



Case Study

Assessment of groundwater pollution in the garages: case study of Cotonou districts

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Abstract

In Benin, waste oils which containing hydrocarbon, additives, and heavy metals are spilled on the soil. In Cotonou, groundwater is flush and the soil has a very high permeability. The aim of this study is to characterize water of wells and assess the extent of groundwater pollution. Samples of well water and soils were collected from three garages in three districts (10th, 11th and 13th). The reducing power ($13,7 < R_H < 14,8$) are less than 15 for all samples indicating a reducing character of groundwater. This was confirmed by low concentrations obtained in dissolved oxygen where the reduction in sulfides and sulfates create respectively the reduction in nitrates and nitrites ions. Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC) revealed high organic load with migration of pollutants into groundwater. The absorbance and SUVA index revealed the presence of aromatic hydrocarbons with high aromaticity in the 13th district site. Copper and lead values showed a solubility of migrant lead to groundwater with concentration equal to 14mg/L. We note that the grounds under the garages in Cotonou city were heavily polluted.

Keywords: Garages, groundwater, aromatic hydrocarbons, heavy metals, pollution.

Introduction

Socio-economic development motivated by the development of port activities in coastal countries such as Benin has facilitated the acquisition of means of locomotion whose maintenance requires emptying. Drainage oils before use consist of 80% to 90% base lubricating oil and 10% to 20% additives to improve their performance. During use, their composition changes due to factors such as the physical and chemical modification of the molecules due to the rise in temperature of some parts of the engine, the degradation of additives, the addition of metals from motor wearing and infiltration of foreign substances such as solvents, glycols and gasoline¹⁻³. These oils contain many elements that are toxic to health and are likely to contaminate the environment, especially due to heavy metals, organic acids, phenols, phthalates and aromatic compounds including polycyclic aromatic hydrocarbons⁴. In Benin, about 90% of the oils produced have a final destination of nature, it mean that 4,468, 563.9 liters of oil or 4,469m³ of oils per year⁵. There is a proliferation of large quantities of used oil from automobile and many motorcycles. These oils, which consist of aliphatic hydrocarbons, aromatic hydrocarbons, heavy metals and

decomposition products of additives, are not very biodegradable and are suspected of being carcinogenic precisely by skin contact⁶⁻⁹. Also their density being lower than water; one liter of oil can cover 1000m² area of water, or contaminate one million liters of water, thus causing inhibition of animal and plant biomass^{1,4}. In Cotonou, the water table is one meter, in places less than one meter from the surface of the ground. This sheet is permeable which facilitates the infiltration of rainwater thus generating the risk of pollution. Thus, discharges reaching all spheres of the environment, we are witnessing a contamination of soil and groundwater by infiltration and leaching of the oil drain. Several studies have reported both chemical and microbiological pollution of groundwater that is under the automobile garages in the city of Cotonou¹⁰⁻¹¹. However none of these studies has quantitatively showed the degree of pollution of these aquifers and the correlation between groundwater pollution under car garages and surrounding wells. It is within this framework that this research aims is to evaluate the water table quality in the garage size in Cotonou. The choice of the sites is made according to the sizes of the garages. They are draining both gasoline and diesel cars. Thus, three boroughs are

targeted among the five that have more flushes, according to the report of the survey conducted by PDGSM¹². Soil collections are made at different depths and water samples are taken from the wells surrounding the garages.

To better qualify the impact, the organic and metallic loads, the aromatic hydrocarbon content and the physicochemical parameters were determined at the level of the different study areas chosen (10th, 11th and 13th districts).

Materials and methods

Area of study and sample sites: **Area of study:** The choice of sites is based on the size of the garages in Cotonou in southern Benin. They are draining both gasoline and diesel cars. In the 10th arrondissement, the Kouhounou district was identified; as for the 11th district, the Vodje district has been identified. In the 13th district, the Agla district has been identified. These targeted boroughs are among the five that are overflowing with more oils, according to the report of the survey conducted by PDGSM¹². These neighborhoods are found in the municipality of Cotonou which climate is subequatorial with two rainy and dry seasons from January to December. Rainfall and temperature vary around 1100mm per year and 32°C respectively.

Sample sites: Soil: Sampling took place during the small rainy season between September and November. It consisted of taking soil samples from 3 garages, 1 garage per district. These samples are taken respectively at different depths (0, 0.25, 0.50,

0.75meters) on the platform of the garages. These points are shown in Table-2 with their identification number.



Figure-1: Garages and wells sites.

Sampling of water samples: The water observed at 0.50m and at 0.75m from the soil collection points was taken. In addition, 9 wells were sampled, it means that 3 wells per garage (Table-2), one at the site and two in the immediate vicinity in order to study the mechanisms of Heavy metal migration in the subsoil and determining the possible interaction between garages (the source of pollution), underground or surface flow (the pollution vector), and surrounding wells or humans indirectly (target). The water samples were taken until overflow in the polyethylene bottles and capped. These flasks are rinsed beforehand with distilled water and then with water to be sampled. Preserving samples requires the addition of a few drops of nitric acid.

Table-1: Releases from garages.

Garages	Activities	Releases			
		Oil change quantity (L/jour)	Waste (kg /jour)	Metals	Polycyclic Aromatic Hydrocarbons (HAP)
Arr 10	Repair of motorcycles, cars, welding, engine oil change	2 L per motorcycle / month 6 L per car / month	Worn wheel, metal objects, carcasas of motorcycles and cars	Lead, Cadmium, Iron, Copper, Mercury, Aluminum, Chromium etc ...	Polycyclic Aromatic Hydrocarbons (PAHs), heavy metals, organic acids, phenols, phthalates, polycyclic aromatic hydrocarbons (PAHs) ...
Arr 11					
Arr 13					

Arr: Arrondissement¹³⁻¹⁴.

Table-2: Sites retained (garages and wells) and their identification.

Borough District		Identification number							
		Soil				Water			
10	Kouhounou	A ₀	A ₁	A ₂	-	A ₂	A _a	A _b	A _c
11	Vodjè	B ₀	B ₁	B ₂	-	B ₂	B _a	B _b	B _c
13	Agla	C ₀	C ₁	C ₂	C ₃	C ₃	C _a	C _b	C _c

A: 10^{eme} Borough, B: 11^{eme} Borough, C: 13^{eme} Borough.

Table-3: Geographical coordinates of sampling sites.

Kouhounou	Geographical coordinates		Vodjè	Geographical coordinates		Agla	Geographical coordinates	
	Longitudes	Latitudes		Longitudes	Latitudes		Longitudes	Latitudes
A _a	2°37572	6°37337	B _a	2°38959	6°36532	C _a	2°36957	6°37852
A _b	2°37577	6°37405	B _b	2°38980	6°36547	C _b	2°36961	6°37827
A _c	2°37583	6°37312	B _c	2°38968	6°36566	C _c	2°36991	6°37876
A ₂	2°37568	6°37338	B ₂	2°38966	6°36527	C ₃	2°36972	6°37840

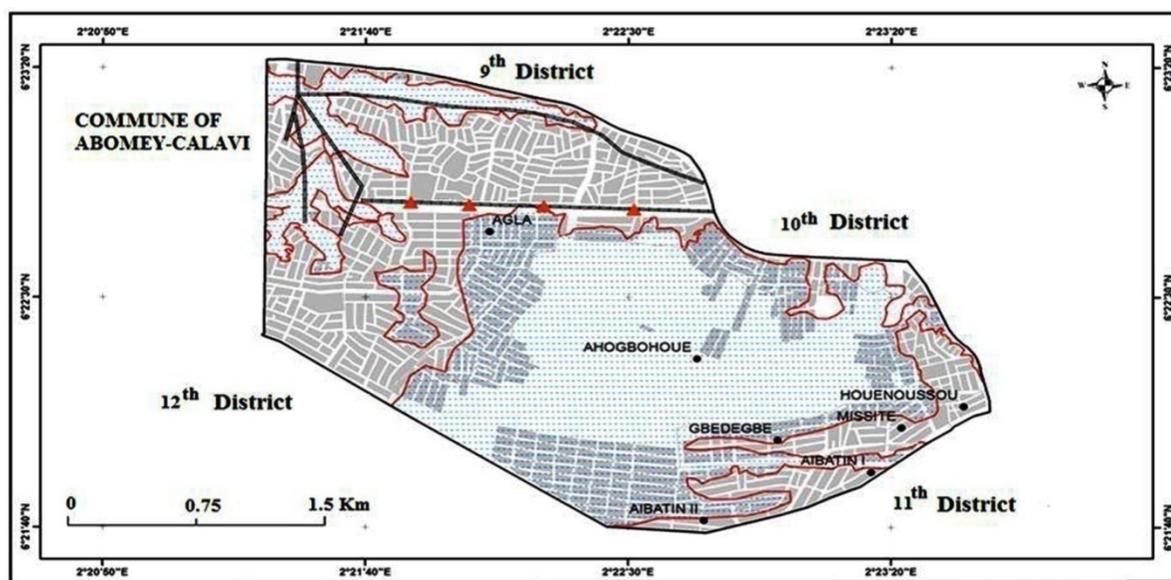


Figure-2: Sampling points in a borough¹⁵.

Physico-chemical parameters: Water and soil samples were analyzed at the Laboratory of Water Science and Technology (LSTE) of Abomey Calavi. The Excel 2007 data analysis software was used for statistical analysis. The physicochemical parameters of well and soil water, such as: temperature (T), conductivity (CE) and dissolved oxygen (dissolved O₂) were measured electrochemically according to NFT 90-106 standards respectively and NF EN 27888 with the Innolab 740i WTW pH/O₂.

The oxidation-reduction potential (E_H, equation 1) and pH were determined by the potentiometric method with multiparameter (WTW pH / E_H 340i) and pH meter (Mettler Toledo) equipped with a LE 409 probe according to the standard NF EN 27888 and NFT 90-008. Turbidity (Turb) was determined by the light scattering according to the standard NFT 90-033. The SUVA index is deduced from the absorbance and calculation of COD by the equation-2.

$$R_H = \frac{E}{0,0992 \cdot T} + 2 \times \text{pH} \text{ avec } E \text{ en mV et } T \text{ en } ^\circ\text{K} \text{ (Equation-1)}$$

$$\text{SUVA} = \text{Abs} (254\text{nm}) / \text{COD} \text{ (Equation-2)}$$

Polluted parameters: The nitrates (NO₃⁻), nitrites (NO₂⁻), sulphate ions SO₄²⁻ were respectively determined according to

French standards NFT 090-012, NFT 090-013 and NFT 090-009 by molecular absorption spectrophotometry with a HACH LANGE DR 2800.

COD, permanganate index (Ip) and BOD₅ were respectively determined by volumetric and manometric methods according to the standards NFT 90-101, NF EN ISO 8467 and NFT 90-103.

Metallic elements (Copper, Lead) were measured using Atomic Absorption Spectrophotometer SAFAS AA181 according respectively to standards NF EN 17294-2 and NF EN 12498.

Dissolved oxygen and turbidity were determined in all well water samples in addition to the other parameters in the table. While after leaching in 48 H according to the 1/10 ratio these same other parameters were evaluated in the leachates of the soils.

Absorbance was measured by visible UV spectrophotometry mC2 SAFAS double beam bandwidth 1nm and the TOC meter was used to determine the Total Organic Carbon (TOC) according to the Apha 2005 method. To identify well water contamination, the values obtained are compared to the Beninese water quality standards.

Results and discussion

Study characteristics of tablets under garages: Physico-chemical parameters: Physico chemical parameters in samples: Tables-4 show the reducing power, the dissolved oxygen, the temperature, the turbidity and the conductivity of the water samples per site.

The reducing power is between 13.70 and 14.90 in all the samples. These values remain below 15. We note a high redox potential (R_H : 14.85) in the well sample (Aa) closest to the 10th Arrondissement garage (site A) and a low value (R_H : 13.74) in the well sample (Ca) closest to the garage of the 13th arrondissement (site C). The values of the reducing power account for the reducing nature of the layers in the three localities. This reducing character is more noticeable on site A compared to the others. The low concentrations of dissolved oxygen obtained testify to it. Such a finding was made by Akowanou and Yovo¹⁶⁻¹⁷. The study sites are therefore highly charged environments with high oxygen consumption that can be linked to microbiological activity due to the presence of bodywork. Wild trucks and dump sites in the vicinity of the sites¹⁸⁻¹⁹. The temperature of the medium (27°C and 31°C) shows that analyzes were made under adequate climatic conditions, conducive to microbiological activities²⁰.

Moreover, the conductivity vary between 500 and 1000 μ S/cm, with high values (1017 μ S/cm) at the level of the sample of the 3rd well (Ac) of the 10th district site. At the 13th borough, we have a low conductivity at the sampling point (C₃) with a depth of 0.75m. This fact reflects a strong mineralization of these waters according to Rodier²¹. The strong mineralization leads to a decrease in dissolved oxygen levels (2.10mg/L) at this site²². In this study, the physico-chemical parameters show that samples are polluted according to European Water Framework Directive of 23 October 2000²³. The potentials obtained are also indicators of presence of pathogenic germs. From the analysis of this section, the low dissolved oxygen value of the sites Aa and Ca wells (wells closest to the 13th arrondissement garage) can be explained by their proximity to the emptying sites. However, the value observed compared to the well closest to the garage of the 11th district (Ba) is explained by the fact that this garage has known in the past backfill with solid waste according to our investigations. This household waste contains more than 50% biodegradable organic matter. So this low value is explained by microbiological activities related to the degradation of organic matter. Outside the well Aa and Ca, where the turbidity is high (especially very high in Ca: 76 NTU), we find that the turbidity values of others sites comply with the WHO standard (5 NTU). There is therefore a strong presence of suspended solids (clay, silt, silica grains, organic matter) in these well waters¹⁸.

Table-4: Physicochemical content of samples from sites A, B, C.

Parameters	Units	Precision	A _a	A _b	A _c	A ₂	B _a	B _b	B _c	B ₂	C _a	C _b	C _c	C ₃
R _H	–	±0,01	14,85	14,41	14,46	14,42	14,59	14,43	14,66	14,44	13,74	13,83	14,52	14,47
O ₂ dissous	mg/L	±0,1	0,40	3,40	2,10	5,80	2,50	2,00	4,50	3,30	2,30	4,00	3,00	5,70
Conductivity	μS/cm	± 1	657	549	1017	904	830	693	698	808	489	479	289	421
pH	–	±0,1	7,2	6,7	6,9	7	7,3	6,8	7,6	7	6,7	6,8	7,1	6,4
Temperature	°C	±0,1	31,6	30,3	30,8	28	27,5	28,3	27	27,6	28	28,2	29,8	27,8
Turbidity	NTU	±0,01	5,46	1,68	2,56	718,7	4,11	1,78	1,58	295,9	76	4,3	3,04	275

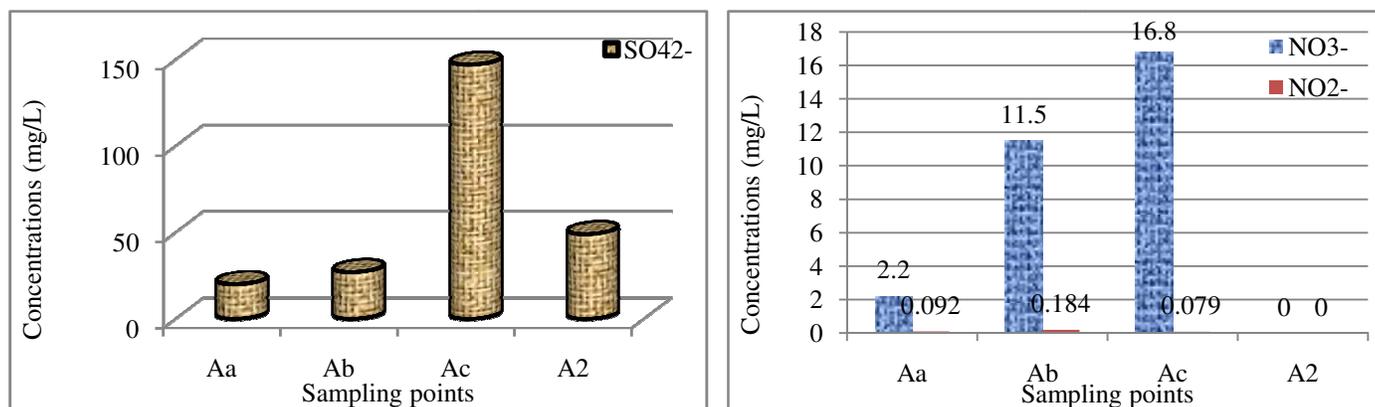


Figure-3: Sulphate, nitrate and nitrite contents of samples Aa, Ab, Ac and A₂.

Polluted parameters: Sulphate, nitrate and nitrite content of site A water samples: Figure-3 shows a low nitrite content of the water samples. The level of histogram of the point Ac has a high size compared to the points A₂, Ab and Aa. It can be said that the Ac sample has high sulphate content (147mg/L) in nitrates (16.8mg/L) and nitrites (0.079mg/L). This corroborates the reducing nature of the medium deduced from the values of the redox potential. This can be explained by the fact that it would reduce sulfates to sulphides and nitrates to nitrite. The presence of these nitrites in water could lead to the formation of methemoglobin on the one hand at the level of consumers and the other to contribute to the endogenous synthesis of N-nitroso compounds²⁴. The presence of these sulphides predicts metal complexes such as metal sulphides due to the affinity of metals such as copper and lead for sulfur²⁵. The case of the Ac well seems more worrying given its high concentration of sulphate. The high conductivity of the Ac sample (1017µS/cm) can be related to the high sulfate ion content (147mg/L).

Determination of the total organic carbon of water samples A₂, B₂, C₃: Figure-4 shows histograms of large sizes and particularly at C₃. This shows high organic carbon content (490 mg/L) in the water sample taken from point C₃ in garage C, while the histogram of point B is small. Therefore, the low organic carbon content (280mg/L) is given by the water sample taken from B₂ in garage B. This observation shows that organic pollution is greater at site C than at site B²⁶. This content may be related to the presence of aromatic compounds from garbage oil from garages.

The waters collected at points B₂ (Ip: 891.6, 10⁻⁴mgO₂/L) and C₃ (Ip: 1534.6, 10⁻⁴mgO₂/L) from sites in the 11th and 13th districts have permanganate superior to those of other points. These sites would be more charged aromatic compounds than the other points having these same depths (Table-5). It means that certain organic loads contained in these soils were dissolved by water at the same depth.

Absorbance measurements and calculation of SUVA: The Absorbance measurement found that points A₂ and B₂ have values that are almost identical but lower than the C₃ site. These absorbances are indicative of the presence of aromatic organic matter in the water samples. And this presence is more remarkable at the Agla site (C). Furthermore, the values obtained for COD and particularly that of the C₃ site (COD: 392 mg.C.L⁻¹) confirm the previous remark. It could be said that it would be hydrocarbon pollution with aromatic nuclei. In addition, the SUVA index is also high for the C₃ site (4.06, 10⁻⁴L.m⁻¹.mg⁻¹.C⁻¹) compared to the A₂ (2.46. 10⁻⁴mg⁻¹.C⁻¹) and B₂ (2.95, 10⁻⁴L.m⁻¹.mg⁻¹.C⁻¹) sites. A comparative analysis with respect to the SUVA index (2L.m⁻¹.mg⁻¹.C⁻¹) obtained by Aina²⁷, allows us to say that we are in the case of a non-negligible aromaticity. We observe through this table that the aromaticity at site C is higher than in the other sites. From this analysis it can be seen that the increasing pollution order of the three organic pollutant research sites starts from site B to site C via A and that organic pollution is therefore more important at site C which is the site of Agla. This could be due to the fact that this site is full of several garages and that substances rich in organic compounds are regularly spilled.

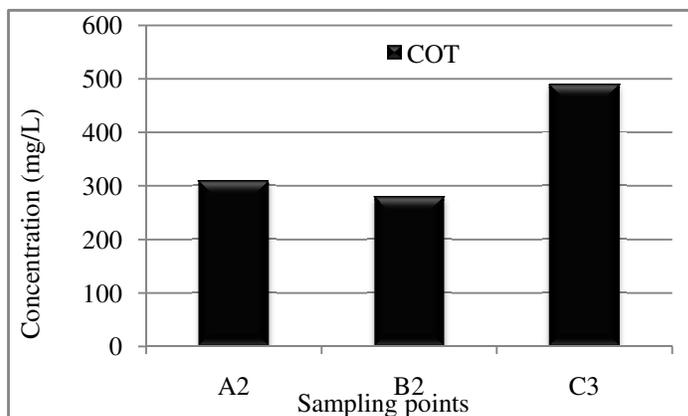


Figure-4: Total organic carbon content of water samples A₂, B₂ and C₃.

Table-5: Measurement results of the permanganate index of water and soil samples at the same depth.

Sampling points	Precision	A _{2s}	A ₂	B _{2s}	B ₂	C _{3s}	C ₃
Ip (10 ⁻⁴ mgO ₂ /L)	0,01	37,9	498,6	100,3	891,6	160,1	1534,6

A_{2s}, B_{2s}, C_{2s}: Soils of the 10th, 11th and 13th borough.

Table-6: Absorbance measurements and calculation of SUVA.

Parameters	Unit	Precision	A ₂	B ₂	C ₃
Absorbance 254nm	cm-1	± 0,001	0,061	0,066	0,159
DCO	mg.C.L ⁻¹	±1	248	224	392
SUVA Index	10 ⁻⁴ L.m ⁻¹ .mg ⁻¹ .C ⁻¹	-	2,46	2,95	4.06

Metallic pollution of water samples at Site B: The figure below shows lead content of well water that is taken at 0.5m depth from the garage B platform.

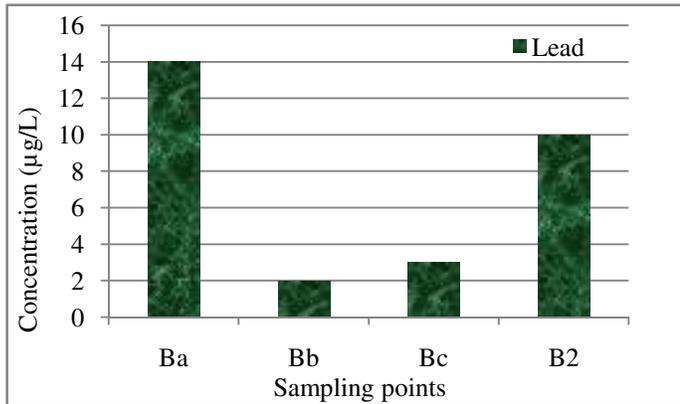


Figure-5: Lead content of Ba, Bb, Bc and B₂ samples.

The analysis of the figure shows that the histogram of the lead content (14µg/L) of the well Ba is higher than those of the other wells. This shows that the Ba well has a high lead content compared to other wells. This well is then polluted with lead based on the latest recommendations of the World Health

Organization (WHO) which set guide value 10µg/L lead²⁸. From Figure-5 we can say that the lead content of the water of the well Ba exceeds the required standards. This presence would result from the contact of water with the materials of the pipes because of its use in the manufacture or the constitution of many metallic or organic materials²⁸. However, given the wells situation and especially the absence of the pipes, the high lead content can be explained by the soil properties in this site that are favorable for the infiltration of lead-rich wastewater. Thus the populations consuming this water are exposed to pulmonary, digestive and psychic diseases such as lead poisoning due to the storage of lead in the red blood cells, liver, kidneys and brain²⁹.

Organic soil pollution of sites A, B, C: Through Figure-6, it can be seen that the COD and the permanganate index Ip of the points A₂ and B₂ are respectively five and nine times higher than those of the other points. This means that these sites have a significant degree of pollution compared to others. The same observation is observed at point C₃ which has COD and Ip levels eight times higher. The levels of BOD₅ obtained at the A₂, B₂ and C₃ sites are representative of the oxidizable organic matter present in the water³⁰. From this analysis, it is noted that the concentrations of COD appear to be greater at the surface of the dump sites than at depth.

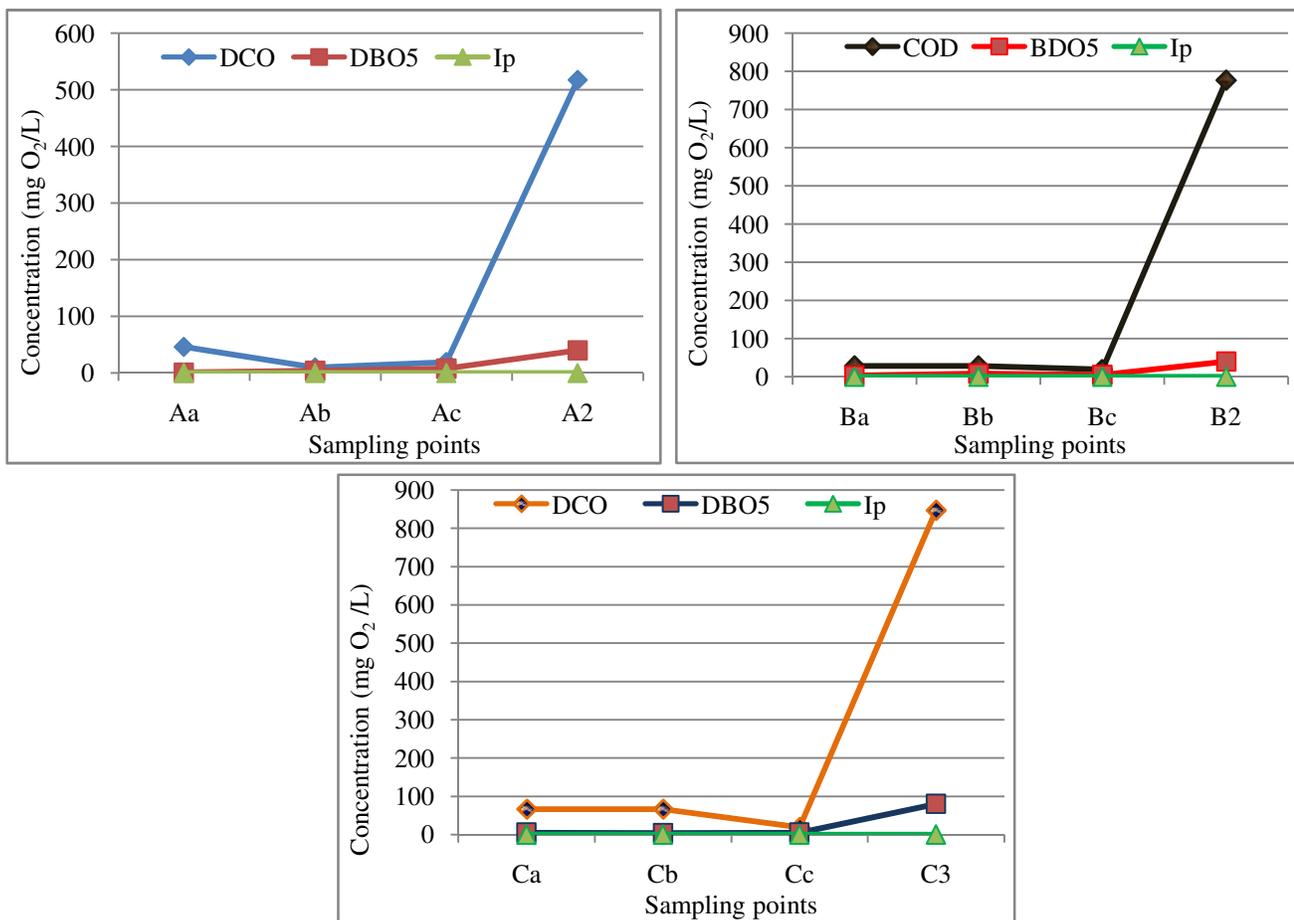


Figure-6: Evolution of COD, BOD5 and Ip at sites A, B, C.

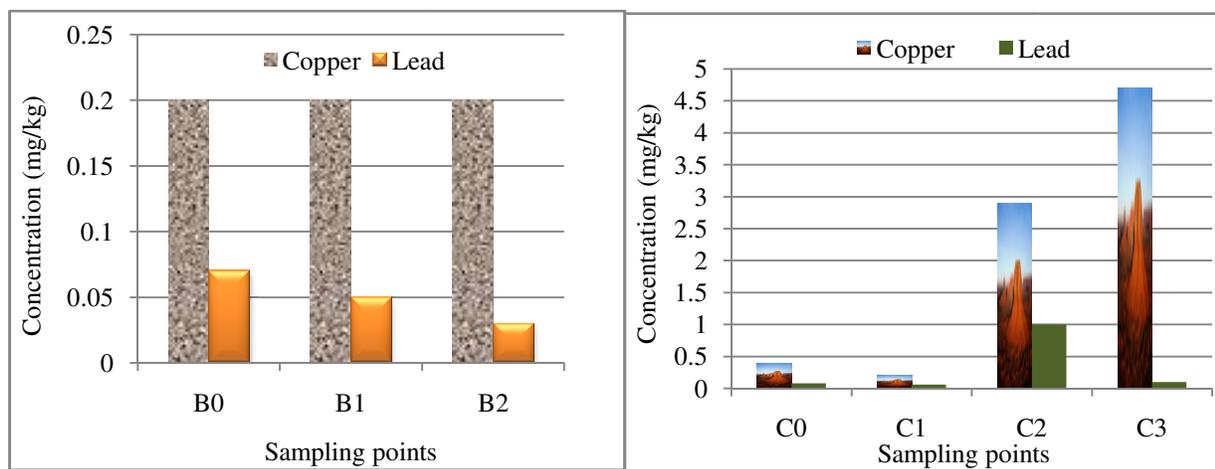


Figure-7: Copper and lead content of Soils of Sites B and C.

Metallic soil pollution at sites B and C: We observe that the metal content of soils varies at site level. All bags have the same copper content (0.02mg/L), while the lead content (7µg/L) decreases from the surface of the deep dump sites. These copper and lead values remain below 2mg/L and 0.05mg/L respectively, which are standards accepted by WHO.

This figure shows a low copper content; while the lead content varies from one pocket to another. The high lead value is observed at 0.50m from the platform at the point of discharge at the C₂ sampling point. In addition, there is a dispersion of lead and a linear migration of copper towards the depth. This can be explained by the fact that lead settles in the soil⁶. On the other hand, these metals adsorbed by the solid matrix will be less available for biodegradation³¹.

It appears that although items such as batteries and scrap metal are the most important carriers of heavy metals, the fact remains that used oils are a potential source of soil contamination with heavy metals.

Conclusion

At the end of this study, it appears that car, gasoline or diesel garages are full of many organic fillers and non-negligible metal loads with lead concentrations exceeding the norm. This pollution is more remarkable at site B and C compared to other sites. In addition it is revealed a migration of pollutants to the subsoil thus affecting the water tables. This study showed that these pollutants are composed of aromatic hydrocarbons and that aromaticity is high at the C site. Populations face enormous risks of contamination. But given the heterogeneous and composite nature of the oils used in Benin, and the heavy metals associated with them, it would be difficult to reduce or limit the contamination observed in the different districts of Cotonou and the big cities.

However, concerted actions must be done by Organizations and Ministries in charge of environment in case to make sensitize

the populations. Thus, studies on metal speciation and organic compound management as well as modern remediation technologies such as phytoremediation will provide solution approaches for soil decontamination.

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