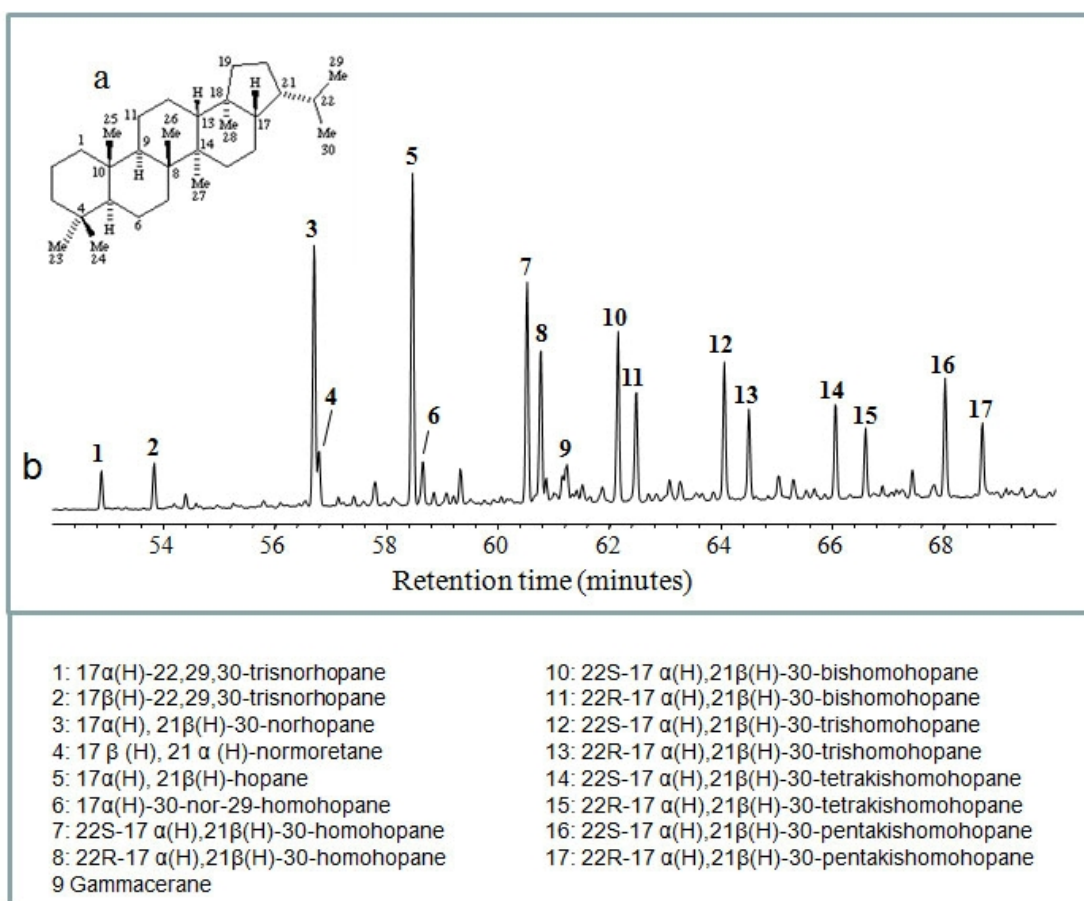

1: 17α(H)-22,29,30-trisnorhopane
2: 17β(H)-22,29,30-trisnorhopane
3: 17α(H), 21β(H)-30-norhopane
4: 17 β (H), 21 α (H)-normoretane
5: 17α(H), 21β(H)-hopane
6: 17α(H)-30-nor-29-homohopane
7: 22S-17 α(H),21β(H)-30-homohopane
8: 22R-17 α(H),21β(H)-30-homohopane
9 Gammacerane
10: 22S-17 α(H),21β(H)-30-bishomohopane
11: 22R-17 α(H),21β(H)-30-bishomohopane
12: 22S-17 α(H),21β(H)-30-trishomohopane
13: 22R-17 α(H),21β(H)-30-trishomohopane
14: 22S-17 α(H),21β(H)-30-tetrakishomohopane
15: 22R-17 α(H),21β(H)-30-tetrakishomohopane
16: 22S-17 α(H),21β(H)-30-pentakishomohopane
17: 22R-17 α(H),21β(H)-30-pentakishomohopane

Fig. 4. (a) Example of pentacyclic triterpane structure (C_{30}-Hopane) and (b) typical distribution of pentacyclic triterpanes (m/z = 191) in soils - case of Vc 02

Table 3. Carbon preference index (CPI), odd-even predominance (OEP(16)), pentacyclic triterpanes/*n*-alkanes ratio and low molecular weight UCM/heavy molecular weight UCM ratio (LMW UCM / HMW UCM)

Samples	CPI	OEP(16)	Pentacyclic triterpanes/*n*-alkanes	LMW UCM / HMW UCM
Ref 01	4.94	0.88	0.00	-
Ref 02	1.14	32.59	0.01	-
Ref 03	1.54	19.12	0.01	-
Br 01	1.09	0.81	0.70	0.10
Br 02	0.95	0.95	7.19	0.03
Br 03	1.16	1.16	2.01	0.05
Br 04	2.01	1.46	1.32	0.12
Br 05	1.97	0.97	1.40	0.11
Br 06	1.23	0.90	0.23	0.38
Br 07	1.65	1.39	1.80	0.04
Br 08	1.16	0.83	1.25	0.14
Br 09	1.27	1.11	0.88	0.14
Br 10	1.08	1.07	0.17	0.09
Br 11	0.91	1.59	0.85	0.04
Vc 01	1.57	0.85	4.64	0.02
Vc 02	1.13	1.35	0.11	0.31
Mm 01	1.43	1.10	1.39	0.03
Mm 02	1.01	1.27	0.89	0.02
Mc 01	1.26	0.88	3.06	0.02
Mc 02	1.11	1.20	2.09	0.16
Mc 03	1.01	1.52	1.40	0.02
Mc 04	1.77	0.85	1.62	0.13
Mc 05	1.32	10.91	0.09	0.64

Specific soil samples and road soil samples show CPI close to 1 and exhibit all, the low and the high molecular weight UCM. This suggested a contribution of thermal mature organic matter: it thus reveals a contamination by petroleum products: crude oils and especially petroleum by-products (Durand et al., 2004; Volkman et al., 1997).

The diagram "pentacyclic triperpane/n-alkane ratio vs EOM content" for all sample (Fig. 5) indicated two distinct lines: The first corresponds to the specific soils with high EOM content and also an elevated pentacyclic triterpanes/*n*-alkane value. This suggests a contamination of these soils by products containing a high proportion of pentacyclic triterpanes probably inherited from heavy petroleum by-products (used engine oils, road asphalts…). The second line characterises road soils with low EOM content and low proportion of pentacyclic triterpanes. Those samples are probably less contaminated by heavy oil products. The reference samples are located at the origin of the two lines with a very low content of EOM and pentacyclic triperpane proportion.
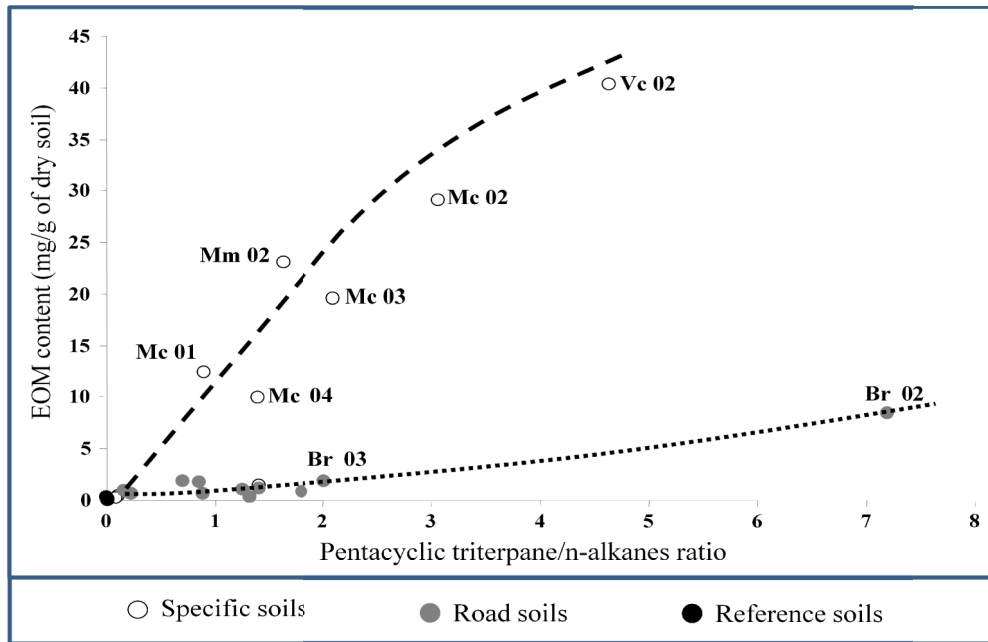
Fig. 5. EOM ratio in function of pentacyclic triterpanes/*n*-alkanes abundance ratio

For specific soils and road soils, the plot of EOM content versus LMW UCM / HMW UCM ratio shows two groups (Fig. 6): (i) the group corresponding to specific samples with the predominance of a high molecular weight UCM and (ii) the group of road samples with the occurrence of a low molecular weight UCM. The occurrence of a high molecular weight UCM can be associated to contamination of petroleum by-products refined (such as road asphalts) and/or degraded (such as draining oils and heavy fuels; Volkman et al., 1997).
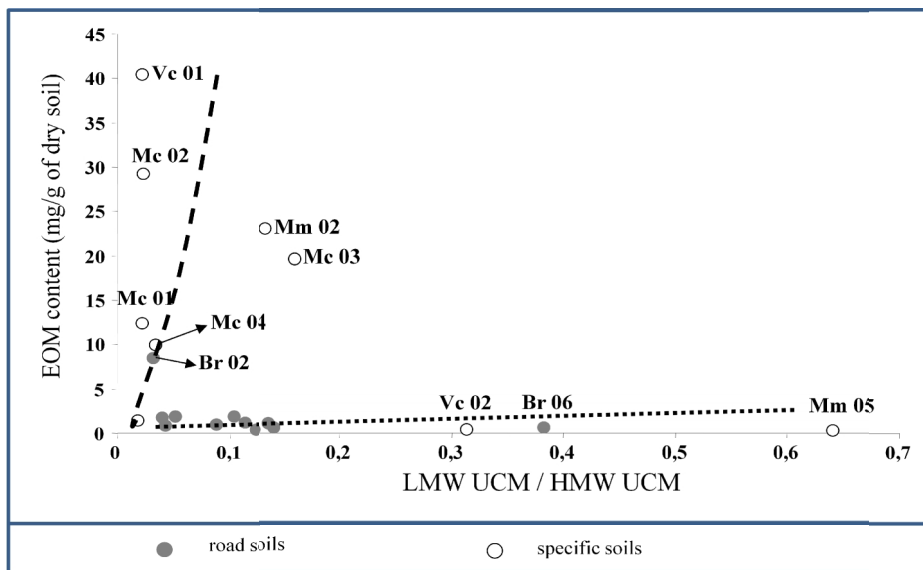
Fig. 6. EOM ratio in function of LMW UCM / HMW UCM abundance ratio

These products can be directly poured on the ground because of the absence of waste evacuation system. The origin of low molecular weight UCM is not yet well elucidated but this latter can be inherited to the degradation of fuel (low molecular weight distillation fraction) sold directly in the streets.

4. CONCLUSION

The analysis of the extractable organic matter in surface soil from Cotonou town reveals a marked contamination by anthropogenic products. The aliphatic hydrocarbons show distributions of *n*-alkanes which are related to a contamination by petroleum by-products: draining oil, heavy fuel and road asphalts, etc. Reference sites samples; considered as non-contaminated, show specific signatures. The other groups remain rather heterogeneous, even if characteristic signatures are recognized, in particular, for the mechanics workshops. This diversity is to relate to the variable organic sources, mainly anthropogenic but also natural and to the evolution of the contamination in these soils (evaporation, biodegradation, leaching…). It would be interesting to carry out molecular isotopic analysis to complete our results in order to be able to identify more precisely the different anthropogenic contributions. The occurrence of low molecular weight UCM encountered in some contaminated soils need also to be elucidated.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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