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Forensic analytical approach for hydrocarbon fingerprinting in soil vapor samplings: Example of a residential neighborhood in Brazil

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ABSTRACT

Conventional analytical methods determine the concentration of compounds used to estimate the presence of environmental contamination capable of posing risk to human and ecological receptors. While these target analytes help regulators and environmental professional identify and manage potentially harmful conditions, these compounds can be generated by many natural and anthropogenic (man-made) sources and conventional methods alone fail to compositionally differentiate subsurface sources of contamination in complex environments. This case study demonstrates the advantage of using both conventional and forensic testing methods to accurately identify the source(s) of volatile hydrocarbon contamination in soil vapor samples for the development of an accurate conceptual site model in a neighbourhood near industrial facilities in Rio de Janeiro State, Brazil. The goal of this study was to differentiate potential impacts from a local steelmaking plant from fugitive hydrocarbons associated with more generic human activity in urban settings. This case study demonstrated the advantage of constructing chemical fingerprints from conventional volatile organic compound (VOC) method TO 15 and a forensic volatile hydrocarbon method using an enhanced version of method TO 15 (PIANO). The chemical fingerprints of vapor samples collected from subsurface soil gas and sewers were analysed and compared to laboratory reference samples. These data determined that the VOCs detected in neighbourhood soil vapor samples were associated with fugitive petroleum products migrating in the sewer pipelines and not with the steelmaking wastes emplaced near the residential area. This article discusses the forensic data and chemical signatures that support these findings, and the use of environmental forensic techniques to evaluate environmental data associated with complex scenarios, involving multiple contamination sources.

KEYWORDS

Soil gas; vapor intrusion; hydrocarbon chemical fingerprinting; environmental forensic; VOCs; PIANO

Introduction

Environmental forensics is a rapidly growing field of study, primarily directed towards determining the origin of environmental contamination and identifying the entity responsible for remedying the environmental impacts (Murphy and Morrison, 2007). Assigning responsibility is an important point of concern, because a wide range of contaminants are continually being released into many environments (Philp, 2014). The conventional environmental testing methods determine the concentration of a limited number of contaminants. Some contaminants, like hydrocarbons, belong to a large class of compounds potentially derived from petroleum, tar, and natural sources. Conventional testing results differentiate subsurface

sources of contamination in relatively clean environments with a limited number of potential sources. However, specialized forensic methods designed to measure dozens of hydrocarbon compounds at low concentrations are better suited for identifying hydrocarbon origins for petroleum and tar releases in areas with urban fill and chronic anthropogenic impacts attributed to ambient background sources. The need for high resolution data is particularly acute when distinguishing overlapping hydrocarbon plumes (e.g. soot, low-level tar residues, coke, gasoline, fuels, and other petroleum products) that require two or more lines of evidence to deconvolute the mixture. Forensic chemists developed specialized methods for assessing the nature, origin, and degradation of different

hydrocarbon releases in a variety of matrices (e.g. non-aqueous phase liquid [NAPL], soil, sediment, groundwater, tissue, vapor, and others). These techniques greatly improve the identification of pyrogenic materials generated by combustion and carbonization, as well as petrogenetic materials generated by geological processes and modified by human refining (Morrison, 2000; Wang and Fingas, 2003; Morisson et al., 2006; Galperin and Kaplan, 2007; Wang et al., 2011; Emsbo-Mattingly and Litman, 2016; Department of Environmental Protection, 2017; Gouvêa Jr et al., 2019).

The identification of hydrocarbon sources in ephemeral matrices, like soil vapor and indoor air, benefits from a tiered analytical approach using multiple gas chromatography (GC) methods, which determine a wide range of hydrocarbons eluting between *n*-pentane (*n*-C₅) and *n*-pentadecane (*n*-C₁₅). Conventional VOC methods scan for a limited number of compounds from a variety of petrochemical and halogenated solvents, adhesives, refrigerants, fumigants, and fuels. These data also help identify degradation and metabolic by-products, such as alcohols and aldehydes. Forensic methods provide greater source signature richness by measuring a wider variety of compounds over a wider concentration range within a specific product class, but these specialized methods are used selectively because of their higher cost and extended time of analysis.

The assessment of indoor air contamination and the potential for vapor intrusion from subsurface soil and groundwater received substantial attention during the past decade. Chemical fingerprinting techniques proved exceptionally valuable for determining VOC sources, migrations pathways, and degradation states in complex environments with multiple historical and potential ongoing releases. Vapor phase impacts from petroleum and tar products are particularly amenable to chemical fingerprinting using conventional and forensic methods because of the large number of non-target hydrocarbon compounds exhibiting diagnostic compositional patterns. Vapor phase signatures of petroleum fuels, solvents, or tar-derived wastes can be chemically fingerprinted, spatially mapped, and forensically attributed to products used by on-site homeowners or migrating from off-site sources, such as industrial wastes or commercial releases. Commonly encountered products include automotive gasoline, common and specialty solvents, paints, and waterproofing chemicals (Douglas et al., 2007).

This study used hydrocarbon chemical fingerprints to investigate the sources of hydrocarbons detected in the subsurface soil vapors in a residential neighbourhood.

The goal was to determine if the chemical fingerprints of soil gas near residential dwellings matched vapor phase impacts from steelmaking waste (e.g. coal tar residues) or other sources in the residential community. Accordingly, residential soil gas samples were compositionally compared to samples collected from the steelmaking waste area and neighbourhood sewer lines. Additional reference samples from industrial facilities outside the study area were added to the analysis for comparison purposes (Morisson et al., 2006; Douglas et al., 2007). The research conducted for this study contributes to the advancement of the use of forensic chemical tools for the identification of patterns related to the presence of wastes related to steelmaking industrial processes, in scenarios with the presence of multiple sources of contamination in varying states of weathering (e.g. evaporation and biodegradation).

Use of forensic analytical techniques for hydrocarbons chemical fingerprinting

The technical challenges associated with methods for hydrocarbons chemical fingerprinting are primarily associated with the fact that the goal of the standard US EPA methods is to minimize risk to potential toxins. By contrast, environmental forensic chemistry is primarily focused on pollution source identification. Because the methods are focused on different outcomes, target compounds and the sensitivity required to quantify the concentration of those compounds in environmental media, especially in soil vapor samples are not perfectly aligned and often require the use of enhancements or modifications to standard US EPA methods.

Gas chromatography is one of the most important chemical fingerprinting methods used in the characterization of hydrocarbons in the environment. The heavy reliance on GC techniques is a function of its extraordinary ability to separate complex mixtures of organic compounds and measure isolated analytes using a wide range of specialized detectors (Douglas et al., 2007). Because petroleum, coal and their by-products contain thousands of compounds, with different concentrations in several orders of magnitude, is it necessary for a successful characterization to consider the use of appropriate sampling techniques, high resolution chromatography methods, and flexible data interpretation strategies (Wang and Fingas, 2003).

Several researchers published analytical methods for characterization and identification of coal and petroleum hydrocarbons in the last two decades (Uhler et al., 1999; Morisson et al., 2006; Oudijk, 2009b; Emsbo-Mattingly and Litman, 2016).

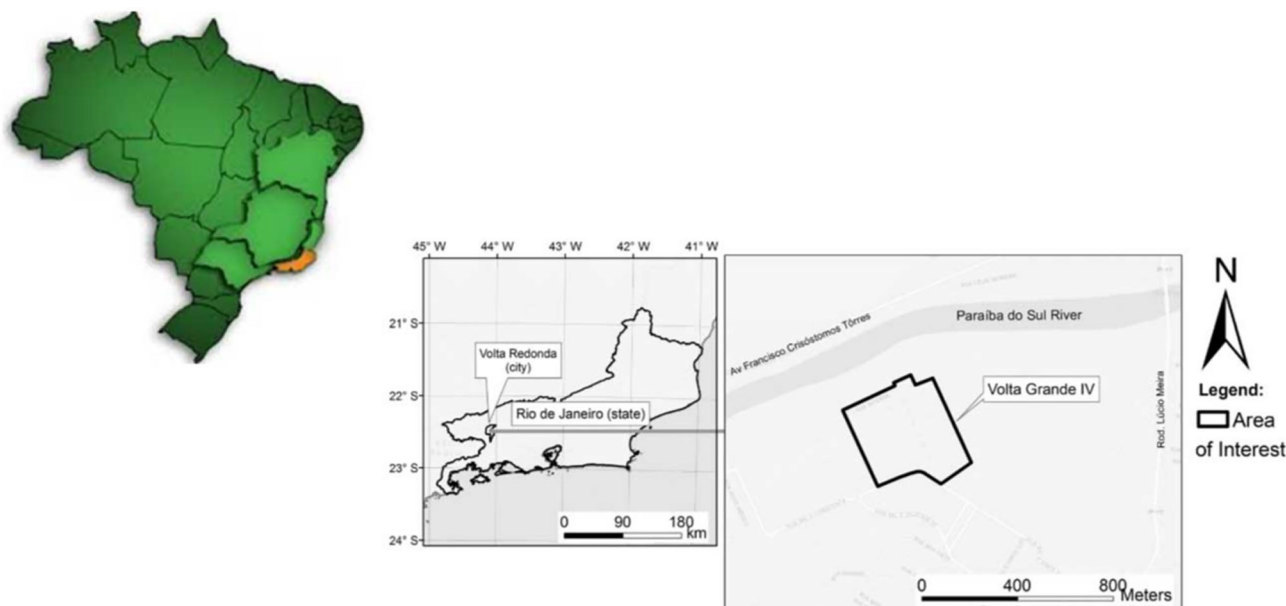


Figure 1. Study area location. Source: Modified from Gouvêa Jr et al. (2019).

The intrusion of soil vapor from subsurface contamination sources into inhabited structures, continues to attract regulatory and environmental agency attention globally. In this context, methods for identifying vapor phase source signatures from candidate sources, tracking the chemical fingerprint and its transformation along migrations pathways, and estimating the magnitudes of indoor air vapor intrusion is an important emerging theme in the environmental forensics field (Morisson et al., 2006; Uhler et al., 1999; Oudijk, 2009b; Emsbo-Mattingly and Litman, 2016).

Study area

The residential neighbourhood Volta Grande IV is located in the city of Volta Redonda, RJ, Brazil (Figure 1). This residential neighbourhood was built in 1995 in an area formerly occupied by the industrial complex operated by Companhia Siderúrgica Nacional (CSN). The plant was originally a national steelworks built in 1940 by the Brazilian government and privatized in 1993.

With the privatization of CSN, the area formerly occupied by contractors' warehouses and temporary storage of materials related to steelmaking processes (the Site) was donated to the Metalworkers' Syndicate. In 1995, after an environmental permitting process, a residential condominium was built on the Site.

Before the establishment of the residential neighbourhood (between 1978 and 1993), a blend of steel slag with by-products of coke oven gas origin, neutralized with calcium carbonate was deposited in a

portion of the Site (Figure 2). Part of this material remained on the site and was covered by clayey soil. The area was levelled and residential houses were built on top of the buried waste.

Previous environmental studies detected the presence of semivolatile organic compounds (SVOCs) in the soil, especially polycyclic aromatic hydrocarbons (PAHs), that exceeded the Brazilian regulatory standards (Conselho Nacional do Meio Ambiente (CONAMA), 2009). Following the publication of these studies, CSN conducted a forensic investigation to delineate the steelworks waste and formulate the conceptual site model (CSM).

Previous work

Beginning in 2000, CSN conducted several soil and groundwater assessments to identifying potential exceedances of Brazilian regulatory standards potentially caused by steelworks waste (CONAMA, 2009). It collected more than 600 soil samples within the study area, at depth intervals ranging from 0 to 7.2 m (~24 ft). It determined the concentrations of a wide variety of parameters, including metals, VOCs, SVOCs, PAHs, polychlorinated biphenyls (PCBs), total petroleum hydrocarbons (TPH), organochlorine pesticides, herbicides, polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/PCDFs). Selected samples were analysed for alkylated PAHs and geochemical biomarkers, which included 53 tri-, tetra- and pentacyclic triterpanes, regular and rearranged steranes, and aromatic steroids to delineate steelwork wastes. The

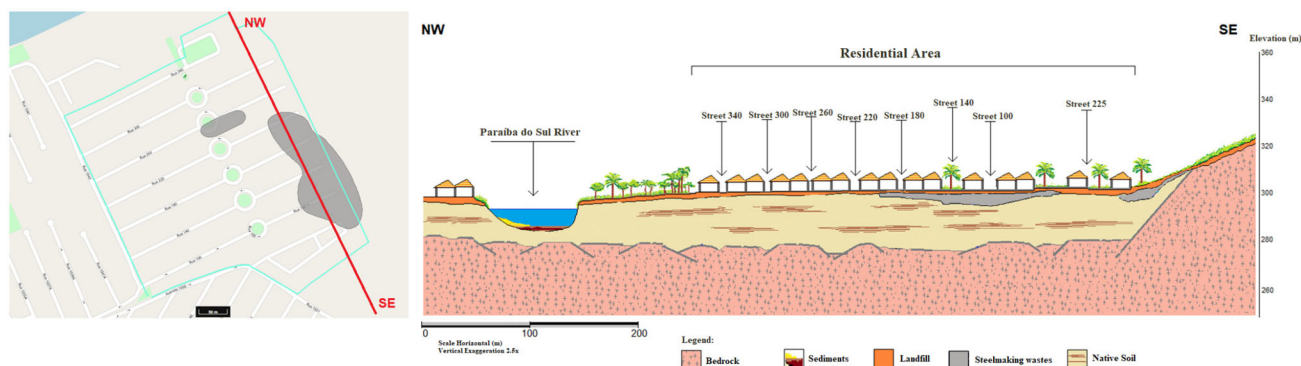


Figure 2. Subsurface area delineated with residues of steelmaking origin.

results from these investigations identified a subsurface layer of steelmaking wastes approximately 1.5 m thick at a depth varying between 1 and 3 m below ground surface in an area of approximately 18,000 m², which occupied approximately 10% of the residential area (Figure 2).

This layer is composed of steelmaking slag mixed with native soil. The steelmaking slag consisted of metals and pyrogenic PAHs produced by the combustion of coal and coke during the thermogenic extraction of iron from iron ore. The concentration of PAHs in the waste layer exceeded regulatory standards. However, discontinuous PAH exceedances occurred in other areas of the residential neighbourhood where steelmaking slag was not identified.

In 2015, a forensic investigation used chemical fingerprints generated from the TPH and PAH results to determine the origin of hydrocarbons throughout the residential neighbourhood (Gouvêa Jr et al., 2019). CSN collected 36 soil samples representing 4 different sample types: urban background, steelmaking wastes, residential soil, and industrial soil. For each sample type, samples were collected at different depths, representative of superficial, subsuperficial and native soils (Figure 3). High resolution hydrocarbon fingerprints were generated from the samples analysed for TPH using modified EPA Method 8015 D (U.S. Environmental Protection Agency, 2003). Additional chemical fingerprints were constructed from the relative abundances of alkylated PAHs and geochemical biomarker concentrations determined using modified EPA Method 8270 D (U.S. Environmental Protection Agency, 2014). The hydrocarbon analyses were conducted in accordance with EPA methods that were enhanced for forensic evaluation purposes.

The results of the initial forensic investigation identified tar-like residues in the steelworks slag. However, the chemical fingerprints from soil samples (Gouvêa Jr et al., 2019) outside the waste layers were attributed to ambient soot and fill with localized releases of

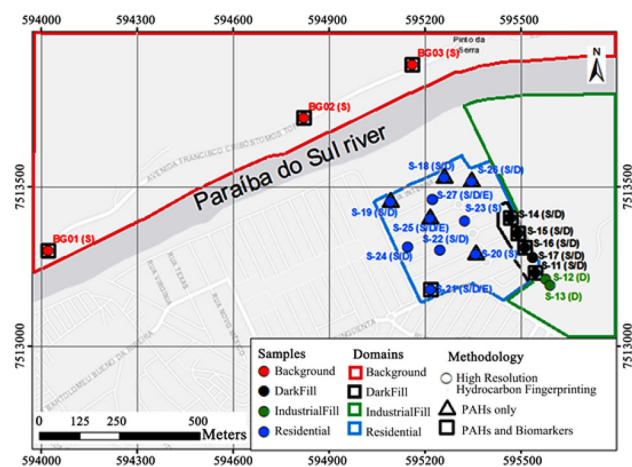


Figure 3. Soil sample locations for hydrocarbon analysis in Volta Grande IV neighbourhood Source: Modified from Gouvêa Jr et al. (2019).

gasoline and possibly diesel fuel from vehicles. The results obtained, therefore, indicated the absence of wastes indicative of steelmaking origin in many residential samples with PAH exceedances.

The concentrations detected in the residential area were less than 560 mg/kg TPH C₉-C₄₄ and 70 mg/kg EPAPAH16, that consist of pyrogenic 3- to 6-ring PAHs (Figure 4a). Although some of the residential soils contained elevated PAHs, they were consistent with samples collected in areas attributed to comparably urban regions unaffected by steelworks waste (Figure 4b, less than 525 mg/kg TPH C₉-C₄₄ and 72 mg/kg EPAPAH16) primarily comprised of pyrogenic 3- to 6-ring PAHs. Their sources are related to pyrogenic PAHs from soot originating from vehicular emissions and wildfires.

The steelmaking wastes samples primarily contain mixtures of background soil; however, some are enriched by a second source of hydrocarbons. The shallow steelmaking wastes samples contain less than approximately 252 mg/kg TPH C₉-C₄₄ 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), contain slightly elevated hydrocarbon concentrations. They are less than approximately 574 mg/kg TPH C₉ C₄₄ and 114 mg/kg

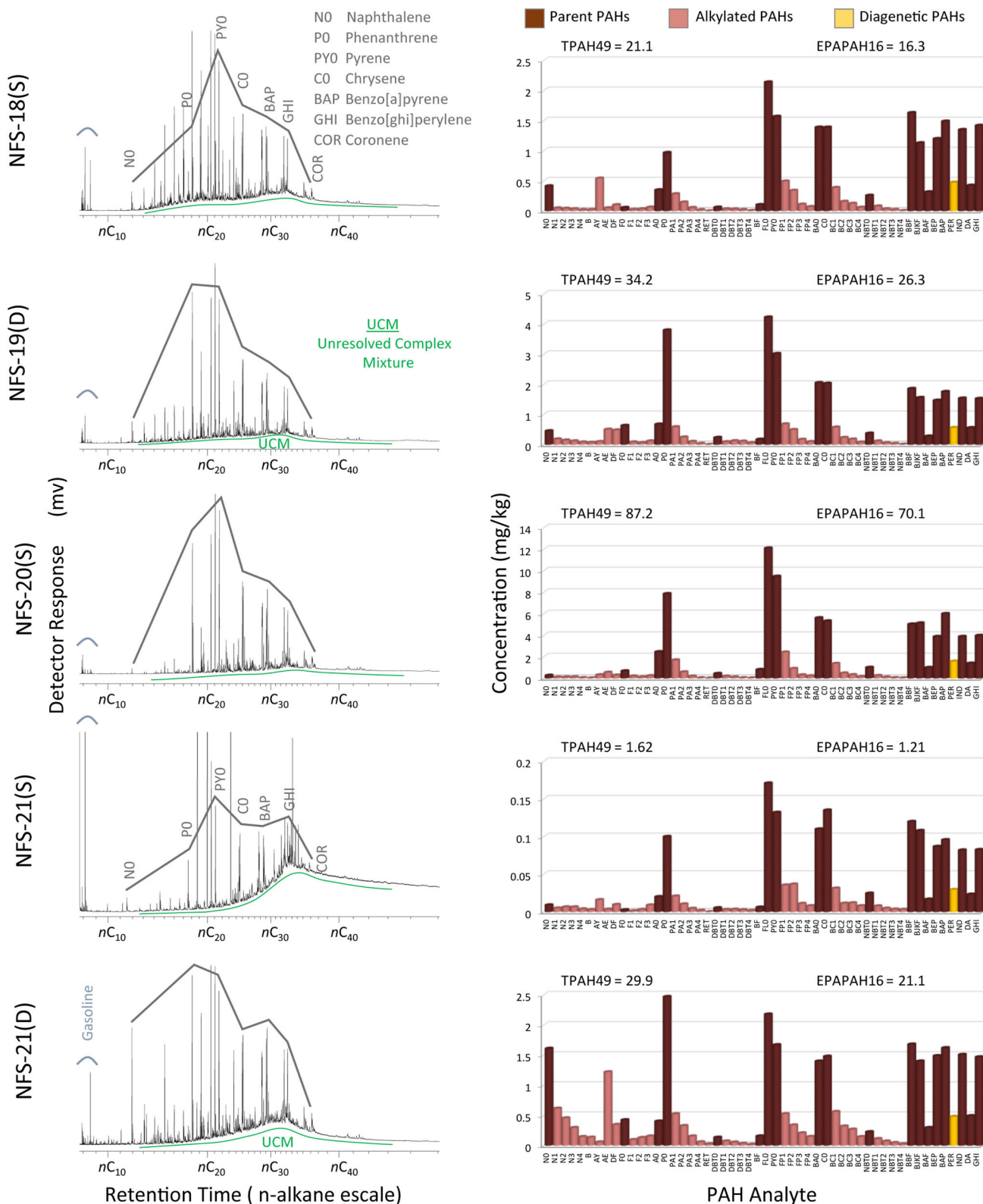


Figure 4a. Hydrocarbon patterns in residential soil samples generated by high resolution hydrocarbon fingerprinting (left) and forensic PAH (right) methods. Source: Modified from Gouvêa Jr et al. (2019).

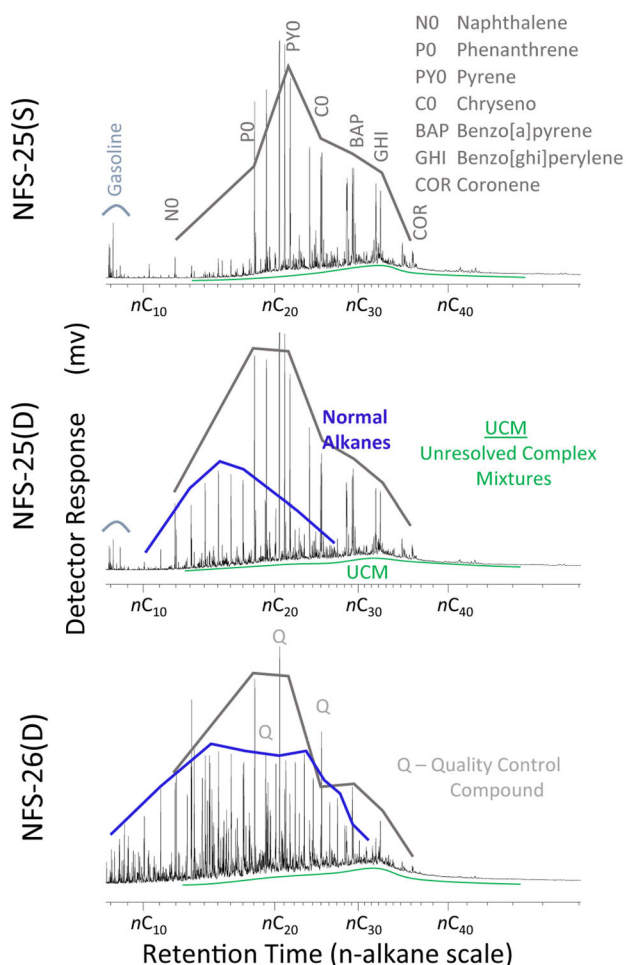
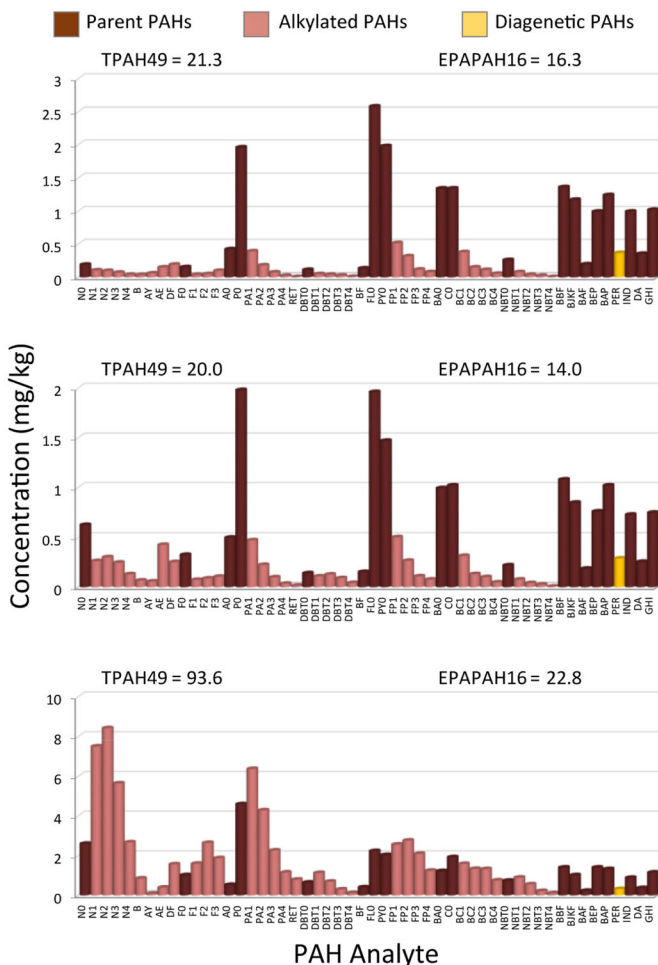


Figure 4a. Continued

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 C₉-C₄₄ (reflecting >99% mineral oil or pavement) and 136 mg/kg EPAPAH16 that primarily consist of pyrogenic 3- to 6-ring PAHs attributable to background (soot).

While the compositional features of regional background was heavily pyrogenic, steelmaking waste contained distinct mixtures of pyrogenic and petrogenic similar to coal by-products, such as coke and coal tar, possibly attributed to steelmaking processes (Figure 4c). Although diluted by anthropogenic fill in all samples, the steelmaking residues were recognized by two or more of the following features: enriched parent PAHs (EPAPAH16 > 100 mg/kg) relative to residual range UCM eluting above *n*-C₂₀, enriched naphthalene (N0/P0 > 0.04), enriched fluoranthene



(FLO/PY0 > 1.3), enriched benzofluoranthenes (BBF + BJF + BKF/BAP), and low geochemical biomarkers (HOP/GHI).

Although the results of the investigation for delineating steelmaking wastes and defining sources of TPHs and PAHs in soil samples were conclusive, some questions related to the detections of VOCs in soil vapor samples remained unclear. Many of the analysed soil vapor samples for regulatory VOCs (U.S. Environmental Protection Agency, 1999a; U.S. Environmental Protection Agency, 1999b) detected compounds that did not correlate with the concentrations detected in soil samples, including 1,2,4-trimethylbenzene, dichloromethane, toluene, ethylbenzene and styrene. Also, the results did not illustrate a relationship between spatial distribution and potential sources of vapors, related to the presence of steelmaking wastes and higher VOC concentrations in soil vapor samples.

The spatial pattern of VOC detections were not entirely random; rather, they loosely followed the sewage galleries and areas with more intense automobile density. A forensic investigation was designed to compare the chemical fingerprint of volatile hydrocarbons

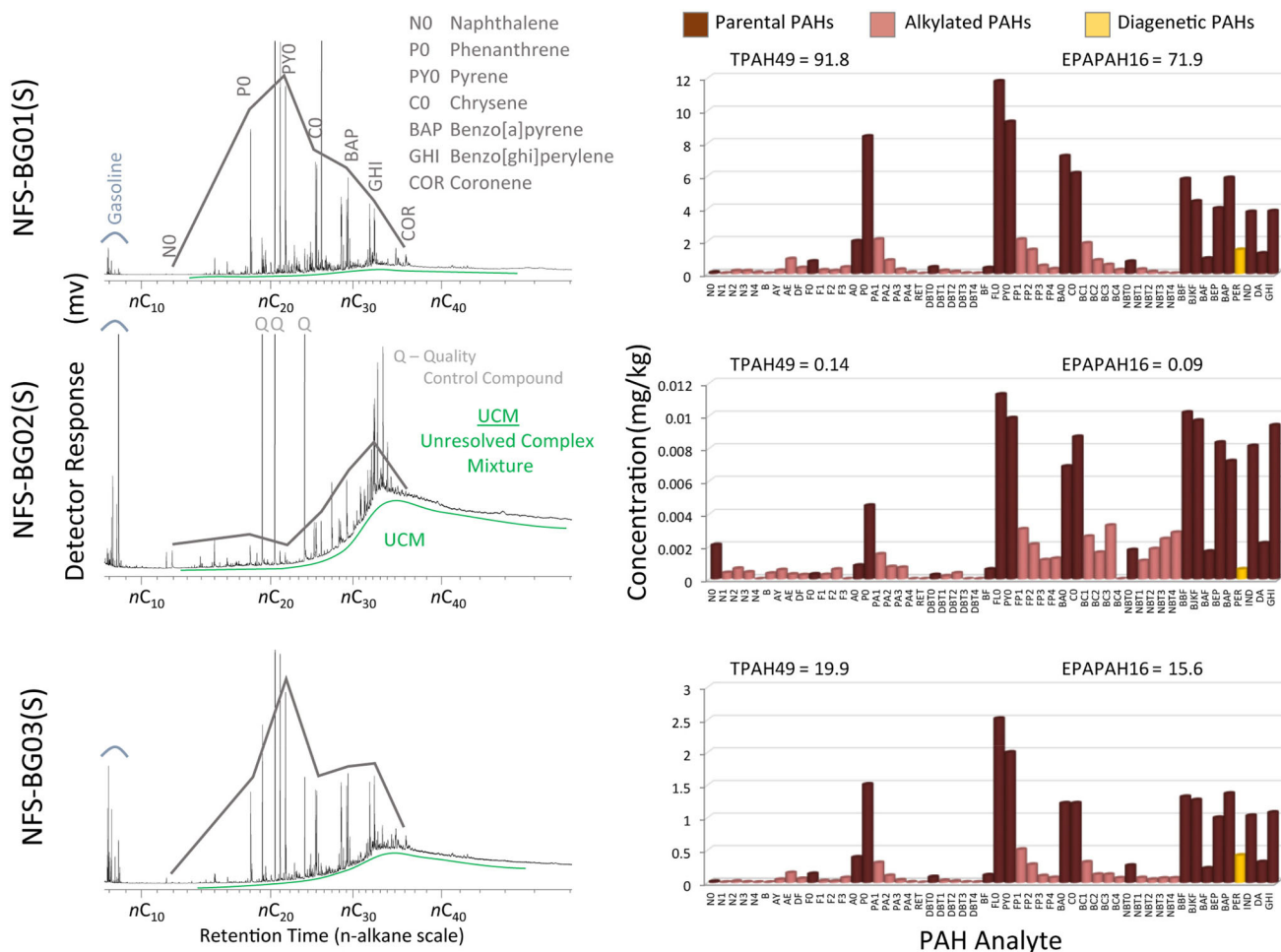


Figure 4b. Hydrocarbons patterns in background soil samples generated by high resolution hydrocarbon fingerprinting (left) and forensic PAH (right) methods. Source: Modified from Gouvêa Jr et al. (2019).

in residential soil vapor samples with steelmaking wastes and urban source samples. The approach provided a better framework to differentiate candidate sources and weathering in the study area.

To meet the objectives of the forensic approach, the hydrocarbon analyses used for identification of soil vapor hydrocarbon sources in the residential area were conducted in accordance with EPA methods that were enhanced for forensic purposes (Douglas et al., 2007). The primary enhancements included lower detection limits, additional quality control samples, and multilevel calibrations for diagnostic hydrocarbon analytes. It is important to note that the methods meet or exceed the quality control provisions of comparable standard EPA methods.

Methods

Sample collection strategy

The sampling strategy was designed to clarify inconsistencies identified in the early investigations that revealed

concentrations that did not match with the potential source area, related to the presence of steelmaking wastes layer, delineated in the residential area. The definition of the spatial domains was based on previous studies (Gouvêa Jr et al., 2019) and included the primary areas of interest. The sampling campaign included (Table 1): (i) five samples from residential domain identified as “Residential”, which represent areas of the neighbourhood previously occupied by the contractors’ warehouses, and therefore less prone to the presence of steelmaking wastes; (ii) seven samples from the area delineated with the presence of a layer of steelmaking wastes at the northeast edge of the residential area, identified as “Steelmaking wastes” and; (iii) three samples from the sewage pipelines existing within the residential area, identified as “Sewer”.

The samples identified as “S” (subslab) and “D” (Deep) represent depths of approximately 0.5 m and 1.0 m respectively. The sewer vapor samples, representative from combined surface runoff and sewage in a shared system, were collected directly from the

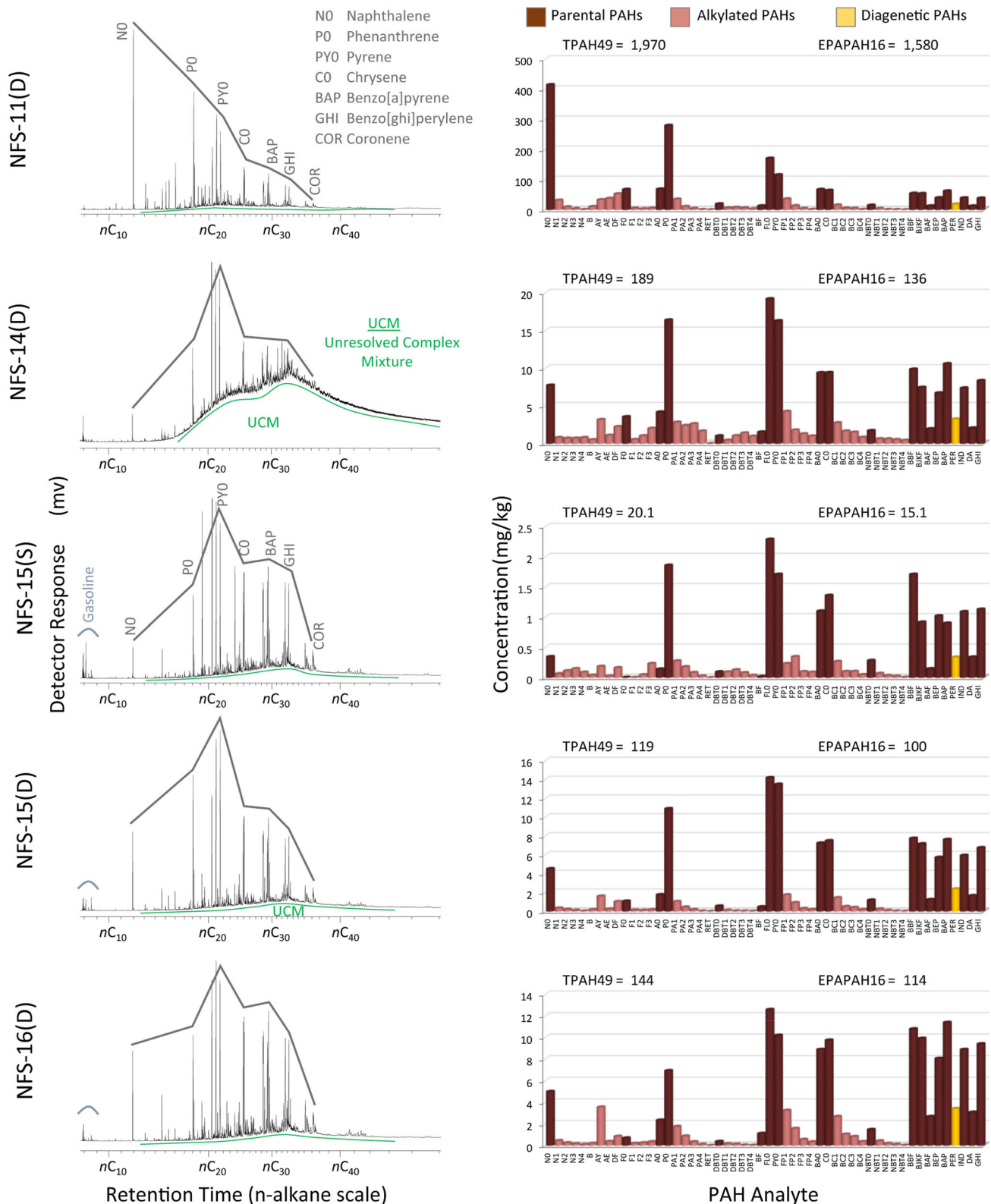


Figure 4c. Hydrocarbons patterns in soil samples from the domain of steelmaking wastes, generated by high resolution hydrocarbon fingerprinting (left) and forensic PAH (right) methods. Source: Modified from Gouvêa Jr et al. (2019).

passing galleries at a depth of approximately 1 m below street surface.

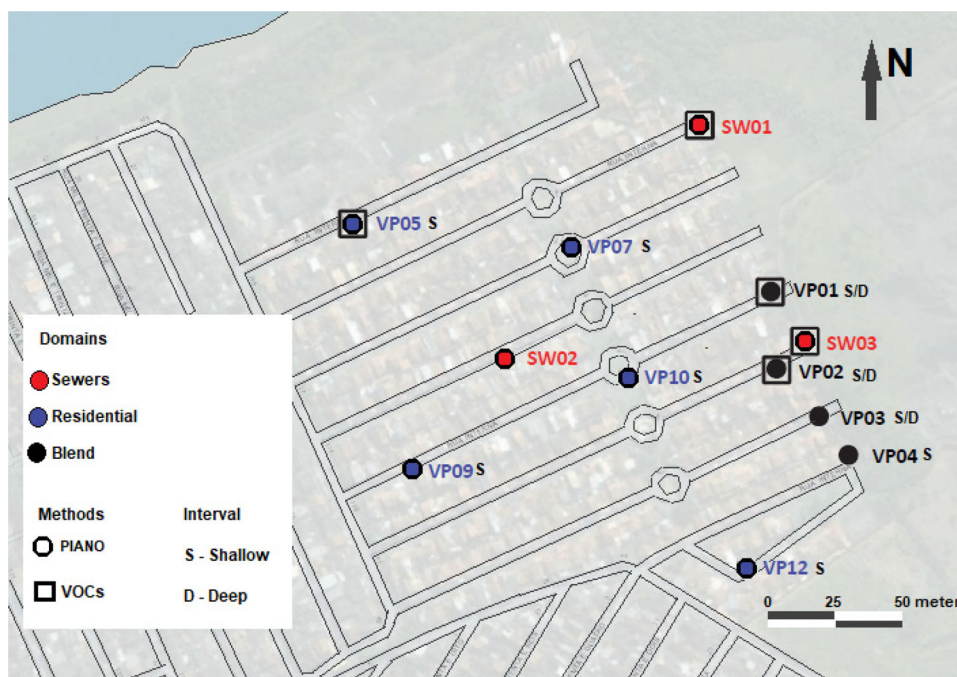
In total, 16 vapor samples (15 samples and 1 field duplicate) were collected and shipped to Alpha

Analytical laboratory (USA) for the Regulatory VOCs in Soil Gas and Air (U.S. Environmental Protection Agency, 1999a) and Forensic PIANO VOCs in Soil Gas and Air (Douglas et al., 2007). The concentration

Table 1. Vapor samples identification and analytical parameters.

Sample	Domain	Matrix	Approx. Depth (m)	Date Collected	Volatile Hydrocarbons PIANO EPA TO15 Mod GC/MS	Volatile Organic Compounds EPA TO15 GC/MS
NF-VP-12 (S)	Residential	Soil Vapor	0,5	09/03/2015	X	
NF-VP-01 (S)	Steelmaking wastes	Soil Vapor	0,5	10/03/2015	X	X
NF-VP-01(D)	Steelmaking wastes	Soil Vapor	1,0	07/03/2015	X	X
NF-VP-02(S)	Steelmaking wastes	Soil Vapor	0,5	09/03/2015	X	X
NF-VP-02(D)	Steelmaking wastes	Soil Vapor	1,0	07/03/2015	X	X
NF-VP-03(S)	Steelmaking wastes	Soil Vapor	0,5	09/03/2015	X	
NF-VP-03(S)fd	Steelmaking wastes	Soil Vapor	0,5	09/03/2015	X	
NF-VP-03(D)	Steelmaking wastes	Soil Vapor	1,0	07/03/2015	X	
NF-VP-04(S)	Steelmaking wastes	Soil Vapor	1,0	09/03/2015	X	
NF-VP-05	Residential	Soil Vapor	1,0	10/03/2015	X	X
NF-VP-07	Residential	Soil Vapor	1,0	10/03/2015	X	
NF-VP-09	Residential	Soil Vapor	1,0	09/03/2015	X	
NF-VP-10	Residential	Soil Vapor	1,0	09/03/2015	X	
NF-SW-01	Sewer	Sewer Vapor	1,0	10/03/2015	X	X
NF-SW-02	Sewer	Sewer Vapor	1,0	10/03/2015	X	
NF-SW-03	Sewer	Sewer Vapor	1,0	10/03/2015	X	X

fd: Field duplicate

**Figure 5.** Location of the sampling points for VOCs and Forensic PIANO VOCs in soil gas samples.

of the compounds detected in the vapors were reported in ppbv and $\mu\text{g}/\text{m}^3$. Figure 5 shows the location of the sampling points.

Vapor monitoring wells installation and sampling procedures

The installation vapor monitoring wells and the procedures for soil gas sampling were based on the guidelines provided by USEPA, 2015 (U.S. Environmental Protection Agency, 2015) and ITRC (2014). Multilevel wells were installed within

steelmaking wastes (Figure 5) to characterize the composition of the vapors at subsurface depths and their diffusion to superficial layers of the soil.

The installation of 12 monitoring wells was performed with a hammer drill to the depth of interest. The sampling tube was inserted 5 cm above the bottom of borehole. The inner space between the borehole and the tube, in the upper portion of the well, was sealed with bentonite and cement grout to prevent the entry of vapors from the wellhead during well purging.

Prior to sampling activities, the monitoring wells were purged to remove stagnant vapors from the well.

The purge flow was maintained between 100 and 200 mL/min to minimize the vapor partitioning of the water retained in the soil pores and to prevent ambient air from diluting the soil vapor samples. A tightness test was then performed to ensure that the ambient air was not introduced into the sample and therefore did not interfere with the composition of the samples collected from monitoring wells. Helium was used as a tracer gas, which has great advantages over other gases considering its molecular size and because it is a light and inert gas, allowing rapid leak detection.

For sampling of soil gas and sewer/stormwater system gas, 2.7-liter canisters equipped with flow controllers were used, adjusted for a sampling time of 2 hours and a sample rate flow of 22,5 mL/min. The canisters used for sampling were clean certified by Alpha Analytical Laboratory. The samples were collected in the stormwater drainage system through sampling tubes connected to the canister at one end and with the other end positioned approximately 1 m below street surface. Quality control procedures for the samples and a rigorous process of equipment decontamination, as described in (Douglas et al., 2007) and (Stout et al., 2010), were followed.

Analytical methods

The hydrocarbon analyses were conducted in accordance with USEPA methods that were enhanced for forensic purposes (Douglas et al., 2007). The primary enhancements included lowering the detection limits, additional quality control samples and multilevel calibrations for diagnostic hydrocarbon analytes. The methods met or exceeded the quality control provisions of comparable standard USEPA methods.

Analytical determination of regulatory VOCs in soil vapors (EPA method to-15)

The conventional VOC analytes represent the most commonly measured compounds found in many products containing light petroleum distillates. The purpose of measuring VOCs was to evaluate the proportions and character of non-petroleum VOCs which were detected in the field samples of previous works. The vapor samples identified as NF-VP 01S, NF-VP 01D, NF-VP 02S and NF-VP 02D, from steelmaking wastes domain, NF-VP 05, from residential domain and NF-SW 01 and NF-SW 03 from sewer/stormwater system (Figure 5) were analysed for determination of regulatory VOCs in accordance with EPA Method

TO-15 (U.S. Environmental Protection Agency, 1999a). The EPA Method TO-15 determined the concentrations of more than 50 volatile organic compounds of traditional regulatory interest (Table 2). The samples were analysed by gas chromatography and mass spectrometer (GC/MS) operated in a full scan and selected ion monitoring modes. In addition to compliance monitoring, these patterns of detected analytes provide a basis to identify likely contributions from solvents, refrigerants, degreasers, adhesives, and other hydrocarbon products. The concentrations of target compounds in air are reported in $\mu\text{g}/\text{m}^3$. A method blank (B), lab control sample (LCS), lab control sample duplicate (LCSD) and laboratory duplicate (LD) were prepared and analysed for quality assurance/quality control (QA/QC).

Forensic PIANO analysis for the determination of chemical fingerprint of hydrocarbons (modified EPA method to-15)

The vapor samples identified as NF-VP 01S, NF-VP 01D, NF-VP 02S, NF-VP 02D, NF-VP 03S, NF-VP 03D, NF-VP 03Dfd and NF-VP 04, from steelmaking wastes domain, NF-VP 05, NF-VP 07, NF-VP 09, NF-VP 10 and NF-VP 12 from residential domain and NF-SW 01, NF-SW 02 and NF-SW 03 from sewer/stormwater system (Figure 5) were analysed for determination of PIANO chemical fingerprint using a modified EPA Method TO-15 (U.S. Environmental Protection Agency, 1999a), enhanced for forensics purposes, according to the procedures described by (Douglas et al., 2007).

A modified EPA Method TO-15 determined the concentration up to 90 volatile hydrocarbons in the five compound classes (paraffins, isoparaffins, aromatics, naphthenes and olefins -PIANO) using purge-and-trap gas chromatography and mass spectrometer (GC/MS), operated in a full scan and selected ion monitoring modes (Table 3). In addition, various oxygenated compounds commonly found in oxygenated and reformulated gasoline were also targeted. These results provided a basis to characterize and distinguish different types of gasoline, light petroleum distillates and tar products. The concentrations of target compounds in air are reported in $\mu\text{g}/\text{m}^3$ from which a distribution profile of the 5 main groups of petroleum constituents was obtained. This profile could be compared to laboratory standards, thus making it possible to characterize and differentiate types of hydrocarbons chemical fingerprints. A method blank (B), lab control sample (LCS), lab control sample duplicate (LCSD)

Table 2. EPA Method TO-15 Analytes.

Analytes	Abbrev	Aromatic	Additive	Bromo	Chloro	Freon	Ketone	Oxygen
Benzene	BZ	X						
Toluene	TOL	X						
Ethylbenzene	EB	X						
Xylene - (m)*	Xm	X						
Xylene - (p)*	Xp	X						
Xylene - (o)	Xo	X						
Styrene	STY	X						
Trimethylbenzene – 1,3,5	TMB135	X						
Trimethylbenzene – 1,2,4	TMB124	X						
Isopropylbenzene (Cumene)	IPPB	X						
n-Propylbenzene	nPB	X						
Tert-Butylbenzene	tBB	X						
n-Butylbenzene	nBB	X						
p-Isopropyltoluene	IPT	X						
Naphthalene	NO	X						
Methyl Tertiary Butyl Ether	MtBE		X					
Bromoform	BFM			X				
Bromomethane	BM			X				
Dibromoethane – 1,2	EDB			X				
Bromodichloromethane	BDCM			X				
Chlorodibromomethane	CDBM			X				
Vinyl Chloride	VC				X			
Methylene Chloride	DCM				X			
Carbon Tetrachloride	CT				X			
Chloroethane	CEA				X			
Dichloroethane – 1,1	DCA11				X			
Dichloroethane – 1,2	DCA12				X			
Trichloroethane – 1,1,1	TCA111				X			
Trichloroethane – 1,1,2	TCA112				X			
Tetrachloroethane – 1,1,1,2	PCA1112				X			
Tetrachloroethane – 1,1,2,2	PCA1122				X			
Dichloropropane – 1,2	DCPA12				X			
Trichloropropane – 1,2,3	TCPA123				X			
Chlorobenzene	CBZ				X			
Dichlorobenzene – 1,2	DCBo				X			
Dichlorobenzene – 1,3	DCBm				X			
Dichlorobenzene – 1,4	DCBp				X			
Trichlorobenzene – 1,2,4	TCB124				X			
Dichloroethylene - (cis-1,2)	DCEc12				X			
Dichloroethylene - (trans-1,2)	DCEt12				X			
Dichloroethylene – 1,1	DCE11				X			
Trichloroethylene	TCE				X			
Tetrachloroethylene	PCE				X			
Dichloropropene - (cis-1,3)	DCPEc13				X			
Dichloropropene - (trans-1,3)	DCPEt13				X			
Chloroform	CFM				X			
Hexachlorobutadiene	HxCB				X			
Chlorotoluene – 2	CT2				X			
Trichlorofluoromethane (Freon 11)	F011					X		
Dichlorodifluoromethane (Freon 12)	F012					X		
Acetone	ACET						X	
Methyl Ethyl Ketone	MEK						X	
Methyl Isobutyl Ketone	MIBK						X	
Diethyl Ether	DEE							X
Tetrahydrofuran	THF							X
Total	55	15	1	5	27	2	3	2

and laboratory duplicate (LD) were prepared and analysed for QA/QC procedures.

Results and discussion

The laboratory reports contain the raw concentrations, spectra and associated quality control results that support the forensic interpretation (see supplemental material). Laboratory reference samples provided examples of hydrocarbon signatures representing the

potential hydrocarbon products in the study area for comparison purposes. These laboratory data provided both qualitative and quantitative lines of forensic evidence as discussed below.

Conventional VOC results

The conventional VOC analytes represent the most commonly measured compounds found in adhesives, solvents, propellants, refrigerants, dry cleaning fluids,

Table 3. Modified forensic PIANO EPA method TO-15 analytes.

Analyte	Abbrev	Paraffin	Isoparaffin	Aromatic	Naphthene	Olefin	Thiophene	Gasoline Additive
Pentane	C5	X						
Hexane	C6	X						
Heptane	C7	X						
Octane	C8	X						
Nonane	C9	X						
Decane	C10	X						
Undecane	C11	X						
Dodecane	C12	X						
Tridecane	C13	X						
Isopentane	IP		X					
2,3-Dimethylbutane	23DMB		X					
2-Methylpentane	2MP		X					
3-Methylpentane	3MP		X					
2,2-Dimethylpentane	22DMP		X					
2,4-Dimethylpentane	24DMP		X					
2-Methylhexane	MHx		X					
2,3-Dimethylpentane	23DMP		X					
3-Methylhexane	3MH		X					
Isooctane	ISO		X					
2,5-Dimethylhexane	25DMH		X					
2,4-Dimethylhexane	24DMH		X					
2,2,3-Trimethylpentane	223TMP		X					
2,3,4-Trimethylpentane	234TMP		X					
2,3,3-Trimethylpentane	233TMP		X					
2,3-Dimethylhexane	23DMH		X					
3-Ethylhexane	3EH		X					
2-Methylheptane	2MHEP		X					
3-Methylheptane	3MHEP		X					
Benzene	B			X				
Toluene	T			X				
Ethylbenzene	EB			X				
p/m-Xylene	MPX			X				
Styrene	STY			X				
o-Xylene	OX			X				
Isopropylbenzene	IPB			X				
n-Propylbenzene	PROPB			X				
1-Methyl-3-ethylbenzene	1M3EB			X				
1-Methyl-4-ethylbenzene	1M4EB			X				
1,3,5-Trimethylbenzene	135TMB			X				
1-Methyl-2-ethylbenzene	1M2EB			X				
1,2,4-Trimethylbenzene	124TMB			X				
sec-Butylbenzene	SECBUT			X				
1-Methyl-3-isopropylbenzene	1M3IPB			X				
1-Methyl-4-isopropylbenzene	1M4IPB			X				
1-Methyl-2-isopropylbenzene	1M2IPB			X				
Indan	IN			X				
1-Methyl-3-propylbenzene	1M3PB			X				
1-Methyl-4-propylbenzene	1M4PB			X				
n-Butylbenzene	BUTB			X				
1,2-Dimethyl-4-ethylbenzene	12DM4EB			X				
1,2-Diethylbenzene	12DEB			X				
1-Methyl-2-propylbenzene	1M2PB			X				
1,4-Dimethyl-2-ethylbenzene	14DM2EB			X				
1,3-Dimethyl-4-ethylbenzene	13DM4EB			X				
1,3-Dimethyl-5-ethylbenzene	13DM5EB			X				
1,3-Dimethyl-2-ethylbenzene	13DM2EB			X				
1,2-Dimethyl-3-ethylbenzene	12DM3EB			X				
1,2,4,5-Tetramethylbenzene	1245TMP			X				
Pentylbenzene	PENTB			X				
Naphthalene	NO			X				
2-Methylnaphthalene	2MN			X				
1-Methylnaphthalene	1MN			X				
Cyclopentane	CYP				X			
Methylcyclopentane	MCYP				X			
Cyclohexane	CH				X			
Methylcyclohexane	MCHx				X			
1-Pentene	1P					X		
2-Methyl-1-butene	2M1B					X		
2-Pentene (trans)	T2P					X		
2-Pentene (cis)	C2P					X		

(Continued)

Table 3. Continued.

Analyte	Abbrev	Paraffin	Isoparaffin	Aromatic	Naphthene	Olefin	Thiophene	Gasoline Additive
1-Hexene	1HEX					X		
1-Heptene/1,2-DMCP (trans)	1H					X		
1-Octene	1O					X		
1-Nonene	1N					X		
1-Decene	1D					X		
Thiophene	THIO						X	
2-Methylthiophene	2MTHIO						X	
3-Methylthiophene	3MTHIO						X	
2-Ethylthiophene	2ETHIO						X	
Benzothiophene	BT0						X	
1,2-Dichloroethane	12DCA							X
1,2-Dibromoethane	12DBE							X
MMT	MMT							X
Tertiary butanol	TBA							X
MTBE	MTBE							X
Diisopropyl Ether (DIPE)	DIPE							X
Ethyl Tertiary Butyl Ether (ETBE)	ETBE							X
TAME	TAME							X
Total	88	9	19	34	4	9	5	8

cosmetics, and products containing light petroleum distillates. The purpose of measuring VOCs in this project is to evaluate the proportions and character of non-petroleum VOCs which appear in the field samples collected in steelmaking wastes domain and residential areas. They are also detected in the sewer vapor samples. The total concentrations of VOC analytes in the soil vapor in the steelmaking wastes area range from $456 \mu\text{g}/\text{m}^3$ to $11,191 \mu\text{g}/\text{m}^3$ (Table 4). The total VOC concentration in the residential soil vapor sample is $419 \mu\text{g}/\text{m}^3$. The total VOC concentrations among the sewer samples range from $2,788 \mu\text{g}/\text{m}^3$ to $3,277 \mu\text{g}/\text{m}^3$. Paraffins, isoparaffins, aromatics and oxygenates attributable to gasoline comprise the majority of the VOCs; however, varying proportions of non-petroleum solvents are also present (Figure 6). Carbon disulfide (CD) is one of the most frequently detected non-petroleum VOC in all of the samples (Figure 7). Historically, CD was used as an industrial solvent, fumigant and insecticide. Currently, it is primarily used as an industrial solvent (Harrison et al., 2006). Oxygenated solvents, such as acrolein (ACL) and acetone (ACE) are detected in many field samples (Figure 7) and attributable to adhesives, building materials, and other industrial applications (Daughton, 2018). Acetaldehyde (ACT) is detected in the sewer vapor and attributable to the metabolic activity of bacteria or other organisms (Grosjean et al., 1990; Caballero et al., 1997). Chloromethanes are solvents detected in most of the field samples possibly from paint strippers, refrigerants, propellants, automotive products, and others (Tsai, 2017). Chloroethenes are present in the residential and steelmaking wastes areas and likely represent releases from dry cleaners, degreasers or other solvent products

(Grischek et al., 1996; Myszkowski et al., 2007). Freons are commonly detected at low levels in many field samples and likely represent incidental releases of refrigerants and propellants (Barber et al., 1998). Collectively, the observation of VOCs from petroleum and non-petroleum sources are consistent with results described by (Morisson et al., 2006; Douglas et al., 2007; Oudijk, 2009b; Emsbo-Mattingly and Litman, 2016), and may indicate widespread sewage leaks in the residential and steelmaking wastes areas. Alternatively, the non-petroleum VOCs may also indicate the infiltration of untreated wastewater from the sewers into the proximal subsurface soils.

Forensic piano fingerprints

The PIANO analytes include the dominant compounds in gasoline and petroleum solvents. Many volatile hydrocarbons were detected in the soil vapor samples collected in the domain of steelmaking wastes and in the residential areas. They were also detected in sewer vapor samples. The total concentrations of PIANO analytes in the soil vapor collected in steelmaking wastes area range from $351 \mu\text{g}/\text{m}^3$ to $17,365 \mu\text{g}/\text{m}^3$ (Table 5). The total PIANO concentrations among the residential soil vapor samples range from $166 \mu\text{g}/\text{m}^3$ to $54,847 \mu\text{g}/\text{m}^3$. These analytes occur throughout the residential area (Figure 6). The total PIANO concentrations among the sewer samples range from $3,297 \text{mg}/\text{m}^3$ to $3,988 \text{mg}/\text{m}^3$ (Table 5). The total PIANO concentrations are relatively uniform, with two exceptions (NF-VP-02(D) and NF-VP-09 representative from deeper interval in the steelmaking wastes domain and the higher concentration detected in the residential area, respectively), and

Table 4. Conventional TO15 VOC results.

Sample	Domain	Total TO15 Concentration (ug/m ³)	Relative proportion of Conventional TO 15 VOC analytes divided by classes										Signature Pattern				
			Chlorinated (%)	Fluorinated (%)	Brominated (%)	Oxygenated (%)	Sulfonated (%)	Hydrocarbon (%)	Metabolites	Solvents	Refrigerants/Propellants	Adhesives	Gasoline/Fuel				
NF-VP-01	Steelmaking Wastes	831	4.675	0.978	0.000	11.092	3.313	79.942	-	-	-	-	-	-	-	+	+
NF-VP-01(D)	Steelmaking Wastes	3,796	2.894	0.244	0.000	12.056	8.815	75.991	-	-	-	-	-	-	-	+	+
NF-VP-02(S)	Steelmaking Wastes	456	13.873	0.675	0.000	20.564	2.752	62.136	-	-	-	-	-	-	-	+	+
NF-VP-02(D)	Steelmaking Wastes	11,191	0.266	0.000	0.000	2.705	5.511	91.517	-	-	-	-	-	-	-	+	+
NF-VP-05	Residential	419	13.726	0.694	0.000	25.223	1.967	58.389	-	-	-	-	-	-	-	+	+
NF-SW-01	Sewer	3,277	0.471	0.101	0.000	93.755	0.143	5.530	++	++	-	-	-	-	++	+	-
NF-SW-03	Sewer	2,788	0.225	0.096	0.000	94.318	0.043	5.318	++	++	-	-	-	-	++	+	-

Legend: - not detected; + detection; ++ dominant concentration.

occur within the residential and steelmaking wastes areas (Figure 6). The chemical fingerprints of the PIANO data make possible the comparison of field (Figure 7) and reference samples (Figure 8). The PIANO fingerprints clearly demonstrate the presence of gasoline residues in the field samples (Figure 7).

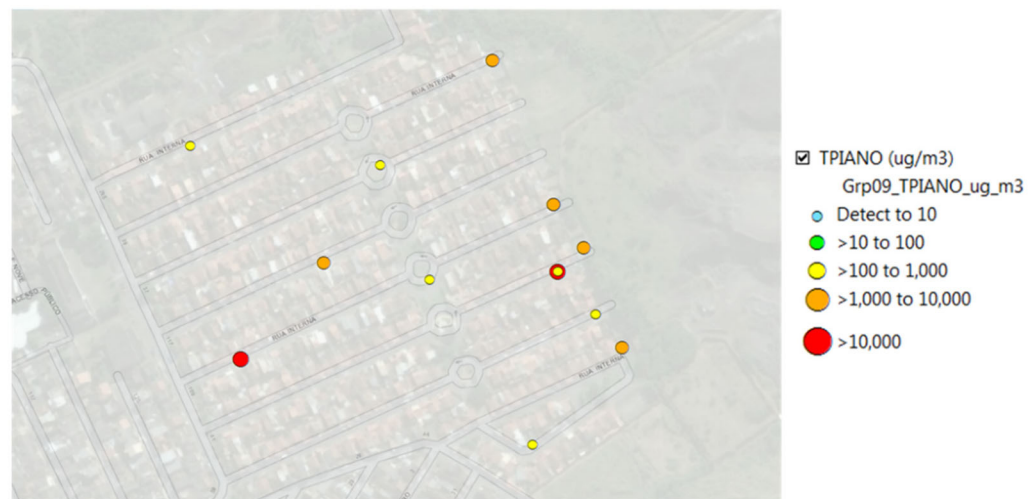
The fresh to lightly weathered gasoline residues are observed widely throughout the residential and steelmaking wastes areas (Figure 4c). The signature of gasoline consists of *n*-C₅ to *n*-C₉ paraffins mixed with isoparaffins, light aromatics (benzene, toluene, ethylbenzene, and xylenes or BTEX), naphthenes and olefins from comparable molecular weight ranges (Figure 4c and 9). The signature of weathered gasoline or diesel fuel is also evidenced in some of the field samples that exhibit high proportions of *n*-C₁₀ to *n*-C₁₃ range paraffins mixed with tri- and tetra-alkylbenzenes (Figure 9). These patterns are most clearly evident in all three sewer samples plus NF-VP 01, NF VP 02(S), NF VP 03(S), NF VP 03(D), NF VP 05, NF VP 07, NF VP 10, and NF VP 12. The absence of diesel signatures (Figure 4) in the hydrocarbon signatures of soil samples collected near the soil vapor samples suggests that the mixture of *n* C₁₀ to *n* C₁₃ range paraffins and tri and tetra-alkylbenzenes is most likely weathered gasoline. For example, a comparison of closely located pairs of soil gas and soil samples, like NF VP 02 and NFS S15, NF VP-03 and NFS S16 (Figure 4c and 7), and NF VP 05 and NFS S19 (Figures 4a and 7), demonstrate that the mixture of *n* C₁₀ to *n*-C₁₃ range paraffins and tri and tetra-alkylbenzenes are derived from weathered gasoline with no evidence of diesel fuel. The very high concentrations of ethanol (ETOH), isopropyl alcohol (IPA) and tertiary butanol (TBA) may indicate the release of ethanol based automotive fuel (Morisson et al., 2006; Douglas et al., 2007; Oudijk, 2009b; Emsbo-Mattingly and Litman, 2016). It is important to note that ethanol percentage in gasoline is typically higher than 26% in Brazil. These oxygenated compounds appear at high and relatively uniform concentrations in the sewer vapors.

These compounds readily evaporate and dissolve into groundwater; therefore, the high concentrations of them in the sewer vapor suggest a recent release of gasoline that experienced little to no evaporation. Indeed, the presence of ETOH, fresh gasoline and weathered gasoline in many of the samples suggests a long-term chronic gasoline release, which is distributed widely through the residential and dark soil areas by the sewer system.

(A)
Conventional
T015 VOCs
by Source



(B)
Total
Volatile
Hydrocarbons
in Air
($\mu\text{g}/\text{m}^3$)



(C)
PIANO
Distribution
by
Compound
Class

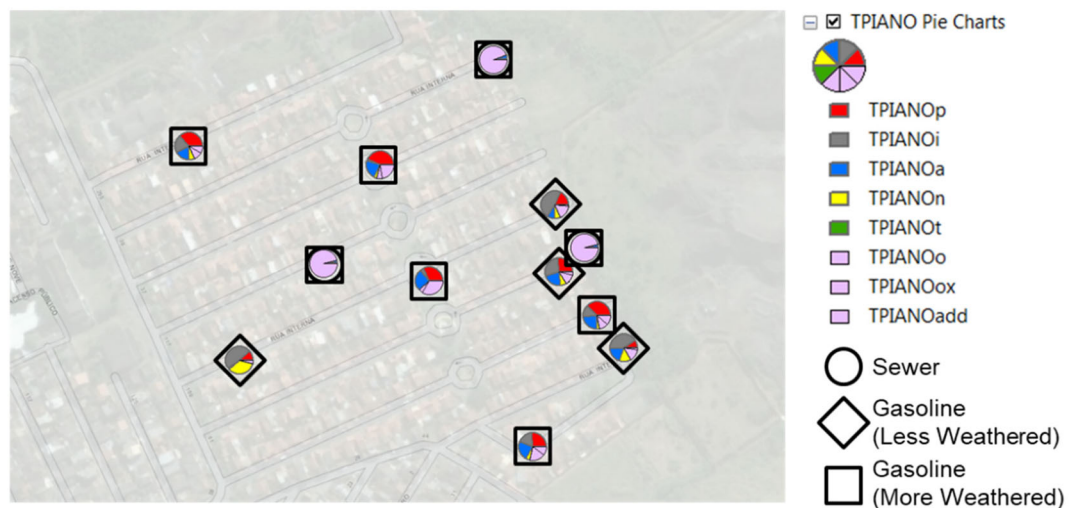


Figure 6. Volatile organic compound distributions.

Conclusions

Hydrocarbons products contain many individual compounds and patterns capable of identifying the source

of VOC in the vapor samples, degree and type of weathering, and relative amounts of each product when mixing occurs. Advanced forensic analyses

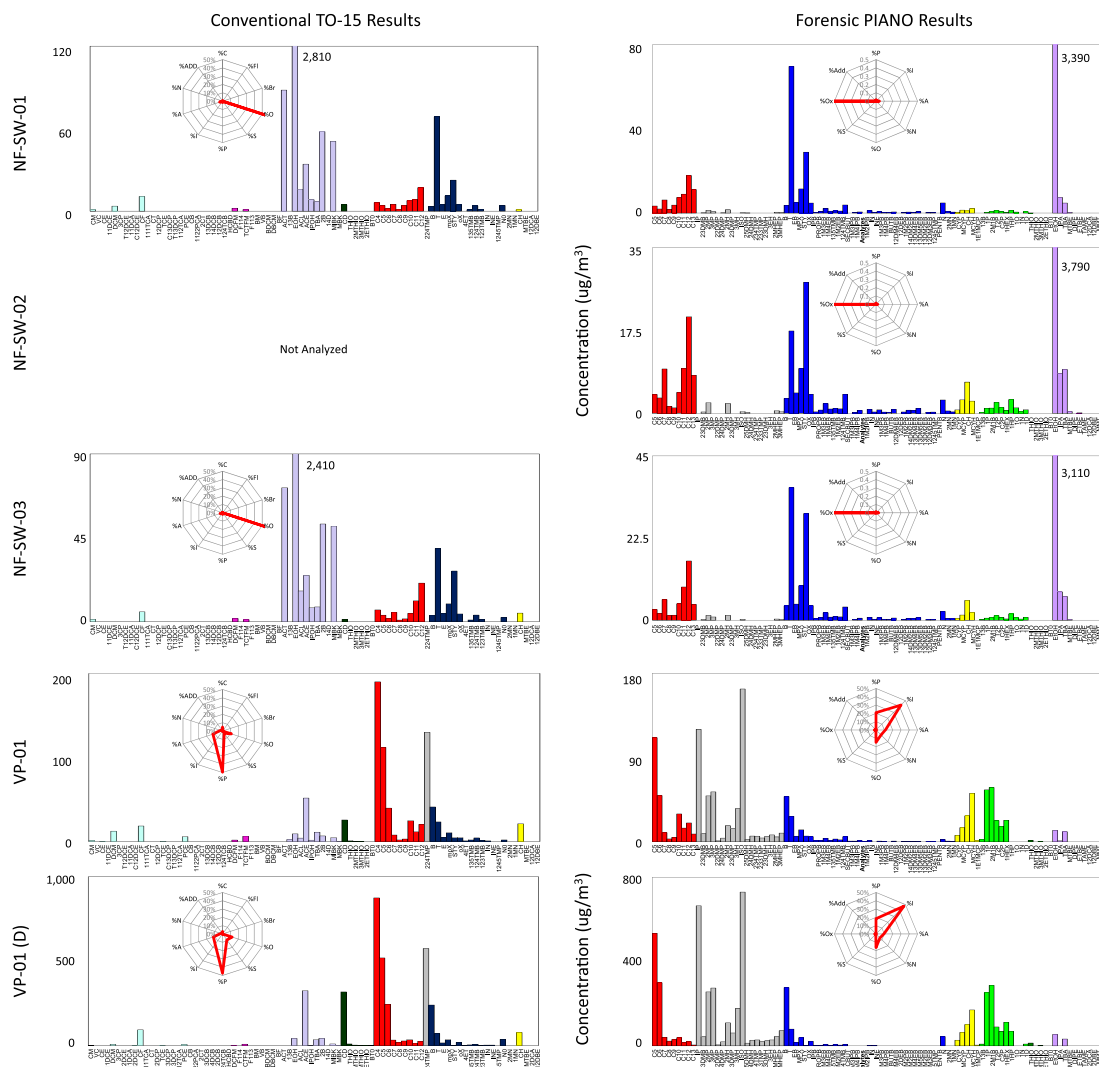


Figure 7. Volatile organic compound compositions in field samples.

further demonstrated the relationship between the steelmaking wastes and the hydrocarbon chemistry with a sufficient resolution for accurately identifying and differentiating pyrogenic and petrogenic products in the environment from soil samples collected during the prior works. The wide range of volatile hydrocarbon signatures helped determine the type, origin, and source of the hydrocarbons in vapor samples collected within a residential neighbourhood of Volta Grande IV, Brazil.

The forensic testing results supported several specific conclusions. First, the volatile hydrocarbon fingerprint in soil vapor samples collected from the residential area predominantly contained gasoline (i.e. n -C₅ to n -C₉ paraffins mixed with isoparaffins, BTEX, naphthenes, olefins, and ethanol - used in very high proportions in some Brazilian gasolines) and diesel

fuel (i.e. n -C₁₀ to n -C₁₃ range paraffins mixed with tri- and tetra-alkylbenzenes). Second, previous investigations demonstrated the steelmaking residues were composed of tar, which exhibited a volatile hydrocarbon fingerprint dominated by aromatics (i.e. BTEX, styrene, N0, 1MN, and 2MN) with little to no petroleum hydrocarbons (i.e. paraffins, isoparaffins, naphthenes, olefins, or gasoline additives). These starkly contrasting vapor signatures confirmed the presence of diffuse anthropogenic sources typical of active human activity in the residential area. Third, previous PAH fingerprinting identified some tar residues in the deeper dark soil layer, however, the volatile hydrocarbon in the subsurface vapor samples demonstrated little to no off-gassing of steelmaking waste into soil gas capable of posing risk of vapor intrusion and adverse indoor air impacts.

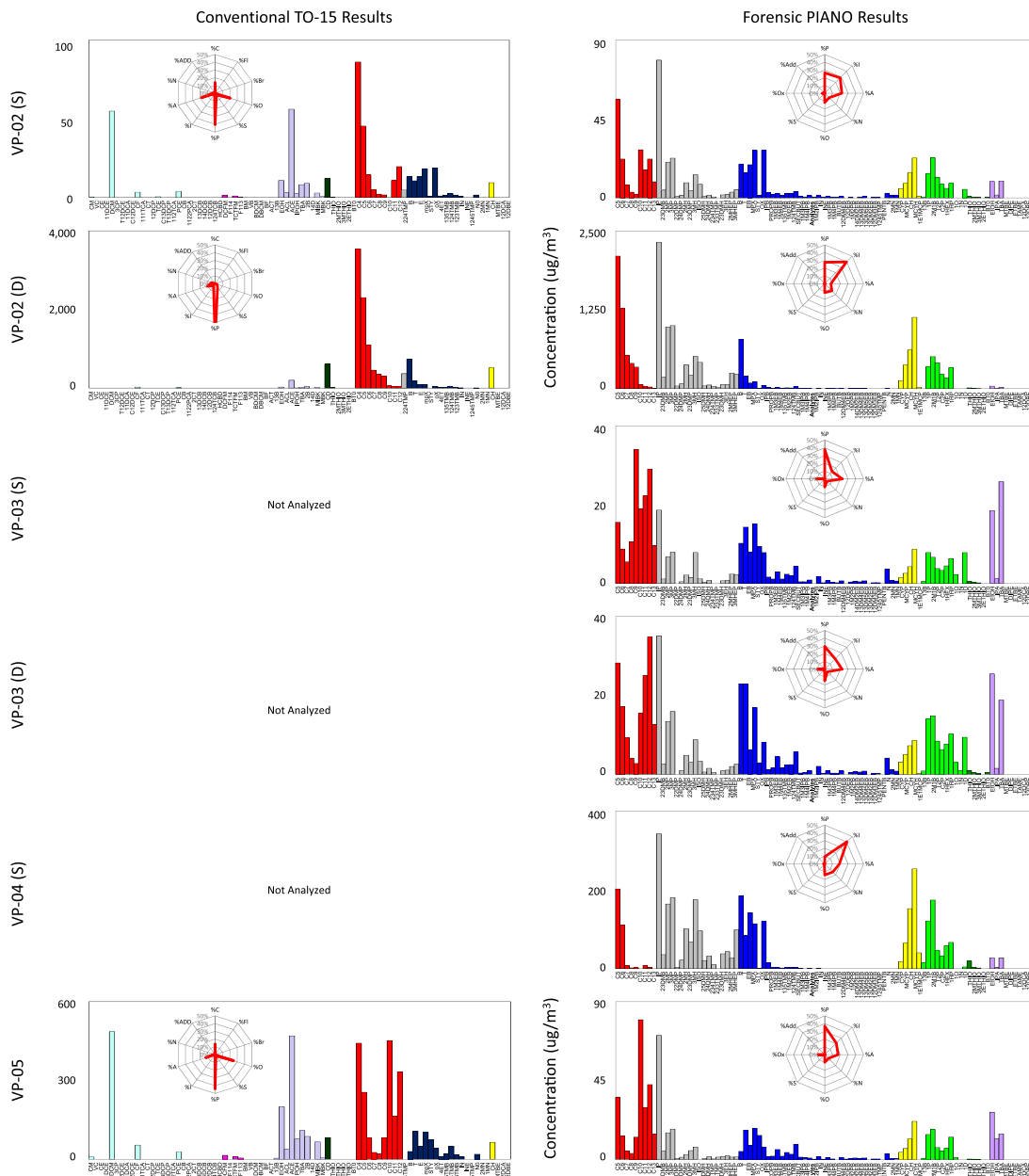


Figure 7. Continued

There are several possible reasons why steelmaking wastes failed to generate soil vapor signatures capable of migration in the soil gas. First, the tar residues were devolatilized during the steelmaking process and contained little to no volatile hydrocarbons at the time of disposal in the residential area. Second, environmental weathering degraded the volatile hydrocarbons in the tar residues over time. Third, volatile hydrocarbons vapors were rapidly degraded within close proximity of the deeper dark soil deposits by micro bacteria. Fourth, the organic carbon content of the subsurface soils substantially

adsorbed and effectively immobilized the volatile hydrocarbon vapors.

Consideration of multiple lines of evidence suggested that the absence of steelmaking vapors in the residential soil gas was most likely due to devolatilization during the steelmaking process and environmental weathering. In part, this conclusion is based on the initial PAH characterization, which demonstrated that almost all of the tar residues were depleted in N0 and/or P0 relative to the 4- to 6-ring PAHs. The low relative abundances of N0 and P0 is consistent with devolatilization and environmental weathering. In

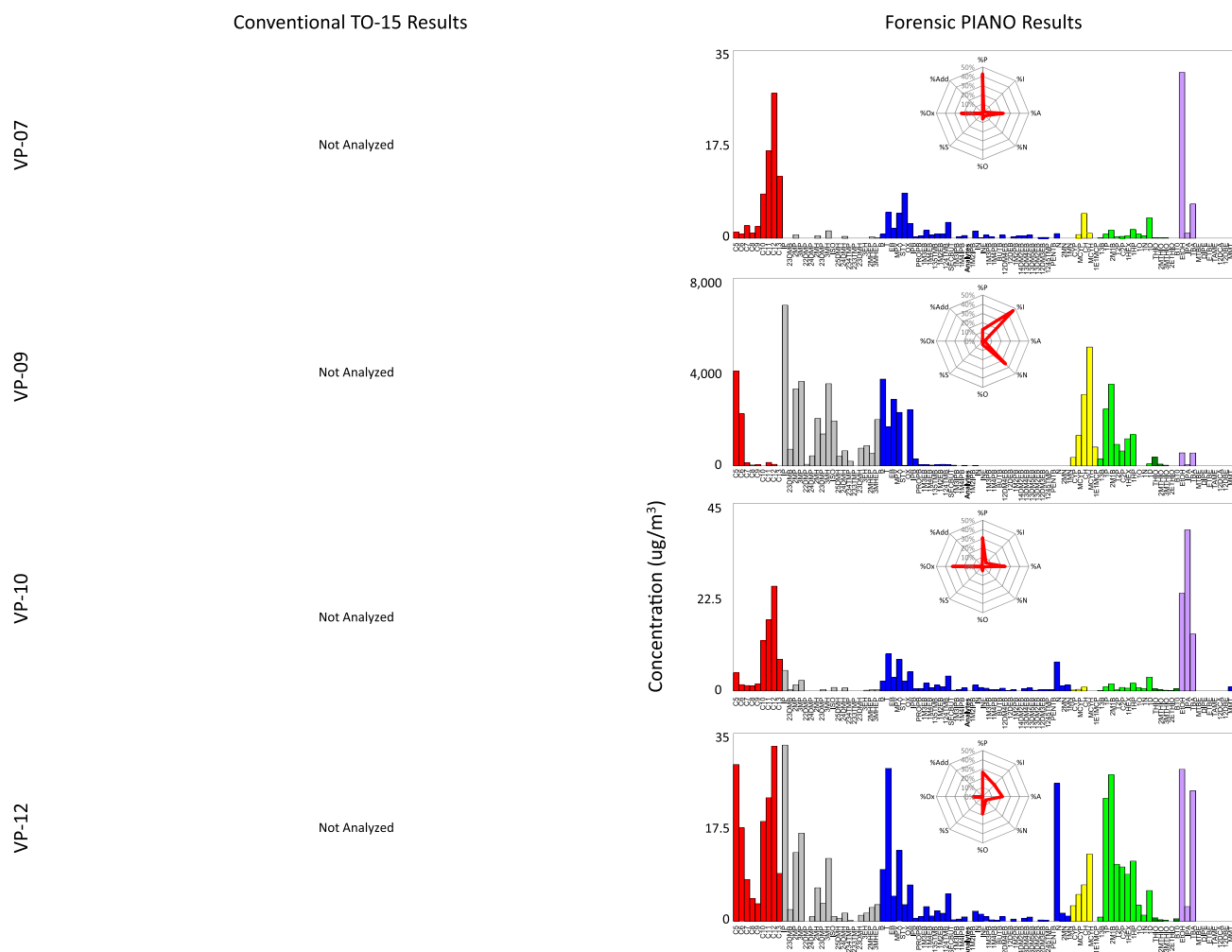


Figure 7. Continued

addition, the widely observed gasoline vapors in the residential soil gas samples contain variable proportions of n -C₅ to n -C₉ paraffins, which readily degrade in the environment. The variable proportions of n -C₅ to n -C₉ paraffins relative to comparable isoparaffins, naphthenes, and aromatics suggested biotic and abiotic degradation.

Collectively, the volatile hydrocarbon fingerprints discussed in this work generated significant information about hydrocarbon residues in this residential neighbourhood that heretofore posed significant unanswered questions for site investigators, conceptual site modellers, and remediation specialists. Although many previously identified anthropogenic hydrocarbon sources were known or suspected to exist in the residential area, the volatile hydrocarbon fingerprints clarified that the overwhelming sources of volatile hydrocarbons in soil gas were fugitive automotive gasoline and other petroleum hydrocarbon emissions. In general, higher concentrations occur at the deeper

depth interval proximal to the groundwater table. The gasoline derived hydrocarbons in soil gas ranged from $166 \mu\text{g}/\text{m}^3$ to $54,847 \mu\text{g}/\text{m}^3$ and consisted of paraffin, isoparaffin, aromatic, naphthene, olefin (PIANO) compounds mixed with ethanol. The mixtures of gasoline with different weathering patterns were consistent with multiple independent sources, possibly over long periods of time. The non-petroleum volatile organics likely reflected variable releases of solvents, adhesives, metabolic by-products, building materials, paint strippers, refrigerants, propellants, automotive products and others commonly observed in raw sewage.

This volatile hydrocarbon fingerprinting study also demonstrated that the sewer pipelines likely enhanced the distribution of petroleum products throughout the residential area. The sewer vapor samples contain relatively uniform mixtures of fresh and weathered gasoline mixed with volatile organics from a variety of non-petroleum sources. The gasoline derived

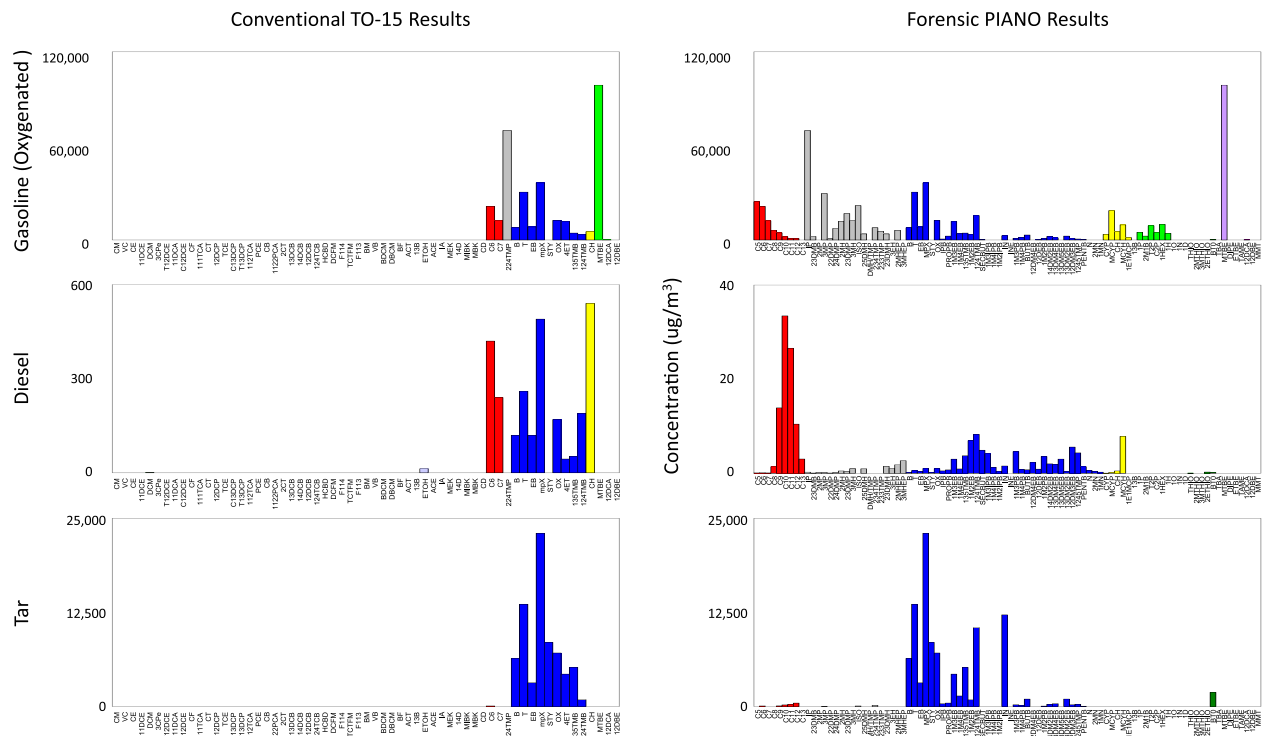


Figure 7. Continued

Table 5. Volatile forensic hydrocarbon (PIANO) results (EPA TO15M GC/MS).

Sample	Domain	Total PIANO Concentration (ug/m ³)	Relative proportion of Forensic Hydrocarbon PIANO analytes divided by classes							Signature Pattern		
			Paraffin (%)	Isoparaffin (%)	Aromatic (%)	Naphthene (%)	Olefin (%)	Sulfur (%)	Additive (%)	Gasoline	Diesel	Tar
NF-VP-01	Steelmaking Wastes	1,204	20.811	42.494	11.238	8.537	14.789	0.147	1.984	++	+	-
NF-VP-01(D)	Steelmaking Wastes	5,469	18.388	47.341	9.381	6.672	16.365	0.267	1.585	++	+	-
NF-VP-02(S)	Steelmaking Wastes	628	26.280	28.046	22.051	8.182	11.917	0.261	3.263	++	+	-
NF-VP-02(D)	Steelmaking Wastes	17,365	27.492	39.584	7.950	13.031	11.477	0.108	0.358	++	+	-
NF-VP-03(S)	Steelmaking Wastes	408	37.733	13.381	22.831	4.129	10.515	0.253	11.157	++	+	-
NF-VP-03(S)fd	Steelmaking Wastes	351	34.873	13.123	22.645	4.142	11.208	0.311	13.697	++	+	-
NF-VP-03(D)	Steelmaking Wastes	506	29.444	19.045	22.471	4.728	14.886	0.401	9.024	++	+	-
NF-VP-04(S)	Steelmaking Wastes	3,599	9.319	40.447	18.921	14.665	14.352	0.678	1.618	++	+	-
NF-VP-05	Residential	642	36.771	20.991	17.212	6.792	9.879	0.055	8.299	++	+	-
NF-VP-07	Residential	166	42.571	1.965	22.346	3.757	6.126	0.155	23.080	+	++	-
NF-VP-09	Residential	54,847	12.489	46.654	2.020	34.914	3.800	0.000	0.122	++	++	-
NF-VP-10	Residential	231	31.048	5.163	24.424	0.663	4.842	0.739	32.696	+	++	-
NF-VP-12	Residential	545	26.588	17.914	21.476	4.982	18.600	0.294	10.146	+	++	-
NF-SW-01	Sewer	3,628	1.732	0.134	4.039	0.141	0.158	0.003	93.793	+	++	-
NF-SW-02	Sewer	3,988	1.548	0.153	2.188	0.321	0.300	0.000	95.488	+	++	-
NF-SW-03	Sewer	3,297	1.425	0.133	3.191	0.284	0.212	0.000	94.755	+	++	-

Legend: - not detected; + detection; ++ dominant concentration; fd field duplicate.

hydrocarbons range from 3,297 $\mu\text{g}/\text{m}^3$ to 3,988 $\mu\text{g}/\text{m}^3$ and consist of paraffin, isoparaffin, aromatic, naphthene, olefin (PIANO) compounds mixed with ethanol. The non-petroleum volatile organics likely reflect variable releases of solvents, adhesives, metabolic by-products, building materials, paint strippers, refrigerants, propellants, automotive products and others commonly observed in raw sewage. The sewer vapor is greatly enriched in ethanol, ketones, and weathered gasoline compared to most of the soil vapor samples.

In summary, this work utilized complementary forensic chemical fingerprinting techniques to discern the sources of volatile hydrocarbons present in the soil vapors of an urban area with suspected presence of steelmaking wastes. While most environmental forensic case studies focus on volatile petroleum hydrocarbon releases in the US and Europe, this case study demonstrated the application of modern chemical fingerprinting techniques to determine the type, origin, and source of volatile hydrocarbons in Brazil.

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