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Using Principal Component Analysis (PCA) to Interpret Geochemical Composition of Toxic Waste

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Abstract

The Ivorian Antipollution Center discovered toxic waste from Probo Koala ship in August 21, 2006. This ship had been used by the Trafigura company to refine oil called naphtha of cokéfaction at sea. The refining process involved caustic sodium carbonate washing, which produced toxic waste. This waste was unloaded in 13 areas of the Abidjan district: Akouédo, Abobo, Abobo-Alépé Road (Djibi village), Civile Prison Road (MACA), the industrial zone of Koumassi, and Port-Bouët-Vridi CAP Logistic (Rue Saint-Sylvestre), among others. This situation caused a socio-political crisis and resulted in the deaths of many people. Initial analysis showed that the substances in the toxic waste originated from petroleum processing. To access the environmental impact of this pollution in the Abidjan district (Ivory Coast), samples of the toxic waste were sent for analysis to the Wessling laboratory in France. The results revealed that the waste contained Polycyclics Aromatics Hydrocarbons (PAH), Volatile Aromatics Compound (VAC), Mercaptans, Sulfur molecules, Aliphatic hydrocarbons, Linear hydrocarbons, Total Petroleum Hydrocarbons (TPH), and heavy metals.

Keywords: Toxic waste, Trafigura, Probo Koala, Polycyclics Aromatics Hydrocarbons (PAH), Volatile Aromatics Compound (VAC), Aliphatic hydrocarbons, Linear hydrocarbons, Total Petroleum Hydrocarbons (TPH), Mercaptans, Sulfur, Heavy metals, Principal Component Analysis (PCA)

Introduction

On August 21, 2006, 540 m^3 of toxic waste were discovered in 13 zones of the Abidjan district in Ivory Coast. The pollutants contained in the toxic waste discharged into the district caused 30,000 cases of intoxication and the deaths of around one hundred people (Amnesty International, 2012). While many PAH-contaminated sites around the world were inherited from the cessation of industrial activities in the last century (mainly between the 1960s and 1980s), in the country of this study, toxic waste has become a primary source of such pollution due to its fatal impact. Coal-related activities, such as coking and gas production, has also been particularly responsible for PAH contamination in industrials oils (Biache et al., 2008). Given that these compounds have carcinogenic, toxic, and mutagenic properties, some have been classified as priority pollutants by the US-EPA (Keith & Telliard, 1979). In the environment, PAHs contribute to the contamination of soil, water, and air worldwide (US-EPA, 1999). To study the environmental impact of these pollutants in Ivory Coast generally, and particularly, in the Abidjan district, toxic waste samples were sent to the Wessling laboratory in France for analysis. Until today, the Ivorian authorities and the population still seek clarity on the true composition of the toxic waste. Therefore, the survey focuses on determining the chemical composition of the toxic waste. To align with international waste classification standards, the European Commission's waste classification system is used in this study to identify the appropriate code for the toxic waste. Principal Compound Analysis is also applied to examine the relationships between the various chemical components identified in the analysis. First, however, it is important to understand the origin of the toxic waste.

Materials and Methods

Samples

This study concerns the 13 toxic waste-contaminated zones in the southern region of Ivory Coast, located within the Abidjan district. The samples analysed were collected from these zones. The geographical coordinates are presented in Table 1.

Table 1. The geographic position of 13 contaminated toxic waste zones

Zone	Unloading geographic position
Cocody: Akouédo	-Akouédo I : N 05°21.429’ - W 03°56.095’ -Akouédo II : N 05°21.077’ - W 03°56.206’ -Akouédo III : N 05°21.425’ - W 03°56.028’
Abobo	-Abobo (Coco services) : N 05°24.092’ - W 04°01.167’ -Abobo Sagbé : N 05°24.409’ - W 04°01.593’ -Plateau Dodui I : N 05°23.403’ - W 04°00.367’
Abobo Alépé Road (Djibi Village)	-Alépé 1 : N 05°27.373’ - W 03°58.344’ -Alépé 2 : N 05°27.572’ - W 03°58.280’
Yopougon : Civile Prison Road (MACA)	-MACA I : N 05°23.354’ - W 04°04.710’ -MACA II : N 05°24.811’ - W 04°04.674’ -MACA III : N 05°25.309’ - W 04°04.405’
Koumassi	-Koumassi Industrial Zone : N 05°17.547’ - W 03°56.783’
Port-Bouet	-Vridi CAP Logistic : N 05°15.832’ - W 03°59.980’

Soils were sampled in these 13 zones. Extractable organic matter was recovered by extracting portions of the soil using a Soxhlet apparatus with chloroform (CHCl3) for 24 hours. The extract contained PAHs, VACs, mercaptans, sulfur, heavy metals, and various organic compounds ranging from macromolecules (e.g., asphaltenes) to mono-aromatic units. These analyses were conducted using a photometer-equipped microscope to determine the proportion of volume occupied by different mineral and organic particles. Soil samples were freeze-dried, sieved at 2 mm, and crushed to 500 µm to ensure homogeneity. To obtain the EOM, portions of the soil were again extracted using the Soxhlet apparatus with chloroform for 24 hours.

Analytical

Extraction-fractionation

The toxic waste fraction was recovered by Soxhlet extraction in chloroform for 48 hours. Aliphatic, aromatic, and polar fractions were separated by liquid chromatography on a silica column through successive elution with pentane and a pentane/dichloromethane mixture. Polar compound were recovered using a methanol/dichloromethane mixture. After each step, the recovered fractions were weighed and the mass differences were calculated.

Gas Chromatography-mass Spectrometry

Aliphatic and aromatic hydrocarbons, along with polar compounds, were analyzed by gas chromatography–mass spectrometry (GC–MS) using an HP 5890 Series II GC coupled to an HP 5971 mass spectrometer. An on-column injector, a 60 m DB-5 J&W fused silica column (0.25 mm i.d., 0.1 mm film thickness), and a temperature program of 40–300 °C at 3 °C/min followed by an isothermal stage at 300 °C for 15 minutes (with constant helium flow at 1 ml/min) were employed. Due to the presence of carboxylic acids in the polar fractions, silylation using BSTFA + 1% TMCS (99/1) was performed to enhance chromatographic resolution (Biache et al., 2014). A small aliquot of the sample was dissolved in the derivatizing solution at a concentration of 4 mg/ml and heated for 15 minutes at 50 °C. One microliter of the solution was then directly injected into the gas chromatograph (Biache et al., 2014). Geochemical analytical techniques such as GC-FID and ICP-MS were also applied in this study. Details of all analytical methods are provided in Table 2.

Table 2. Parameters and analytical methods

Parameters	Norme	Technical	Laboratory
Benzene and aromatics (VAC - BTEX)	NF ISO 11423-1(#)	GC-MS	Wessling Lyon (F)
Volatile Halogenated Hydrocarbons Compounds (VHOC) on water	NF EN ISO 10301(#)	GC-MS	Wessling Lyon (F)
Polycyclics Aromatics Hydrocarbons (HAP)	Internal method HAP-PCB adapted de NF T90-115(#)	GC-MS GC-FID	Wessling Lyon (F)
Hydrocarbons Idication (GC) on water / leached (HCT)	NF EN ISO 9377-2(A)	GC-FID	Wessling Lyon (F)
Metals / Elements on water / leached	DIN EN ISO 11885 / DIN EN ISO 17294-2(A)	(ICP-MS)	Wessling Altenberge (D)
Metals on water / leached	NF EN ISO 17294-2(#)	(ICP-MS)	Wessling Lyon (F)
Metals on water / leached (ICP-MS)	NF EN ISO 17294-2(#)	(ICP-MS)	Wessling Lyon (F)
Mercaptans on water	WEX 100	(ICP-MS)	Partner Laboratory

Statistical methods

To interpret the results, Principal Component Analysis (PAC) was applied as the primary statistical method.

Principal Component Analysis

Principal Component Analysis (PCA) is an exploratory statistical method used to provide a graphical description of information within large datasets. In most applications, PCA involves analysing p variables measured on n individuals. When n and p are large, PCA synthesizes the extensive amount of data into a form that is easier to understand (Niang, 1994). Unidimensional or bidimensional studies may be performed on variables using graphical tools (e.g., histograms, box plots) or numerical summaries (e.g., mean, variance, correlation). However, these basic studies are often insufficient in a multidimensional context, as they do not account for the relationships between variables-often the most critical aspect (Niang, 2002). PCA is widely regarded as the foundational method in factor analysis. It identifies linear combinations of the p variables, called components, to simplify the visualization of the observations. By transforming a large number of correlated variables into a smaller set of uncorrelated principal components, PCA serves as a dimensionality reduction method. It may also be used for multivariate outlier detection, particularly by analysing the final principal components, which is beneficial in multidimensional quality control (Saporta, 2006).

Principal Component Analysis Interpretation

PCA results are obtained from active elements-variables and individuals that directly participate in the analysis-as opposed to supplementary elements, which do not. Active variables and individuals are used to compute principal axes; supplementary variables and individuals are then projected onto these axes (Hawkins, 1986). Active variables (numerical) are those with meaningful intercorrelations and are considered the core variables of the study. Supplementary variables offer additional information for characterizing individuals but are not directly used in the analysis (Jolliffe, 1986). Only the correlations between supplementary and active variables, as determined through principal components, are of interest-correlations between supplementary variables themselves are not considered (Lebart et al., 2006). Interpretation involves analyzing results using active variables and individuals, while supplementary elements are considered in the external interpretation phase (Montgomery, 1985).

Variables

PCA produces principal components-new artificial variables defined as linear combinations of the original variables (Schölkopf et al., 1999). These principal components must be interpretable based on the original variables. This is achieved by calculating the linear correlation coefficients r(c, xj) between the principal components and the original variables (Barnett &Lewis, 1984). In standard PCA using standardized data, these correlations are straightforward to compute and follow the relation: $r(c, xj) = \sqrt{\lambda} uj$ (Caussinus et al., 2003).

Typically, the correlation of variables across two principal components are visualized using a correlation display graph. Each variable xj is positioned with its abscissa as r(c1, xj) and its ordinate as r(c2, xj). This graph aids in detecting groups of similar or opposing variables, helping to interpret the significance of the principal axes (De Leeuw & Van Rijckevorsel, 1988).

Observation

Interpreting observations involves examining their coordinates, particularly through graphical representations called principal planes. These help identify how observations are distributed, which ones are similar, and which deviate significantly. In cases involving non-anonymous observations, this can assist in interpreting principal axes by locating opposing individuals along an axis (Gnanadesikan, 1977).

Additionally, insights from the variable analysis can support observation interpretation. For instance, if the first component is strongly correlated with a specific original variable, individuals with large positive coordinates along axis 1 likely exhibit above-average values for that variable (the origin representing the centroid of the data cloud) (Gower & Hand, 1996).

Results

The results of this study concern samples of contaminated soils and water collected from toxic waste-affected zones in the Abidjan district. These samples were sent to the Wessling labolatory in France for analysis. The findings revealed that Polycyclics Aromatics Hydrocarbons (PAH), Volatile Aromatics Compound (VAC), mercaptans, sulfurs-containing molecules, and heavy metals were the primary pollutants present in the contaminated soils.

Polycyclics Aromatics Hydrocarbons (PAH)

Principal Component Analysis (PCA) of PAHs (Figure 1) indicated that the first two axes (Factor 1 and Factor 2) accounted for a total of 90.29% of the variance. Factor 1 represented 80.67% of the total variability in PAH contamination across the sampled zone. A strong correlation ($\alpha=0.9$) was observed for chrysene and fluoranthene along Factor 1. Factor 2 accounted for 9.62% of the total variability, with naphthalene ($\alpha=-1$) strongly correlated along this axis. In summary, two PAHs were closely associated with Factor 1, while fourteen PAHs were strongly correlated with Factor 2.

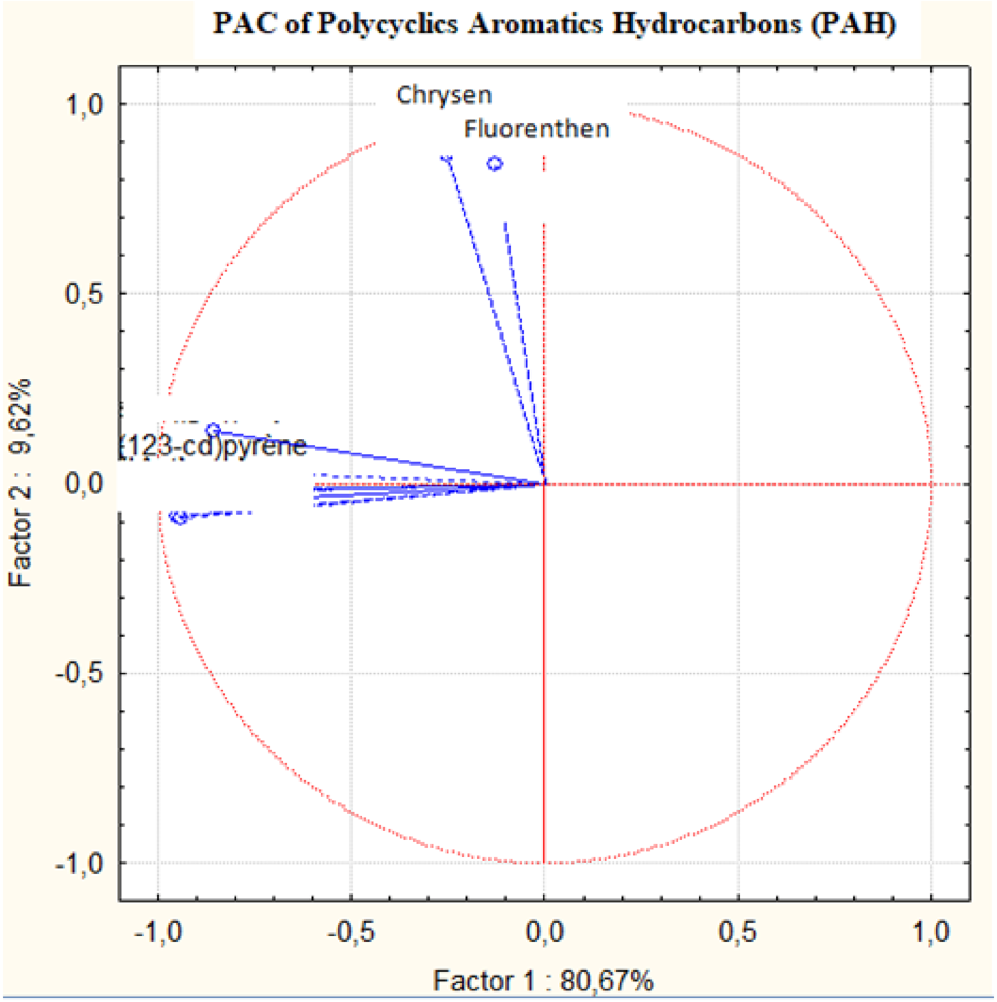

Figure 1. Principal Component Analysis (PCA) of Polycyclics Aromatics Hydrocarbons (PAH)

Volatile Aromatics Compound (VAC)

PCA of VAC (Figure 2) showed that the two first axes explained 93.47% of the variance. Factor 1 accounted for 83.54% of the total variability, but no significant correlations were identified along this axis. Factor 2 accounted for 9.93% of the variance, with o-xylene showing a strong correlation (α = -1). All VAC exhibited correlations primarily along Factor 2.

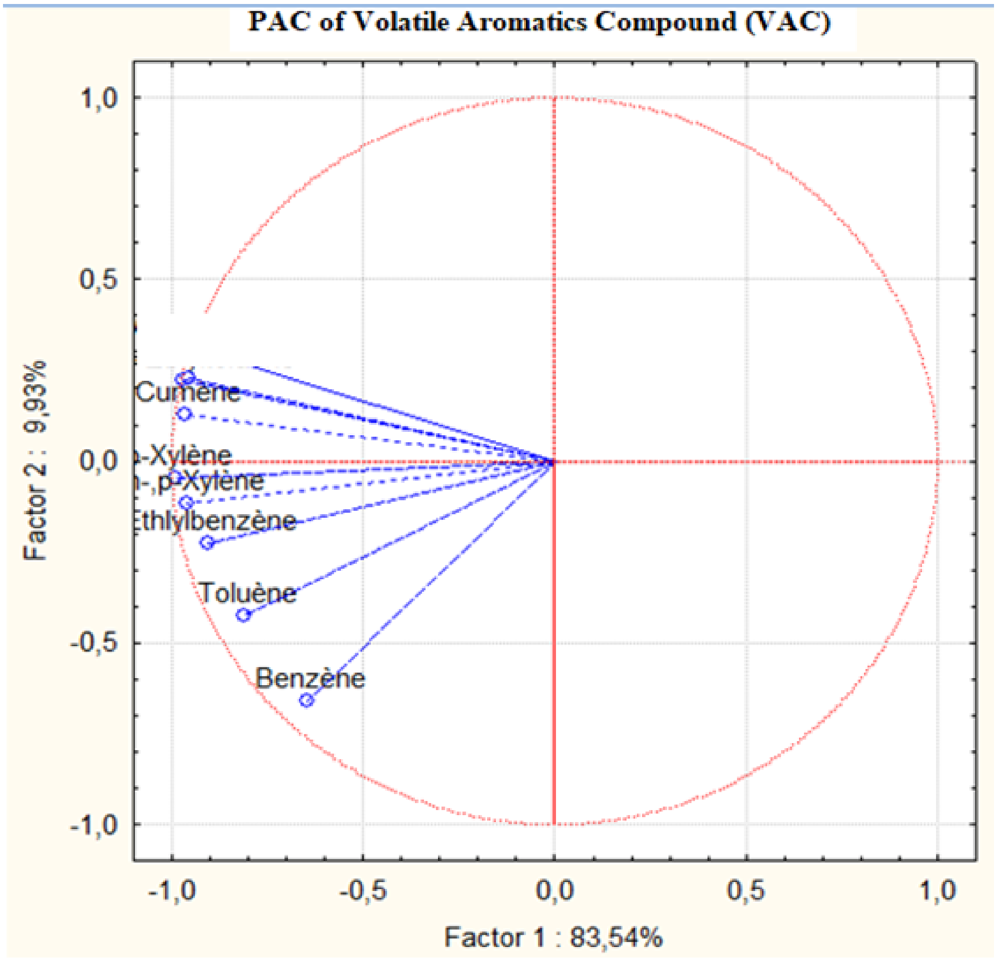

Figure 2. Principal Component Analysis (PCA) of Volatile Aromatics Compound (VAC)

Mercaptans and sulfurs molecules

PCA of mercaptans and sulphur-containing molecules (Figure 3) revealed that the first two axes captured 55.59% of the total variability. Factor 1 explained 37.86%, with some compounds-such as tert-butylmercaptan-showing high positive correlations (α = 1). Factor 2 contributed 17.73% of the variance. Several compounds also exhibited strong negative correlations (α = -) along this axis. Additionally, certain mercaptans and sulfur molecules showed no correlation with either axis and appeared near the center of the figure, indicating no significant contribution to Factor 1 or Factor 2.

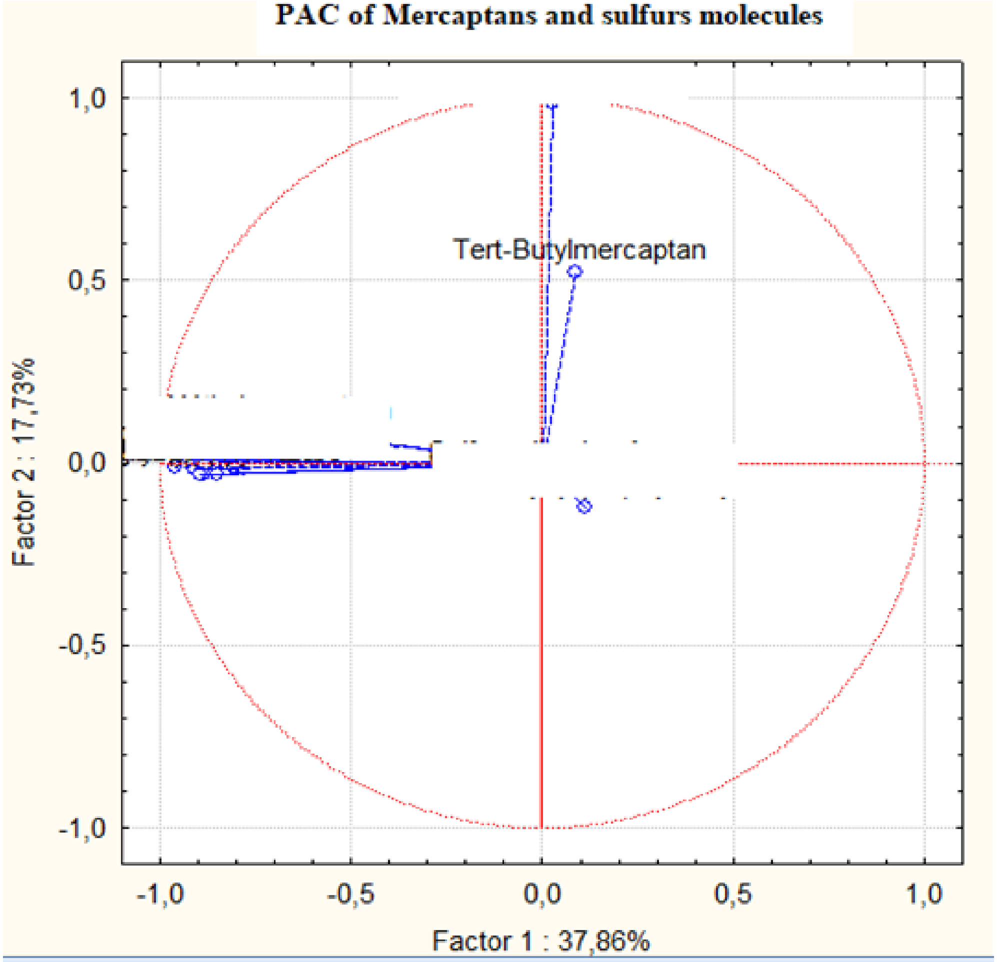

Figure 3. Principal Component Analysis (PCA) of Mercaptans and Sulfur Molecules

Heavy Metal

Principal Component Analysis (PCA) of heavy metals (Figure 4a) shows that the first two axes (Factor 1 and Factor 2) together explain 53.90% of the total variance. Factor 1 accounts for 42.74 % of the variability in heavy metal contamination in samples collected from the waste-contaminated zone. A coefficient α = 0.7 was observed for antimony along Factor 1, indicating an anticorrelation with other metal compounds. Factor 2 accounts for 11.16 % of the variability, with cadmium (Cd) showing a strong association (α=0.8). Notably, all compounds are correlated along Factor 2, except for antimony (Sb).

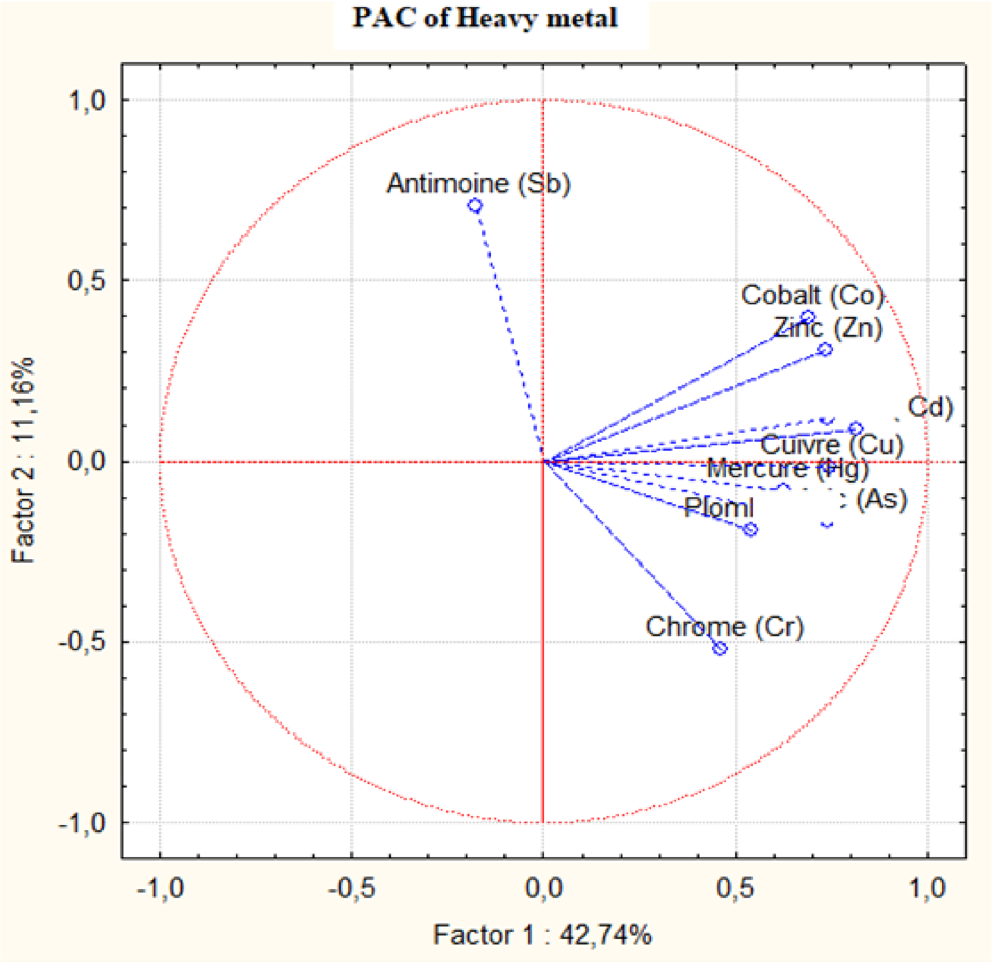

Figure 4a. Principal Component Analysis (PCA) of Heavy Metal

When sulphur is included in the analysis, PCA of heavy metals and sulfur (Figure 4b) indicates that the first two axes explain a total of 49.07 % of the variance. Factor 1 accounts for 38.85 % of the total variability. Antimony (Sb) shows a coefficient α = 0.7 along Factor 1, again demonstrating anticorrelation with other métal compounds. Factor 2 explains 10.22% of the variability, with cadmium (Cd) strongly associated (α = 0.8). Sulfur also shows an anticorrelation with other heavy metals (α = -0.35) and is not aligned with Factor 2.

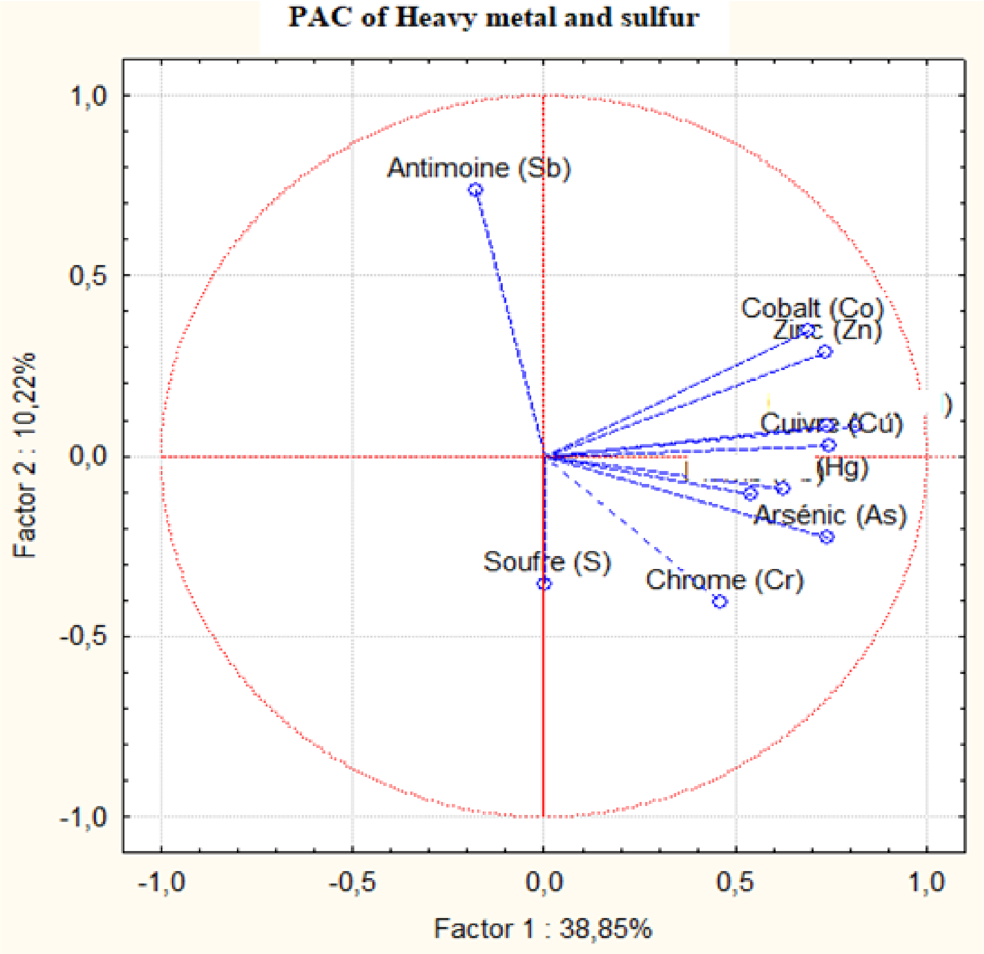

Figure 4b. Principal Component Analysis (PCA) of Heavy Metal and Sulfur

Aliphatic Hydrocarbons

The Principal Component Analysis (PCA) of aliphatic hydrocarbons (Figure 5) shows that the first two principal components (Factor 1 and Factor 2) account for a total variance of 92.87% in the dataset. Factor 1 explains 68.62 % of the total variability in aliphatic hydrocarbons contamination from the toxic waste-affected zone. A high coefficient (α = 0.9) was observed for the C10-C12 aliphatic hydrocarbons along Factor 1, suggesting an anticorrelation with other compounds. Factor 2 explains 24.25% of the total variance. A strong correlation (α = 1) was found for the C8-C10 aliphatic hydrocarbons along Factor 2, which did not include C10-C12 compounds, indicating a distinct behaviour from the compounds described in Factor 1.

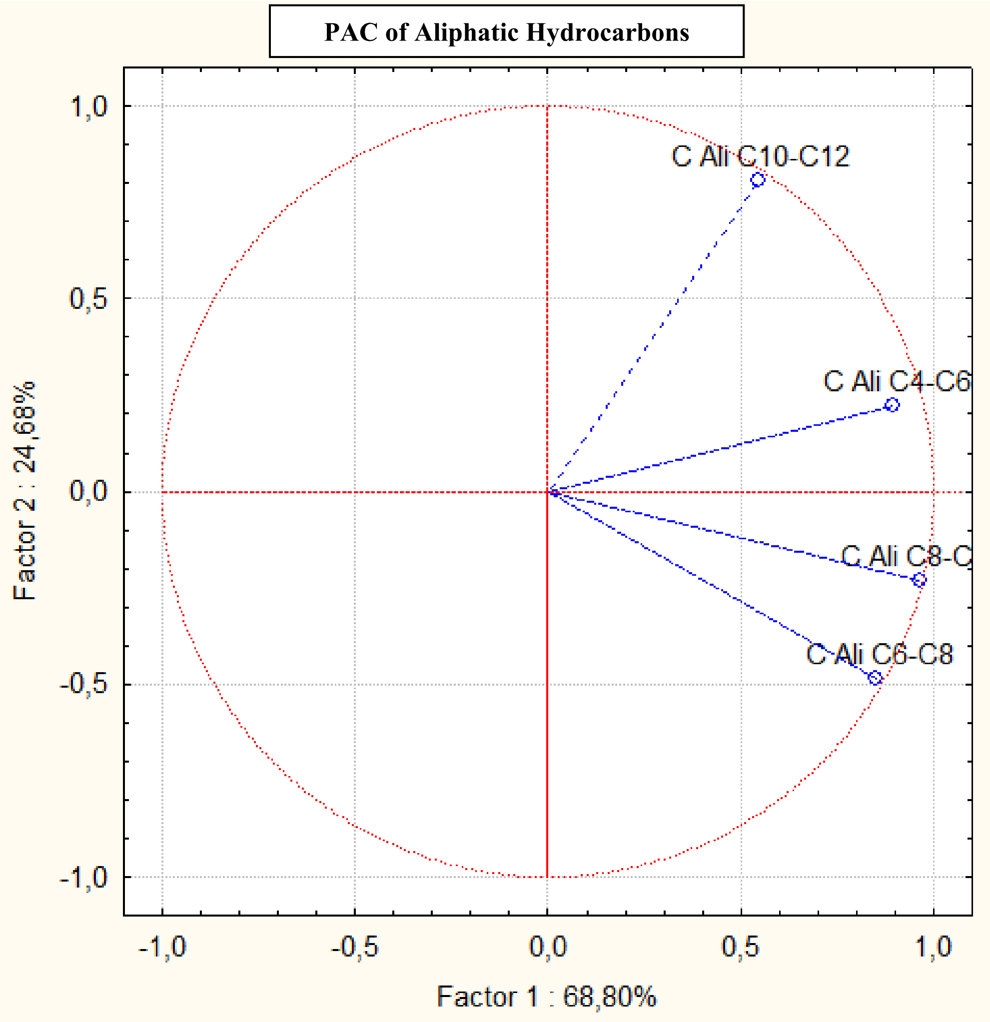

Figure 5. Principal Component Analysis (PCA) of Aliphatic Hydrocarbons

Linear Hydrocarbons

The PCA of linear hydrocarbons (Figure 6) reveals that the first two components contribute to 71.26% of the total variance. Factor 1 explains 49.88%, but no specific linear hydrocarbons compounds were clearly associated with this axis. Factor 2 accounts for 21.38% of the variance and shows strong negative correlations (α = -1) with C10-C12, C12-C16, C16-C21, and C35-C40 linear hydrocarbons.

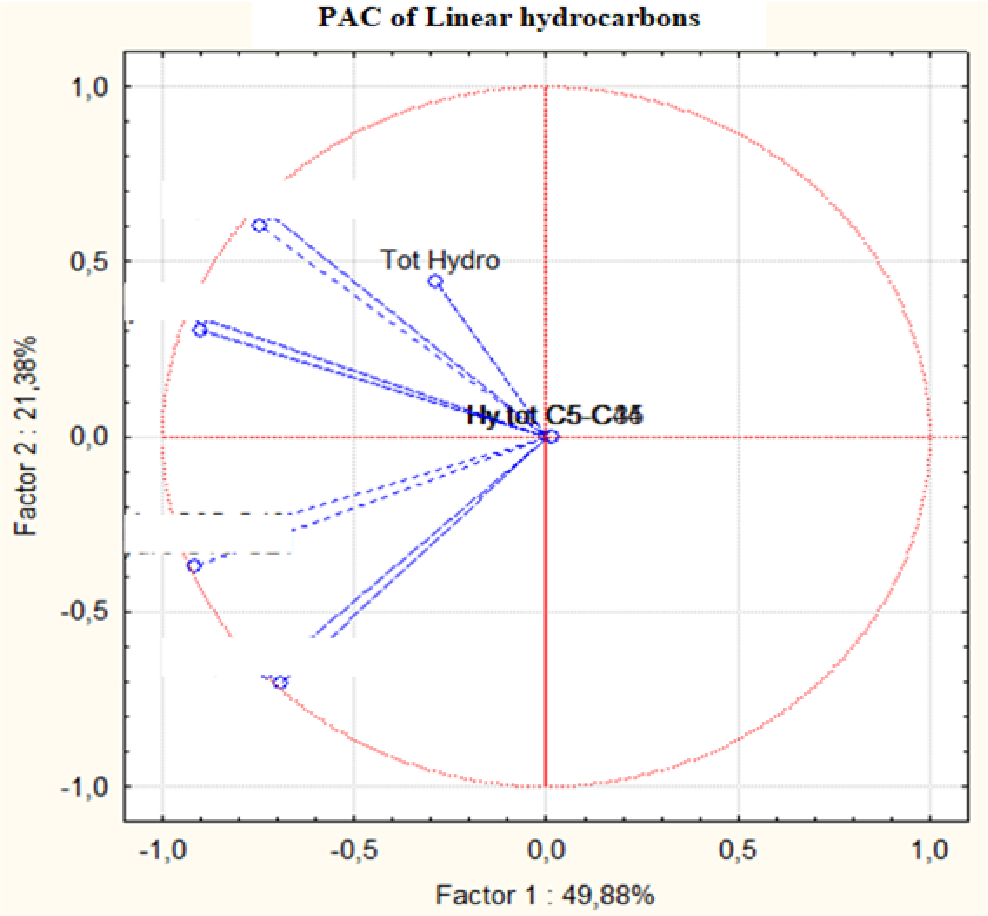

Figure 6. Principal Component Analysis (PCA) of Linear Hydrocarbons

Total Petroleum Hydrocarbons (TPH)

The PCA of Total Petroleum Hydrocarbons (TPH) (Figure 7) indicates that the first two components represent 68.74% of the total variance. Factor 1 explains 50.58% of the variability, but no individual TPH compound was notably associated with this axis. Any Total Petroleum Hydrocarbons (TPH) compound were found around Factor 1. Factor 2, which contributes 18.16% shows a strong negative correlation (α = -1) with C8-C10 TPH, indicating a distinct behaviour compared to the rest of the compounds.

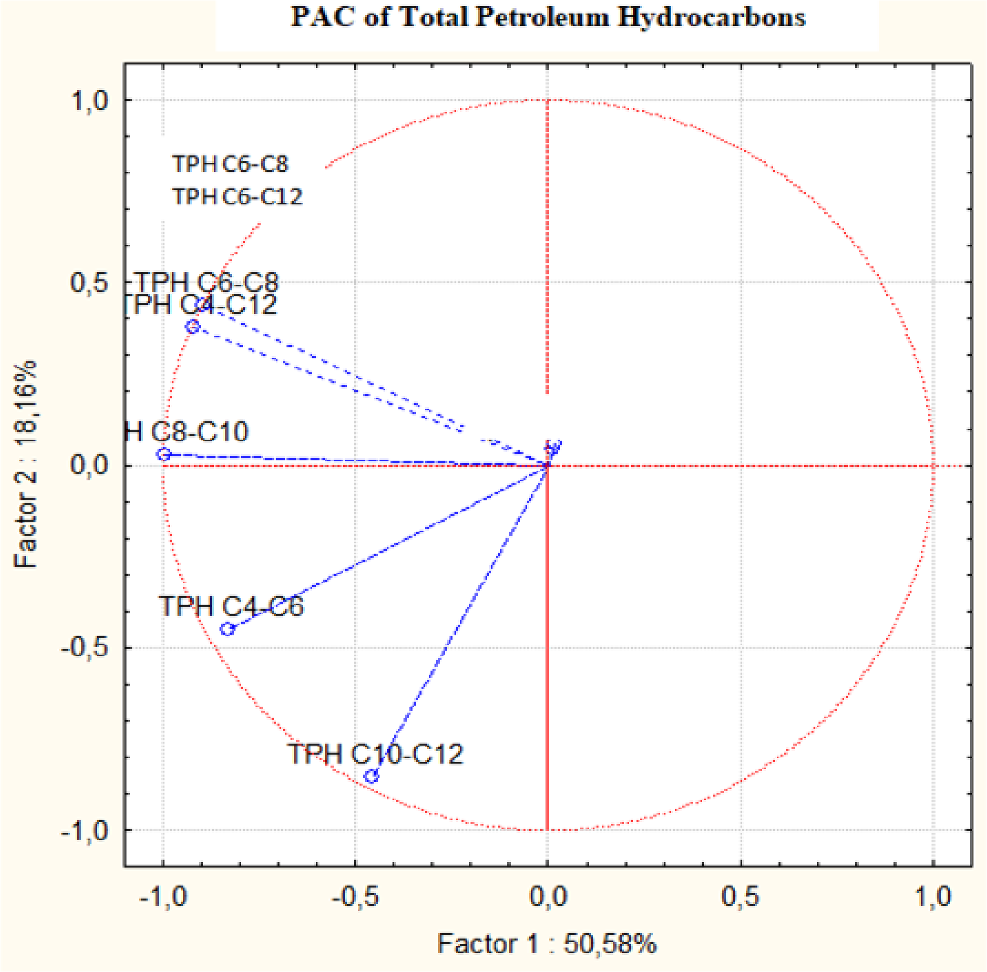

Figure 7. Principal Component Analysis (PCA) of Total Petroleum Hydrocarbons (TPH)

All Chemical Compounds in Toxic Waste

The PCA of all chemical compounds present in the toxic waste shows that the first two axes (Factor 1 and Factor 2) explain 49.7% of the total variance. Factor 1, accounting for 33.92%, includes compounds with strong negative correlations (α = -0.9), such as butylmercaptan. Several heavy metals were also found to be associated with this axis. Factor 2, representing 15.78%, shows very strong correlations (α = -1) with other compounds such as o-xylene, suggesting their dominant influence in the secondary component.

Discussion

This study considered various parameters for determining the geochemical composition of waste in general, and toxic waste in particular. According to the European Commission, the Guideline for Waste Centres, recently amended by Regulation (EU) No. 1357/2014 and Decision 2000/532/EC (later revised by Decision 2014/955/EU), constitutes the official European framework for assessing the hazardous nature of waste. The objective of the recent amendments regarding hazardous waste properties was to align with the new EU regulatory system on the classification and labelling of substances and mixtures, as introduced by Regulation No. 1272/2008, commonly referred to as the CLP Regulation (Classification, Labelling, and Packaging). This alignment seeks to harmonize both approaches as much as possible and to adopt the updated classification system that uses H-statements (Hxxx) instead of the older R-phrases (Rxx) (Flore et al., 2016). At the time of writing this document, a draft decree to transpose these texts into French law under the Environmental Code is under adoption, primarily relying on these European references. According to the European Waste Catalogue, the code for the toxic waste in Abidjan-after analyses-can be written as: 050407*, described as “waste containing hazardous substances from the processing of petroleum and the origin of combustion.

The naphtha from coking proposed for sale by the PMI firm had a high content in sulfur mercaptans. The company’s executives considered two options for refining this coking naphtha: (1) oxidation of mercaptans via the Merox process, and (2) washing with caustic sodium carbonate. In both cases, when coking naphtha is mixed with caustic sodium carbonate to capture the mercaptans, toxic residues are generated. The Merox process includes an essential second essential step that transforms these residues in disulfides, which are more stable and less harmful, through oxidation. This step usually requires a specialized facility. Trafigura initially planned to build a facility for the Merox process. One executive noted that this option "would be expensive, but would function." However, for unclear reasons, Trafigura abandoned the Merox method and opted for washing with caustic sodium carbonate instead-fully aware that this would produce toxic waste. Internal company emails confirm this. One such message explicitly states that terminals in the United States, Singapore, and Europe rejected caustic soda washings because local environmental protection agencies prohibit disposal of the resulting residues. Jorge Marrero, a senior Trafigura executive, sent an email to the company’s Ivorian subsidiary, Puma Energy, warning them of the imminent arrival of the ship and informing them of 528 m^3 of residues to be unloaded. The email clarified that, due to a Chemical Oxygen Demand (COD) greater than 2,000 mg/L, the toxic waste should not be classified as MARPOL waste, but rather as chemical residues. Marrero also described the waste as a “mixture of oil and caustic sodium carbonate with a high concentration of sulfur mercaptans."

According to geochemical analyses conducted at Wessling Laboratory in France, the main components of the toxic waste included: Polycyclics Aromatics Hydrocarbons (PAH), Volatile Aromatics Compound (VAC), Mercaptans and sulfur molecules, Heavy metal, Sulfur, Aliphatic Hydrocarbons, Linear hydrocarbons, and Total Petroleum Hydrocarbons (TPH). Principal Component Analysis (PCA) was used to describe these compounds in this study. The results of the laboratory analyses on samples of soil, water, air, sediments, mollusks, and fruits and vegetables collected from the affected sites are discussed herein.

The following recommendations aim to address and prevent violations of human rights and environmental protections committed by firms and factories around the world. All States must ensure that their legal frameworks allow for holding companies criminally liable as legal entities. They must also allocate sufficient resources to enable investigations and effective prosecution of corporate misconduct. Legal frameworks should be reviewed to ensure they contain appropriate provisions requiring companies to respect human rights and environmental standards across all their operations. These frameworks must also empower States to conduct investigations and prosecute criminal acts committed by companies abroad or those with cross-border consequences. The results of such legal assessments should be made publicly available. Firms must be legally obligated to demonstrate due diligence regarding human rights impacts across their operations and publish annual reports in this domain. Furthermore, enterprises must be legally required to disclose comprehensive information on any materials or substances in their possession or control that could affect public health or the environment.

Conclusion

This article presents the environmental impact of PAH-contaminated soil in the Abidjan district of Ivory Coast. While many PAH-contaminated sites around the world are legacies industrial activities between the 1960s and 1980s, in Ivory Coast-the location of this study-toxic waste became a major pollutant after causing the death of over 100 people and approximately 30,000 cases of intoxication. GC-MS analyses conducted at Wessling Laboratory in France on soil and water samples from 13 locations in the Abidjan district [Akouédo, Abobo, Abobo-Alépé road (Djibi village), Civile Prison Road (MACA), Industrial Zone of Koumassi, Port-Bouët - Vridi CAP Logistic (Rue Saint-Sylvestre)] shows that the sources of contamination are heterogeneous. Findings confirm that the toxic waste originated from the washing of naphtha from coking with caustic sodium carbonate by Trafigura abroad the Probo Koala vessel. Terminals in the United States, Singapore, and Europe had rejected such washings due to environmental regulations prohibiting the disposal of toxic waste residues resulting from this chemical process. Trafigura executives described the residue as a mixture of oil and caustic sodium carbonate with a high concentration of sulfur mercaptans. According to the European List of Waste, the code for the toxic waste analysed in Abidjan is: 050407*, which denotes waste containing hazardous substances from petroleum refining or combustion processes. The Probo Koala arrived at the port of Abidjan on Saturday, August 19, 2006. Trucks and drivers hired by the Tommy company were awaiting the vessel's arrival to unload the waste and operations began that afternoon. A complete mapping of all dumping sites has proven impossible. The fact that drivers dumped waste in multiple locations and subsequently fled made the identification of all affected sites difficult. A map containing the most widely accepted data-complied by UNOSAT (United Nations Operational Satellite Applications Programme) using information from Ivorian authorities, the European Union, and the United Nations Office for the Coordination of Humanitarian Affairs (OCHA)-identifies 18 known dumping points.

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Conflict of Interest: The authors reported no conflict of interest.

Data Availability: All data are included in the content of the paper.

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