Environmental Forensic Investigation in the Residential Neighborhood Volta Grande IV, Volta Redonda, RJ, Brazil, Using TPH and PAHs Analyses in Soil Samples

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Environmental Forensic Investigation in the Residential Neighborhood Volta Grande IV, Volta Redonda, RJ, Brazil, Using TPH and PAHs Analyses in Soil Samples

José C. R. Gouvêa Jr.[1], Fernando Simão e Silva[2], Reginaldo A. Bertolo[1], Tiago R. Moura[2], Stephen Emsbo-Mattingly[3]

[1]CEPAS—Groundwater Research Center, University of Sao Paulo, IGc-USP, Sao Paulo, Brazil
[2]NewFields, Rio de Janeiro, Brazil
[3]NewFields, Rockland, Massachusetts, USA
Email: jose.gouvea@usp.br

Abstract

This article presents the results of a forensic investigation concerning the origin of hydrocarbons detected in the subsurface soil of the residential neighborhood Volta Grande IV, Volta Redonda, RJ, Brazil. Previous investigations identified several areas with concentrations of volatile organic compounds (VOCs) and polycyclic aromatic hydrocarbons (PAHs) above the Brazilian regulatory standards of CONAMA 420/2009 within the study area. Concern was raised that these hydrocarbons might be derived from local steel mill wastes. This forensic investigation determined that the VOCs in the residential soil are associated with gasoline and possibly diesel fuel oil releases into the subsurface soils that are not associated with the steel mill waste. The PAHs in residential subsurface soil generally fell below background concentrations and are likely associated with regional soot. The PAHs in the three samples with concentrations above background (out of a total of thirty-six samples) exhibit compositional features similar to coal byproducts, such as tar and coke, possibly attributable to the steel mill operation. This work discusses the geoforensic data and chemical signatures that support these findings.

Keywords

Environmental Forensic Investigation, Hydrocarbons Fingerprinting, Polycyclic Aromatic Hydrocarbons

1. Introduction

The expansion of urban areas is a recurring problem in many countries. The populational growth increases residential expansion areas, which sometimes occupy territories previously occupied by other use, such as rural or industrial [1]. Volta Grande IV is a residential neighborhood in the municipality of Volta Redonda (RJ, Brazil), known as "the city of steel" (Figure 1). This residential neighborhood was built in 1995 in an area formerly occupied by the Companhia Siderúrgica Nacional (CSN), an originally national steelworks company; the plant was built in 1940 by the Brazilian government and privatized in 1993. The Volta Grande IV area was donated to the employees' union in 1998; the area was previously occupied with contractor's sheds and temporary storage of materials from various steelmaking processes.

Before the establishment of the residential neighborhood (between 1978 and 1993), a blend of steel slag with by-products of carbon-chemical origin neutralized with calcium carbonate was buried in a portion of the area. Part of this material remained in the site and was covered by clayey soil. The area was leveled and the houses were then built. Previous studies detected the presence of hydrocarbons in the soil, especially Polycyclic Aromatic Hydrocarbons (PAHs) above the Brazilian regulatory standards of CONAMA 420/2009 [2]. CSN conducted a geoforensic investigation to delineate the location of the waste from the steelworks company, in which integrated forensic hydrocarbons fingerprinting and data interpretation techniques were used to characterize the chemical compositions.

There is an increasing trend of employing environmental chemistry techniques to determine the source(s) and fate of the contaminants and, in some cases, to determine their age or each source's share. Environmental forensic techniques and databases were originally developed in the oil industry and were initially applied to environmental work with the Exxon Valdez incident. Since then, the techniques have been refined for identification of both petrogenic and pyrogenic materials [3]-[9].
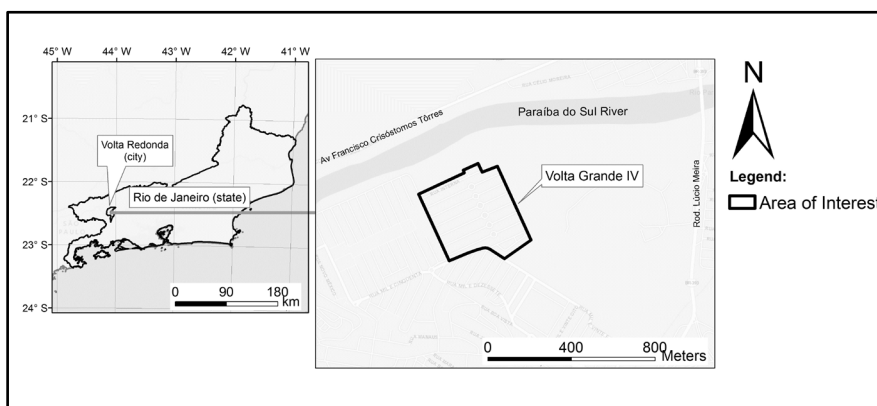

Figure 1. Location of the study area—Volta Grande IV neighborhood—in Volta Redonda (RJ).

Chemical fingerprinting and diagnostic source ratios helped compare the hydrocarbon patterns of residential soils with regional background, soils with suspected steel mill residues (dark soil), and selected reference samples. The application of geoforensic techniques is recent and rare in Brazil. For this reason, this work also aims to contribute with the development and application of the geoforensic tools in Brazil.

Volta Redonda municipality is geologically inserted into the central segment of the Continental Rift of Southeastern Brazil (CRSB), within the area of Volta Redonda sedimentary basin [10]. The basin's basement, as well as all other domains of CRSB, is located over Proterozoic/Eopaleozoic terrains of Ribeira Belt [11]. All those basement units occur invariably in the form of elongated bodies, in the NE-SW direction, following the regional trend of Ribeira Belt (Figure 2).

At least two main sedimentary depocenters are present in the Volta Redonda basin region, controlled by tectonic events. The most expressive depocenter is called Graben Usina, where the urban center and industrial complex of Volta Redonda are located.

There are other important areas filled with quaternary sediments along the Paraíba do Sul river channel, such as the area where Volta Grande IV neighborhood is located, specifically in the floodplain of Paraíba do Sul River. The area was grounded to allow for urban use.

Outcropping sedimentary units are composed by sandy, muddy and gravelly litofacies, due to recent fluvial dynamics. From a morphostratigraphic standpoint, several levels of quaternary-age sedimentation are observed, from lateral accretion bars and other architectural elements related to current Paraiba do Sul river sedimentary dynamics to elevated terraces with older ages.
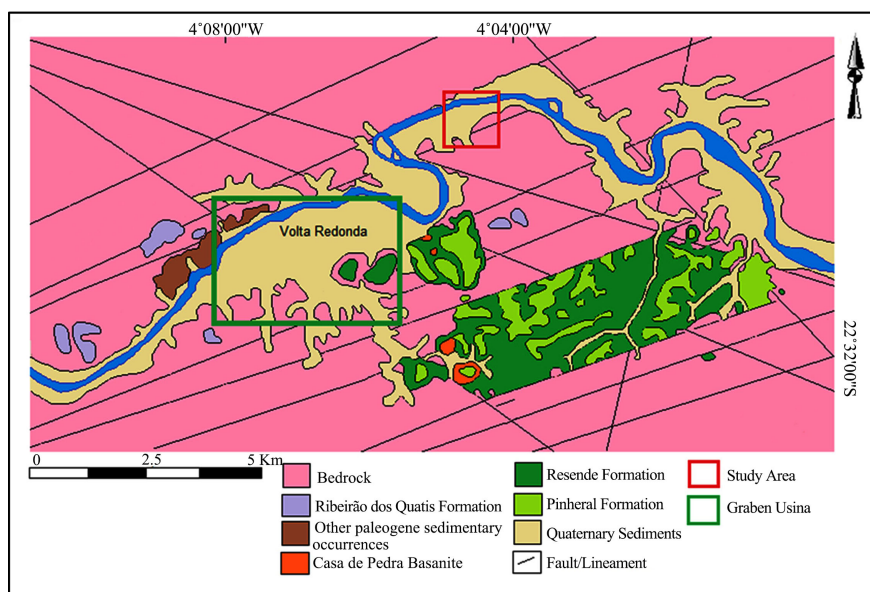

Figure 2. Geological map of Volta Redonda municipality and surroundings (Negrão *et al.*, 2005).

Geophysical studies and soil samples collected during investigative drillings show that the thickness of sediments over the bedrock in the study area varies between 8 to 12 meters. In this context, the several previously environmental investigations carried out in the study area, focused on the shallow geological intervals, on the deep of occurrence of quaternary sediments and in the landfill layer placed over these sediments.

2. Materials and Methods

Environmental geoforensics techniques are most commonly used to determine or assist in determining the age and potential source(s) of contamination. The age and source of contamination should be considered critical lines of evidence in the Conceptual Site Model (CSM) [4] [5] [6] [7] [9]. The diagnostic fingerprinting techniques include several lines of evidence. First, high resolution hydrocarbon fingerprints are generated to classify the dominant hydrocarbon sources using semi-quantitative comparison to reference samples from the study area or a forensic reference material library. Second, the concentrations or relative abundances of diagnostic hydrocarbon compounds, such as saturated hydrocarbons, PAHs, and geochemical biomarkers help distinguish specific fossil fuel products and mixtures. Third, diagnostic ratios of "source-specific marker" compounds help document pattern changes due to environmental weathering or mixing with other hydrocarbon sources and/or "ambient background" [3] [7] [8]. The hydrocarbon analyses were conducted in accordance with EPA methods that were enhanced for forensic purposes. The primary enhancements included lower detection limits, additional quality control samples, and multilevel calibrations for diagnostic hydrocarbon analytes. The methods meet or exceed the quality control provisions of comparable standard EPA methods [3] [4] [5] [7] [9] [12].

2.1. Sample Collection

Sampling locations were selected based on previous studies conducted in 2012 and 2014. Based on visual inspection and TPH concentrations, the area was divided into four different subareas of interest, and sampling locations were defined in order to be representative for each of them.

Thirty-six (36) soils samples were collected from the study area in February and March 2015 for hydrocarbon analysis. The spatial domains included the primary areas of interest. The sampling locations are shown in Figure 3, and Table 1 presents the sampling dates, depths and analyzed parameters. "Landfill" samples reflect the subsurface soils potentially impacted by coal byproducts, solvents, and wastes from the steel mill operation. "Dark Soil" samples were collected in a contiguous zone of dark soil at the northeastern boundary of the residential area, with the likely presence of high content of coal byproduct from the steel mill. "Residential" samples represent soils from the portion of the neighborhood previously occupied by sheds and warehouses, therefore less likely to

Table 1. Analyzed parameters, sampling dates and depths for each soil sample.

Sample ID	Sampling Interval	Sampling Depth (m)	Domain	Sampling Date	Analytical Parameters		
					TPH and TPH Fingerprint	PAH Fingerprint	PAH Fingerprint and Biomarkers
BG01	S	0.50	Background	2/28/2015	X	X	X
BG02	S	0.50	Background	2/28/2015	X	X	X
BG03	S	0.50	Background	2/28/2015	X	X	X
S11	D	1.00	Dark Soil	2/28/2015	X	X	X
S12	D	1.00	Landfill	3/2/2015	X	-	-
S13	D	1.00	Landfill	3/2/2015	X	-	-
S14	S	0.50	Dark Soil	3/2/2015	X	X	X
S15	S	0.50	Dark Soil	3/2/2015	X	X	X
S15	D	1.00	Dark Soil	3/2/2015	X	X	X
S16	S	0.50	Dark Soil	3/2/2015	X	X	X
S16	D	1.00	Dark Soil	3/2/2015	X	X	X
S17	S	0.50	Dark Soil	3/2/2015	X	X	X
S17	D	1.00	Dark Soil	3/2/2015	X	X	X
S18	S	0.50	Residential	2/26/2015	X	X	-
S18	D	1.00	Residential	2/26/2015	X	X	-
S19	S	0.50	Residential	2/26/2015	X	X	-
S19	D	1.00	Residential	2/26/2015	X	X	-
S20	S	0.50	Residential	2/27/2015	X	X	-
S20	D	1.00	Residential	2/27/2015	X	X	-
S21	S	0.50	Residential	2/27/2015	X	X	X
S21	D	1.00	Residential	2/27/2015	X	X	X
S22	S	0.50	Residential	2/25/2015	X	-	-
S22	D	1.00	Residential	2/25/2015	X	-	-
S23	S	0.50	Residential	2/27/2015	X	-	-
S24	S	0.50	Residential	2/25/2015	X	-	-
S24	D	1.00	Residential	2/25/2015	X	-	-
S25	E	1.50	Residential	2/27/2015	X	X	-
S25	D	1.00	Residential	2/27/2015	X	X	-
S25	S	0.50	Residential	2/27/2015	X	X	-
S26	S	0.50	Residential	2/26/2015	X	X	-
S26	D	1.00	Residential	2/26/2015	X	X	-
S27	E	1.50	Residential	2/26/2015	X	-	-
S27	D	1.00	Residential	2/26/2015	X	-	-
S27	S	0.50	Residential	2/26/2015	X	-	-

Legend: Shallow (S), deep (D), and native (E) samples represent depths of approximately the 0.5 m, 1.0 m, and 1.5 m respectively.
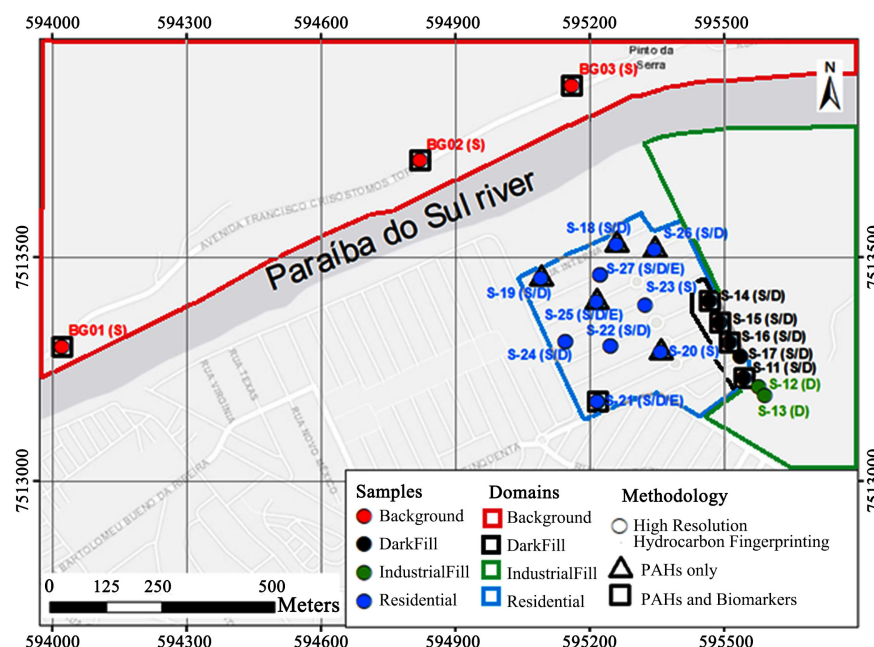
Figure 3. Soil sample locations for hydrocarbon analysis in Volta Grande IV neighborhood.

have buried wastes. "Background" samples represent regional soil conditions from the northern side of the Paraíba do Sul River. Shallow (S), deep (D), and native (E) samples represent depths of approximately the 0.5 m, 1.0 m, and 1.5 m respectively, according to the stratigraphic characteristics observed in the soil boring samples by the field team.

The samples were collected using direct push methods. Samples were transferred from the sampling tube to the appropriate container with a stainless steel shovel; sampling gear was decontaminated with detergent and water, rinsed with water, rinsed with deionized water, left to dry naturally, sprayed with deionized water and wrapped with aluminum foil before being reused. Samples were shipped via overnight courier to Alpha Laboratories (Mansfield, MA) for traditional environmental and forensic hydrocarbon testing.

2.2. PAH Quantification and Fingerprinting

PAH compounds, especially high molecular mass PAHs and their alkylated homologues, are relatively stable. Therefore, the distribution patterns and the diagnostic ratios of these PAHs compounds can be used as fate indicators of hydrocarbons in the environment and hydrocarbons source markers [3] [13] [14] [15] [16] [17]. A modified EPA Method 8270D [18] determined the concentrations of 51 semi-volatile compounds or compound groups, included Priority Pollutant PAHs, alkylated PAHs, and sulfur-containing aromatics. These compounds provide specific information which can be used to match the potential origin/source of PAHs. Following solvent extraction with dichloromethane (DCM) the samples extracts were analyzed by GC/MS selected ion monitoring (SIM) [3] [7] [8].

3. Results and Discussion

Laboratory reference samples provide examples of hydrocarbon signatures representing the potential hydrocarbon products in the study area for comparison purposes. These laboratory data provide both qualitative and quantitative lines of forensic evidence as discussed below.

3.1. Dominant Hydrocarbon Types

The high-resolution hydrocarbon fingerprints demonstrate the dominant hydrocarbon types in each sample. The concentrations of TPH C_9-C_{44} in the ambient background soil samples range from 30 mg/kg to 525 mg/kg (Table 2, Figure 4(a)). Several sources may contribute to TPH concentrations in background samples, including plant debris, naturally occurring oil and coal, use of vehicles (deposition of soot and fuel leakings) and urban runoff. These sources may cause concentrations of several thousand mg/kg in soil and sediment [19].
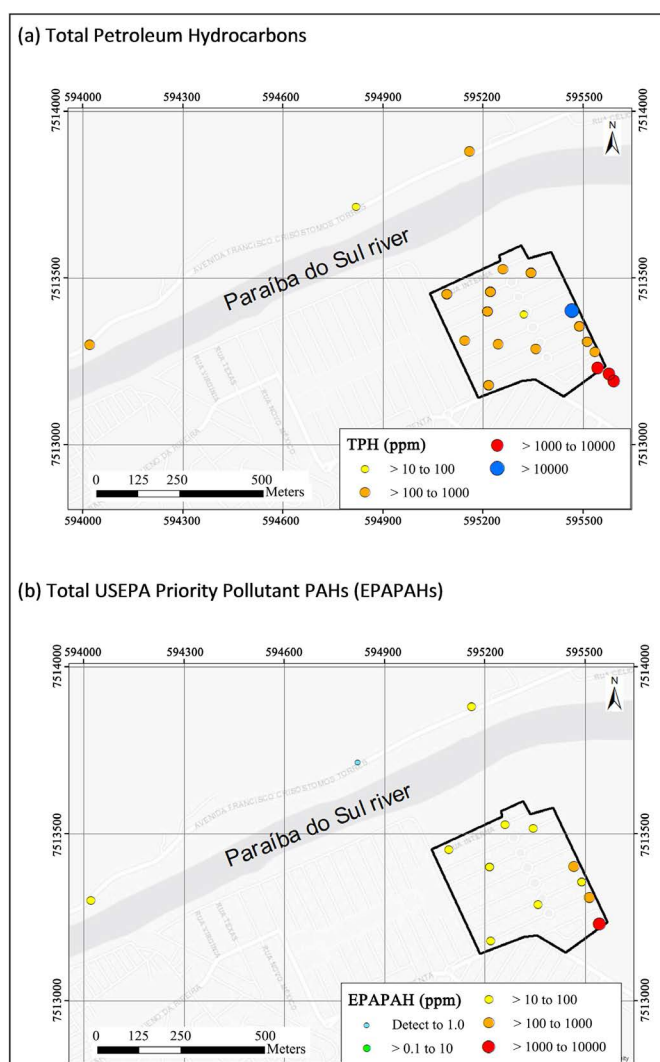

Figure 4. Distribution of total petroleum hydrocarbons and total priority pollutant PAHs from soil samples.

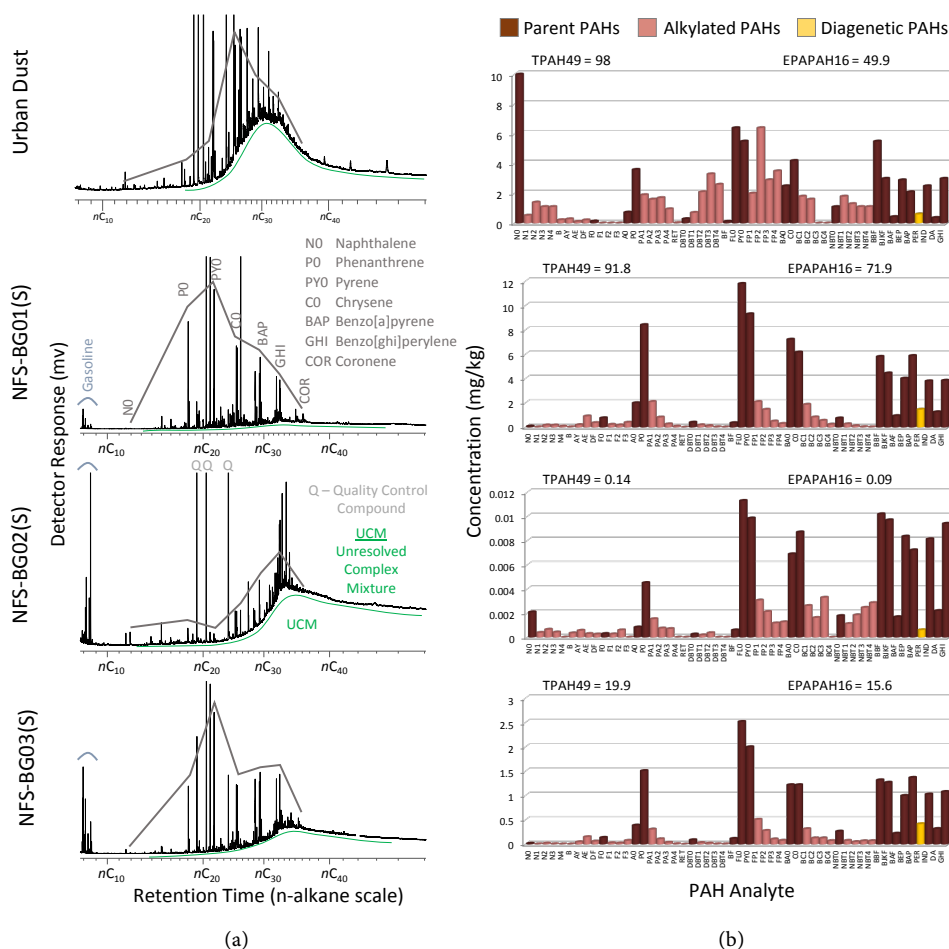Table 2. Dominant saturated hydrocarbon patterns—qualitative analysis.

Sample	Domain	C_9-C_{44} TPH (mg/kg)	1	2	3	4	5	6	7
NFS-BG01(S)	Background	525	-	-	-	-	-	-	++
NFS-BG02(S)	Background	30	-	-	-	-	+	-	-
NFS-BG03(S)	Background	288	-	-	-	-	+	-	+
NFS-11(D)	Dark Soil	7280	-	-	-	-	-	++	-
NFS-12(D)	Landfill	6910	-	-	-	++	-	-	-
NFS-13(D)	Landfill	8210	-	-	-	++	-	-	-
NFS-14(S)	Dark Soil	62	-	-	-	-	+	-	+
NFS-14(D)	Dark Soil	11,600	-	-	-	++	-	-	+
NFS-15(S)	Dark Soil	252	-	-	+	+	-	-	++
NFS-15(D)	Dark Soil	554	-	-	-	-	-	-	++
NFS-16(S)	Dark Soil	114	-	-	-	-	-	-	+
NFS-16(D)	Dark Soil	574	-	-	-	-	-	-	++
NFS-17(S)	Dark Soil	54	-	-	-	-	-	-	+
NFS-17(D)	Dark Soil	111	-	-	-	-	-	-	+
NFS-18(S)	Residential	120	-	-	-	-	+	-	+
NFS-18(D)	Residential	97	-	-	-	-	+	-	+
NFS-19(S)	Residential	130	-	-	-	-	+	-	+
NFS-19(D)	Residential	223	-	-	-	-	+	-	+
NFS-20(S)	Residential	49	-	-	-	-	-	-	-
NFS-20(D)	Residential	332	-	-	-	-	-	-	+
NFS-21(S)	Residential	43	-	-	-	-	-	-	+
NFS-21(D)	Residential	262	-	-	-	-	+	-	+
NFS-21(D) LD	Residential	217	-	-	-	-	+	-	+
NFS-21(E)	Residential	562	-	-	-	-	+	-	+
NFS-22(S)	Residential	65	-	-	-	-	-	-	+
NFS-22(S) LD	Residential	72	-	-	-	-	-	-	+
NFS-22(D)	Residential	147	-	-	-	-	+	-	+
NFS-23(S)	Residential	33	-	-	-	-	-	-	+
NFS-24(S)	Residential	102	-	-	-	-	-	-	+
NFS-24(D)	Residential	65	-	-	-	-	-	-	++
NFS-25(S)	Residential	133	-	-	-	-	+	-	+
NFS-25(D)	Residential	156	-	-	-	-	+	-	+
NFS-25(E)	Residential	163	-	-	-	-	+	-	+
NFS-26(S)	Residential	199	-	-	-	-	-	-	+
NFS-26(D)	Residential	627	+	+	+	-	+	-	+
NFS-27(S)	Residential	296	-	-	-	-	-	-	+
NFS-27(D)	Residential	124	-	-	-	-	+	-	+
NFS-27(E)	Residential	146	-	-	-	-	+	-	+
Crude Oil	Reference	520,000	+	+	+	+	+	-	-

Legend: + detection; ++ dominant concentration; 1-Gasoline Range C_8-C_{12}; 2-Kerosene Range C_9-C_{14}; 3-Diesel Range C_9-C_{28}; 4–Lube Range C_{20}-C_{40}; 5-Pavement Range C_{25}-C_{44}; 6-Tar C_{10}-C_{40} Parent PAHs; 7-Soot/Coke C_{18}-C_{40} Parent PAHs.

The hydrocarbon fingerprint in the background samples consists predominantly of pyrogenic 3- to 6-ring PAHs with varying proportions of heavy hydrocarbons (C_{20+}) comprising the Unresolved Complex Mixture (UCM). These patterns are consistent with used asphalt pavement and soot that accumulate along roadsides and in urban dust. The combustion byproducts are dominated by parent PAHs that include naphthalene (N0), phenanthrene (P0), pyrene (PY0), chrysene (C0), benzo(a)pyrene (BAP), and benzo(g,h,i)perylene (GHI) (**Figure 5**).

The background samples also feature varying proportions of light range hydrocarbons eluting before n-C_{10}. These peaks, as indicated on the left corner of the chromatograms on **Figure 5**, suggest the presence of gasoline.

The concentrations of TPH C_9-C_{44} in the landfill soil samples range from 6910 mg/kg to 8210 mg/kg (**Table 2**, **Figure 4(a)**). These concentrations are significantly higher than the background soil samples. The hydrocarbon fingerprints are also different from the background soil samples. They are dominated by a heavy UCM eluting between n-C_{20} and n-C_{40} with a maximum eluting around n-C_{30} (**Figure 6**), while background samples are dominated by hydrocarbons

Figure 5. Hydrocarbon patterns of urban dust and ambient background soil samples generated by high resolution hydrocarbon fingerprinting (a) and forensic PAH (b) methods.
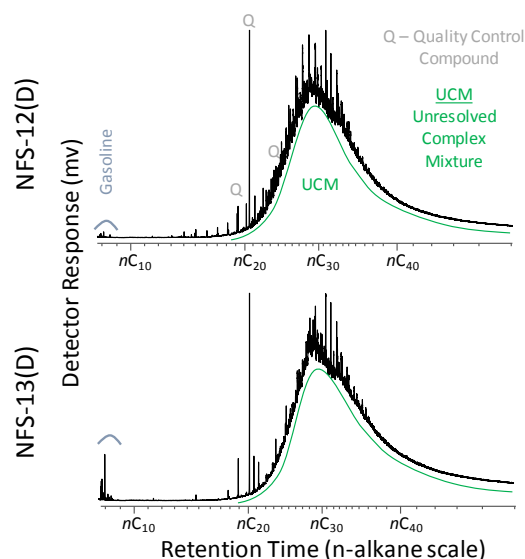
Figure 6. Hydrocarbons patterns in landfill samples generated by high resolution hydrocarbon fingerprinting.

around n-C_{20} (Figure 5). These patterns are consistent with automotive lubricating oil (Figure 5—"Urban Dust") commonly observed in urban dust due to emissions from cars. These heavy mineral oil patterns were not observed in the residential samples; therefore, the landfill samples were not characterized for PAHs.

The concentrations of TPH C_9-C_{44} in the dark soil samples range from 54 mg/kg to 252 mg/kg in the shallow depth intervals and 111 mg/kg to 11,600 mg/kg in the deeper intervals (Table 2, Figure 4(a)). The two samples with the highest TPH concentrations exhibit distinct high-resolution hydrocarbon fingerprints. Sample NFS-11(D) contains 7280 mg/kg TPH C_9-C_{44} comprised of pyrogenic 2- to 6-ring PAHs dominated by N0 with a minimal UCM. This pattern is consistent with coal tar (Figure 7).

Sample NFS-14(D) contains 11,600 mg/kg TPH C_9-C_{44} dominated by middle and heavy range UCMs mixed with low proportions of pyrogenic 3- to 6-ring PAHs (Figure 8). This pattern is consistent with light motor oil or cutting oil mixed with asphalt and soot, as described in previous studies [3] [4] [5].

The remaining dark soil samples, like NFS-15(S), NFS-15(D), and NFS-16(D), present significantly lower concentrations and contain pyrogenic 3- to 6-ring PAHs with lower proportions of heavy UCMs (Figure 9). The dark soil samples also feature varying proportions of light range hydrocarbons eluting before n-C_{10}, which suggest the presence of gasoline residues, which are consistent with previous studies [6] [20]. Therefore, the dark soil samples indicate a mixture of steel mill residues and common urban pollution.

The residential samples are also consistent with the background soils and exhibit little distinction by depth. The concentrations of TPH C_9-C_{44} range from 33 mg/kg to 296 mg/kg in the shallow fill, 65 mg/kg to 627 mg/kg in the deeper fill,

and 146 mg/kg to 562 mg/kg in the deepest depth interval representing the native soil (Table 2, Figure 4(a)). The dominant hydrocarbon patterns among residential soil consist of pyrogenic 3- to 6-ring PAHs with lower proportions of heavy UCMs (Figure 10).

These patterns generally resemble the concentration and compositional features of the background samples and are attributed to common urban soot and used pavement (Figure 6) [3] [4] [5]. Few samples, like NFS-18(S), NFS-19(D), NFS-25(D) exhibit low abundances of normal alkanes and middle weight UCMs in the n-C_{15} to n-C_{28} range suggesting the presence of trace diesel fuel. Sample NFS-26(D) likely contains some coal as evidenced by normal alkanes and UCM eluting in the n-C_{10} to n-C_{35} range. The residential soil samples also feature varying proportions of light range hydrocarbons eluting before n-C_{10} (Figure 11), which suggest the presence of gasoline residues.
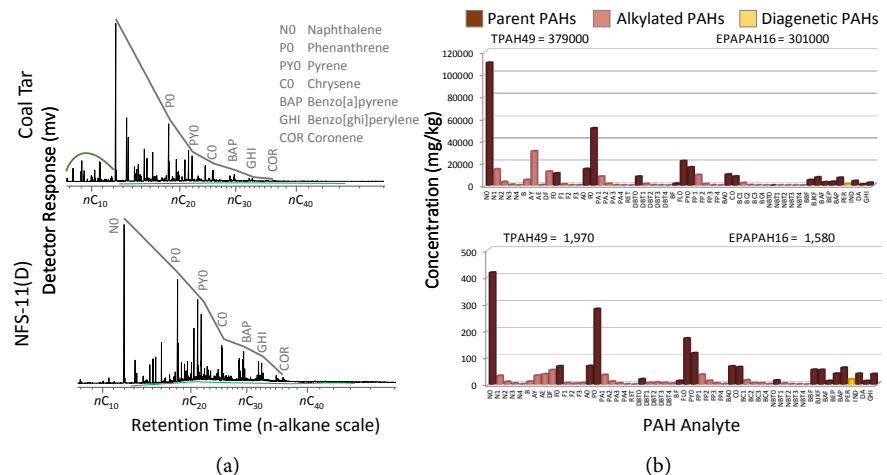

Figure 7. Hydrocarbons patterns of coal tar (reference) and dark soil samples generated by high resolution hydrocarbon fingerprinting (a) and forensic PAH (b) methods.
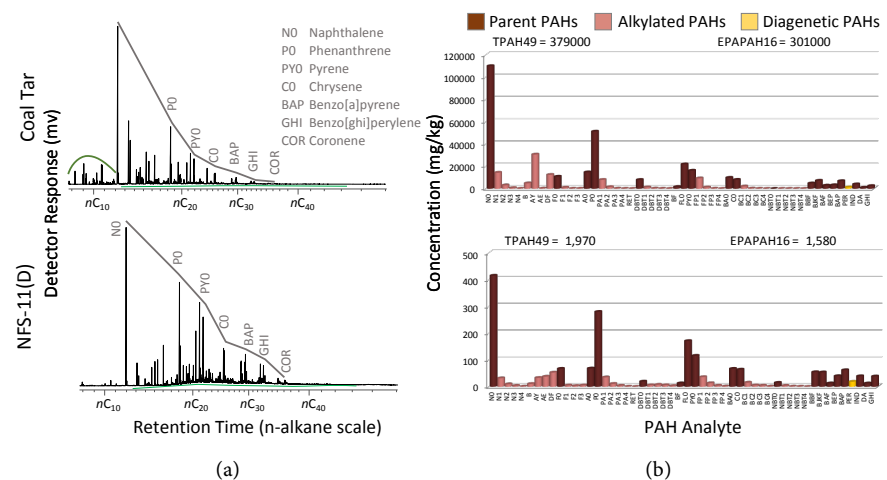

Figure 8. Hydrocarbons patterns of pitch and pavement (references) and dark soil samples generated by high resolution hydrocarbon fingerprinting (a) and forensic PAH (b) methods.
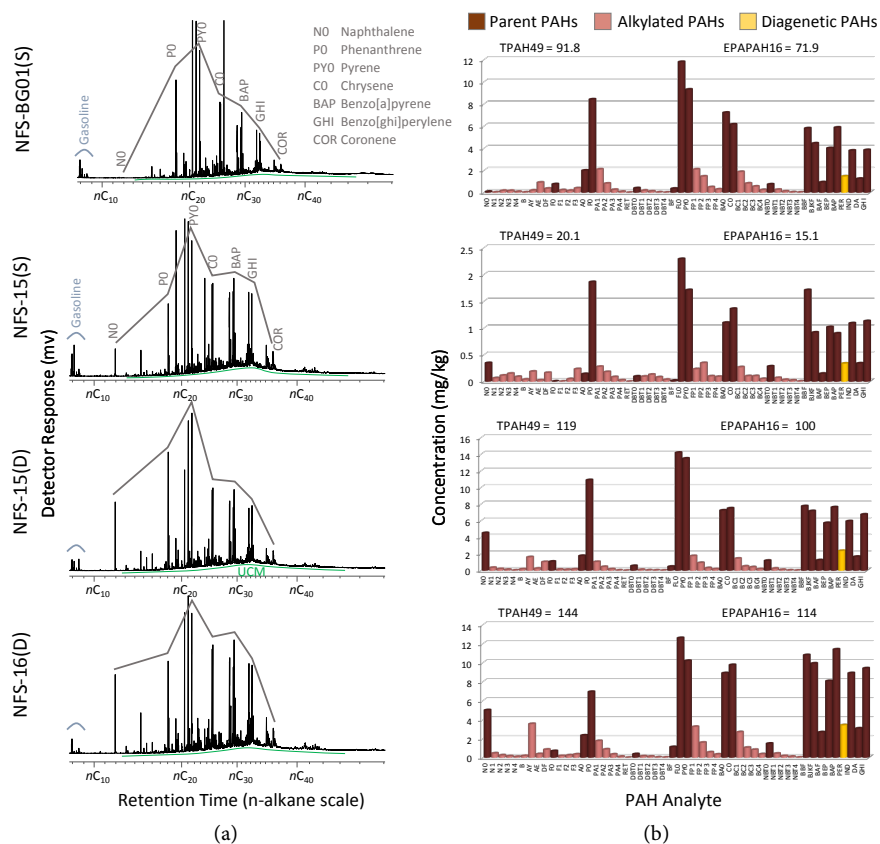
Figure 9. Hydrocarbons patterns in background and dark soil samples generated by high resolution hydrocarbon fingerprinting (a) and forensic PAH (b) methods.
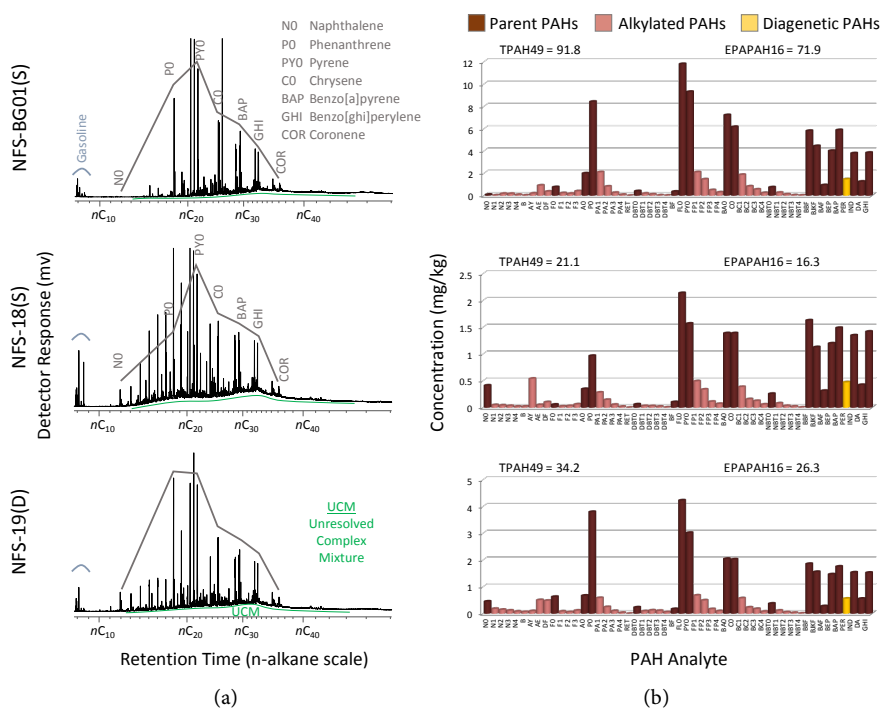

Figure 10. Hydrocarbons patterns in background and residential soil samples generated by high resolution hydrocarbon fingerprinting (a) and forensic PAH (b) methods.
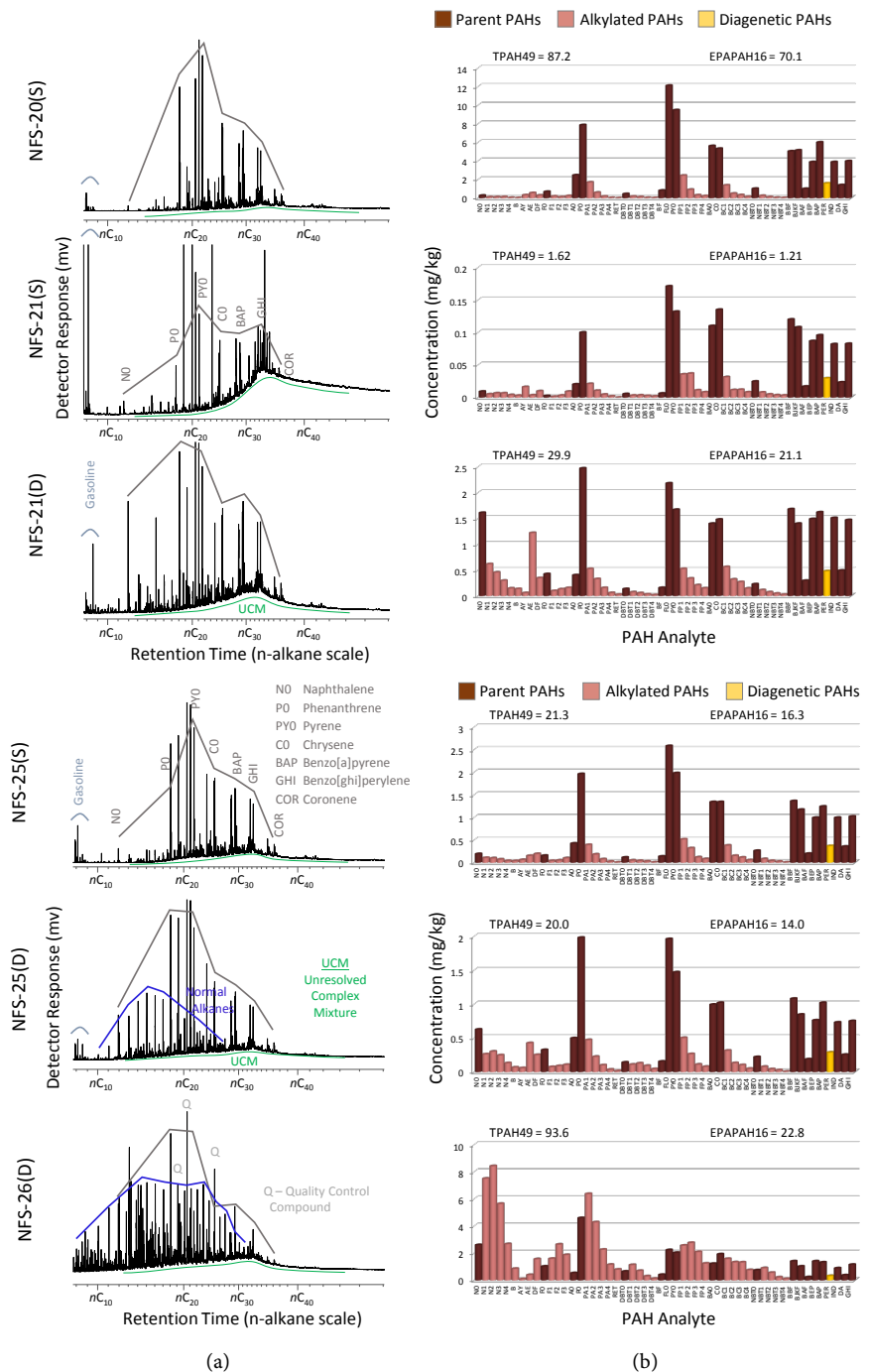
Figure 11. Hydrocarbons patterns in residential soil samples generated by high resolution hydrocarbon fingerprinting (a) and forensic PAH (b) methods.

Collectively, the dominant hydrocarbon fingerprints of residential soil samples resemble the concentration and compositional features of the background samples mixed with isolated residues of common petroleum products likely used by the local residents and businesses. In order to resemble residues from CSN activity, dominant hydrocarbon fingerprints should follow a pattern similar to coal tar.

3.2. PAH Fingerprints

The PAH fingerprints help identify the presence of independent petroleum and combustion signatures at lower concentrations than can be detected in the high-resolution hydrocarbon fingerprints, because the analytical method minimizes many interferences. The PAH signatures are evaluated in terms of concentration and composition. For example, the total concentrations of the 16 EPA Priority Pollutant PAHs in the background samples range from 0.092 mg/kg to 72 mg/kg (Table 3, Figure 4(b)).

Table 3. PAH and hopane features.

Sample	Domain	EPAPAH16 (mg/kg)	Hopane (mg/kg)	N0 P0	FL0 PY0	(BBF + BJKF) BAP	DBT2 PA2	HOP GHI	Description
NFS-BG01(S)	Background	72	0.075	0.001	1.27	1.74	0.15	0.020	Ambient Soil: Pyrogenic 3- to 6-Ring PAHs
NFS-BG02(S)	Background	0.092	0.0061	0.023	1.15	2.76	0.49	0.644	Ambient Soil: Pyrogenic 3- to 6-Ring PAHs
NFS-BG03(S)	Background	16	0.13	0.001	1.26	1.89	0.19	0.119	Ambient Soil: Pyrogenic 3- to 6-Ring PAHs
NFS-11(D)	Landfill	1,583	2.0	0.262	1.47	1.75	0.71	0.050	Ambient Soil with Coal Tar Residue
NFS-14(D)	Dark Soil	136	10	0.057	1.18	1.63	0.44	1.246	Ambient Soil with Coke Possible
NFS-15(S)	Dark Soil	15	0.16	0.023	1.34	2.92	0.72	0.138	Ambient Soil
NFS-15(D)	Dark Soil	100	0.23	0.045	1.05	1.96	0.18	0.034	Ambient Soil with Coke Possible
NFS-16(D)	Dark Soil	114	0.17	0.044	1.24	1.82	0.14	0.018	Ambient Soil with Coke Possible
NFS-18(S)	Residential	16	na	0.025	1.36	1.85	0.21	na	Ambient Soil
NFS-19(D)	Residential	26	na	0.017	1.40	1.94	0.49	na	Ambient Soil
NFS-20(D)	Residential	70	na	0.004	1.28	1.70	0.19	na	Ambient Soil
NFS-21(D)	Residential	21	0.10	0.076	1.31	1.90	0.17	0.071	Ambient Soil
NFS-21(D) Lab Dup	Residential	22	0.077	0.074	1.30	1.73	0.14	0.042	Ambient Soil
NFS-21(S)	Residential	1.2	0.016	0.008	1.30	2.38	0.32	0.199	Ambient Soil
NFS-25(D)	Residential	14	na	0.045	1.33	1.89	0.57	na	Ambient Soil
NFS-25(S)	Residential	16	na	0.012	1.30	2.04	0.21	na	Ambient Soil
NFS-26(D)	Residential	23	na	0.114	1.10	1.83	0.16	na	Ambient Soil
Crude Oil	Lab Reference	1164	150	0.550	2.69	nd	2.7	nd	Petrogenic 2- to 4-Ring PAHs

Legend: na—not analyzed; nd—not detected.

As noted previously, the compositional patterns of the background soils consist of pyrogenic 3- to 6-ring PAHs (Figure 5). Combustion and carbonization processes preferentially destroy the alkylated PAHs (light red histogram bars) and create residues that are enriched in parent PAHs (dark red histogram bars) [3] [4] [5] [21] [22] [23] [24], as evidenced by the pattern differences between fossil fuels (e.g., coal, diesel, and pavement) and pyrogenic byproducts (e.g., coal tar, pitch, and soot from urban dust) (Figure 5, Figure 7 and Figure 8).

As a point of reference, urban soils and sediments collected in the United States commonly contain EPAPAH16 between 0.1 mg/kg and 100 mg/kg consisting of heavy petroleum mixed with pyrogenic 3- to 6-ring PAHs derived from soot and other sources of storm water runoff. In other words, the background soils in the Volta Grande IV study area are consistent with other urban areas. The dark soil samples demonstrate the presence of background PAHs mixed with additional pyrogenic sources at depth.

The EPAPAH16 concentrations range from 15 mg/kg to 136 mg/kg (Table 3, Figure 4(b)). Sample NFS-15(S) fell within the background range (Figure 12(a)); however, the deeper soil samples are slightly higher than background (>74 mg/kg). This signifies the likely mixture of background soil and at least one additional PAH source at depth. All the dark soil samples possess pyrogenic 3- to 6-ring PAHs with subtle pattern differences. Many of these samples exhibit a slight enrichment of N0, which indicates the possible presence of trace coal tar mixed with background soils.

Most of the residential soil samples matched the concentration and composition of background samples. The EPAPAH16 concentrations range from 1.2 mg/kg to 70 mg/kg (Table 3) and represent the extent of background PAHs throughout most of the residential area (Figure 4(b)).

All the dark soil samples possess pyrogenic 3- to 6-ring PAHs with distinct patterns. Source ratios highlight differences in the PAH source signatures that exhibit minimal effects from environmental weathering. Several ratios are well suited for the data in this study. According to described in [3] the ratio of the fluoranthene concentration divided by the pyrene concentration (FL0/PY0) changes with the type of fossil fuel (e.g., coal, gasoline, diesel), the temperature of combustion (e.g., cold engines, warm open fires, hot industrial furnaces). In general, the FL0/PY0 ratio of fossil fuels is less than 0.4, low temperature pyrolytic processes range from 0.5 to 1.0, and high temperature processes exceed 1.0.

A second PAH source ratio also reflects the pyrogenic process. It consists of the sum of benzo(b)fluoranthene and benzo(j,k)fluoranthene concentrations divided by the concentration of benzo(a)pyrene (BBF + BJKF/BAP). The double ratio plot of FL0/PY0 verses (BBF + BJKF)/BAP effectively separates sources of heavy PAHs (Figure 12(a)). The precision of these ratios is ±0.1 on both axes as evidence by the laboratory duplicates.

Like all the samples in this study, the background soils exhibit FL0/PY0 ratios greater than one, which indicates a high temperature origin (e.g. a hot engine or
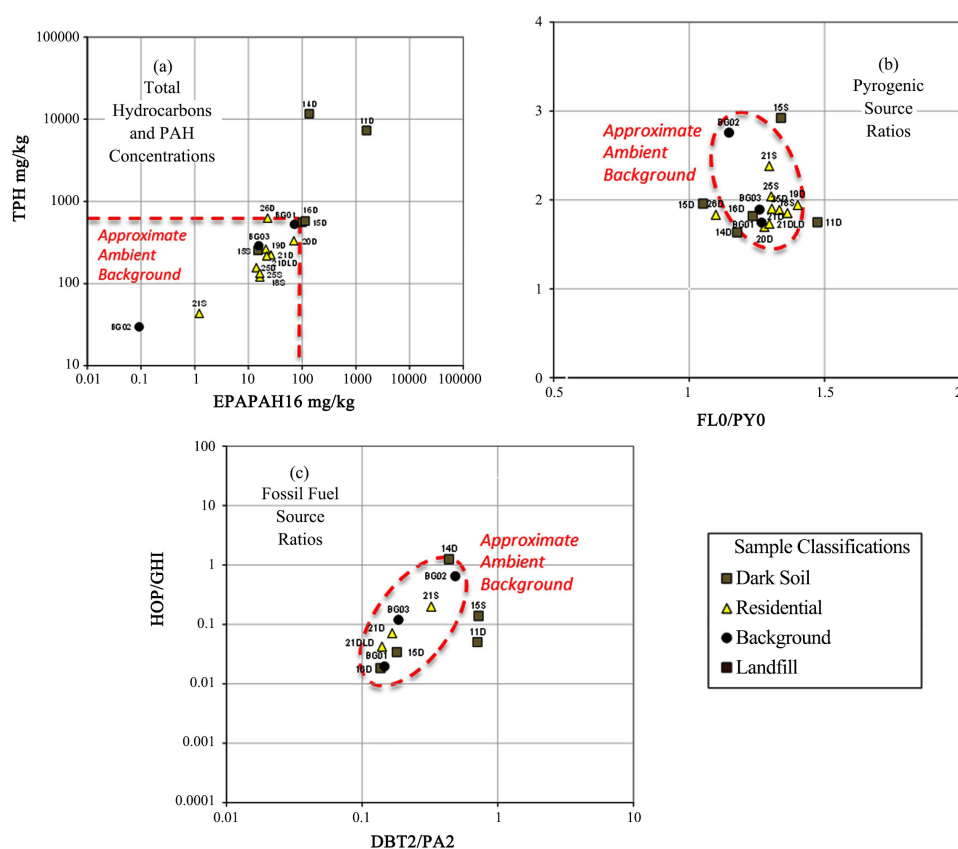
Figure 12. Hydrocarbon ratios among field samples.

furnace). The residential soils fall in the compositional range of the background samples (**Figure 12(b)**); the background samples [black circles] plot in the same area [red dashed circle] as the residential soils [yellow triangles]. Thus, the residential soils reflect the character of the ambient environment. By contrast, the samples from the landfill and dark soil area reflect the presence of PAHs formed at high temperature, but most of them plot outside the signature of the background soils. This finding helps confirm that the dark soils contain elevated PAHs from at least one other secondary source of pyrogenic PAHs.

Other source ratios focus on the degree of fossil fuel decomposition that occurs during pyrolysis. The concentration of dialkyl-dibenzothiophenes relative to dialkyl-phenanthrenes and anthracenes (DBT2/PA2) generally declines during pyrolysis. Similarly, the concentration of the geochemical biomarker, hopane (T19), relative to benzo(g,h,i)perylene (T19/GHI) declines during pyrolysis. The double ratio of DBT2/PA2 and T19/GHI approaches the origin during high temperature pyrolysis (**Figure 12(c)**). As observed previously, the variability among the pyrogenic sources in the background soils match the residential samples. Therefore, the PAHs in the residential area are attributable to the ambient environment. The landfill and dark soil samples plot outside the compositional range of the background soils; therefore, they contain elevated PAHs from at least one other secondary source of pyrogenic PAHs.

4. Conclusions

This environmental geoforensic investigation determined the origin of hydrocarbons observed in environmental samples collected in the Volta Grande IV neighborhood area. The field team collected 36 shallow soil and deep soil samples.

The residential soils match the background soil in terms of concentration and composition. The background soils contain less than approximately 525 mg/kg TPH C_9-C_{44} and 72 mg/kg EPAPAH16 that primarily consist of pyrogenic 3- to 6-ring PAHs. The residential soils contain less than approximately 560 mg/kg TPH C_9-C_{44} and 70 mg/kg EPAPAH16 that consist of pyrogenic 3- to 6-ring PAHs. One residential sample NFS-26(D) contained 627 mg/kg TPH C_9-C_{44} and 23 mg/kg EPAPAH16 due to the mixing of background soil and trace diesel fuel oil, likely caused by a local release. The PAH ratios indicate the background and residential soil samples are derived from similar high temperature combustion (soot) or carbonization (coke oven) sources.

The dark soil samples primarily contain mixtures of background soil; however, some are enriched by a second source of hydrocarbons. The shallow dark soil samples contain less than approximately 252 mg/kg TPH C_9-C_{44} and 15 mg/kg EPAPAH16 that primarily consist of pyrogenic 3- to 6-ring PAHs. These concentrations fall within the background range although the PAH ratios suggest that the background samples represent some, but not all background conditions. The deeper dark soil samples NFS-15(D), NFS-16(D), NFS-17(D), contain slightly elevated hydrocarbon concentrations. They are less than approximately 574 mg/kg TPH C_9-C_{44} and 114 mg/kg EPAPAH16 that primarily consist of pyrogenic 3- to 6-ring PAHs with slightly elevated naphthalene (N0). Slight differences between the background deep dark soil samples suggest a mixture of background and a second source of pyrogenic PAHs. The slight enrichment of N0 suggests a possible mixture with trace quantities of coal tar. Sample NFS-14(D) is distinct. It contains 11,600 mg/kg TPH C_9-C_{44} and 136 mg/kg EPAPAH16 that primarily consist of pyrogenic 3- to 6-ring PAHs attributable to background. This signature matches a mixture of background soil and coal tar. It is possible that the tar residue is associated with the CSN operation.

The landfill samples NFS-12(D) and NFS-13(D) contain unique heavy mineral oil products (between n-C_{20} and n-C_{40} with a maximum eluting around n-C_{30}), likely motor oil, that were not observed in other field samples. The landfill soils contain less than approximately 8210 mg/kg TPH C_9-C_{44}. The PAHs were not measured, because the high-resolution hydrocarbon fingerprint already clearly indicated that these mineral oils signatures are not present in the other field samples, including the proximal residential soil samples.

In summary, this work utilized geoforensic techniques to discern the source of hydrocarbons present in the soil of an urban area with suspected presence of steelworks residues. Despite the vast literature on geoforensic techniques, most

applications are related to petroleum contamination, and mostly outside of Brazil. This work aims to contribute with the advance of geoforensic techniques in different scenarios, including multiple sources of contamination with varying degrees of weathering.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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