RemTech Expo 2019

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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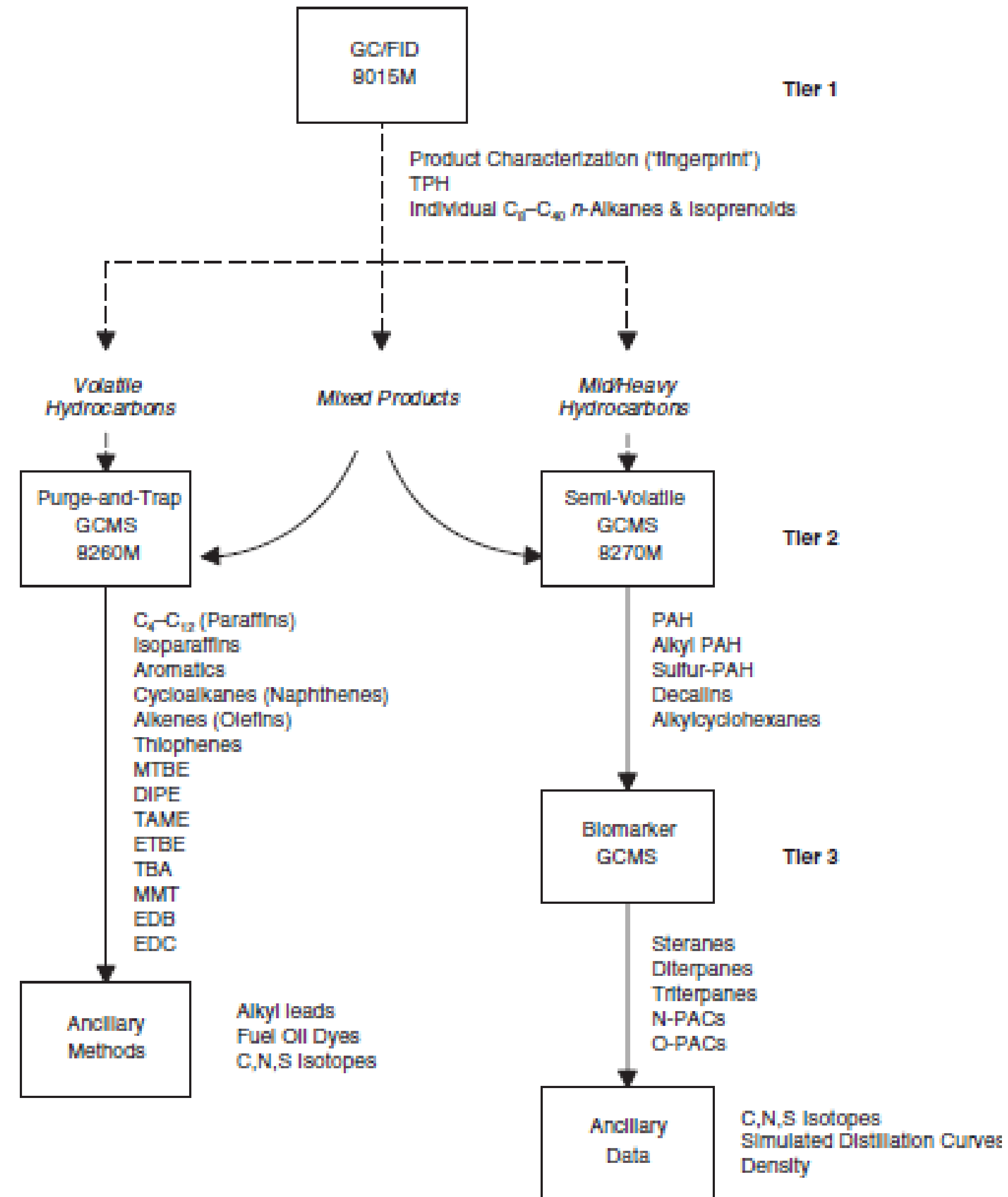NICOLE Latin America
VP Industry Commitee

Environmental Forensic Techniques for Hydrocarbons Chemical Fingerprint

Common uses

Determine or assist in determining the age and potential source(s) of contamination in several environmental matrices

- Discern multiple sources contamination - industrial, urban or background – complex scenarios;

- Age and source of contamination– several environmental matrices;

- Flexible tiered analytical approach, based on GC and
- Ancillary Methods – progressive use of analytical techniques;

- Compositional features of petroleum and coal byproducts;

- Identification petrogenic and pyrogenic materials;

- Chromatographic behavior of the major and minor constituents of each of these assemblages.

Tiered Analytical Approach

Tier 1

GC/FID
8015M

Product Characterization ('fingerprint')
TPH
Individual C_8–C_{40} n-Alkanes & Isoprenoids

Volatile Hydrocarbons

Mixed Products

Mid/Heavy Hydrocarbons

Tier 2

Purge-and-Trap GCMS 8260M

Semi-Volatile GCMS 8270M

C_4–C_{12} (Paraffins)
Isoparaffins
Aromatics
Cycloalkanes (Naphthenes)
Alkenes (Olefins)
Thiophenes
MTBE
DIPE
TAME
ETBE
TBA
MMT
EDB
EDC

PAH
Alkyl PAH
Sulfur-PAH
Decalins
Alkylcyclohexanes

Tier 3

Biomarker GCMS

Steranes
Diterpanes
Triterpanes
N-PACs
O-PACs

Ancillary Methods

Alkyl leads
Fuel Oil Dyes
C,N,S Isotopes

Ancillary Data

C,N,S Isotopes
Simulated Distillation Curves
Density

Tiered Approach – Detailement Level
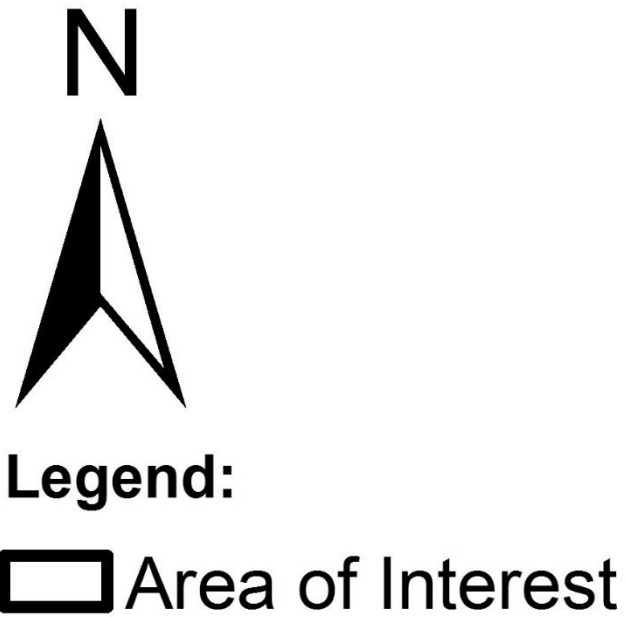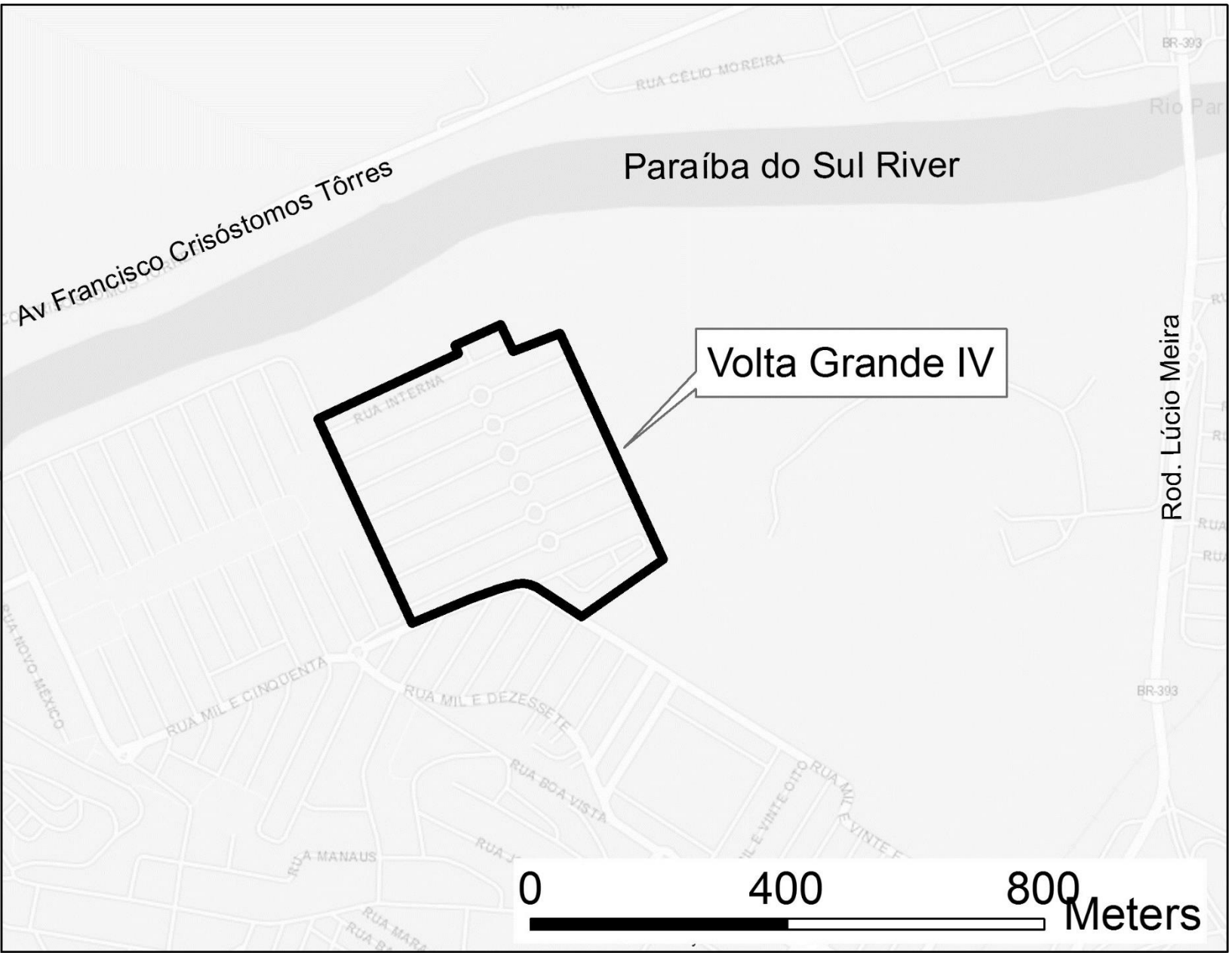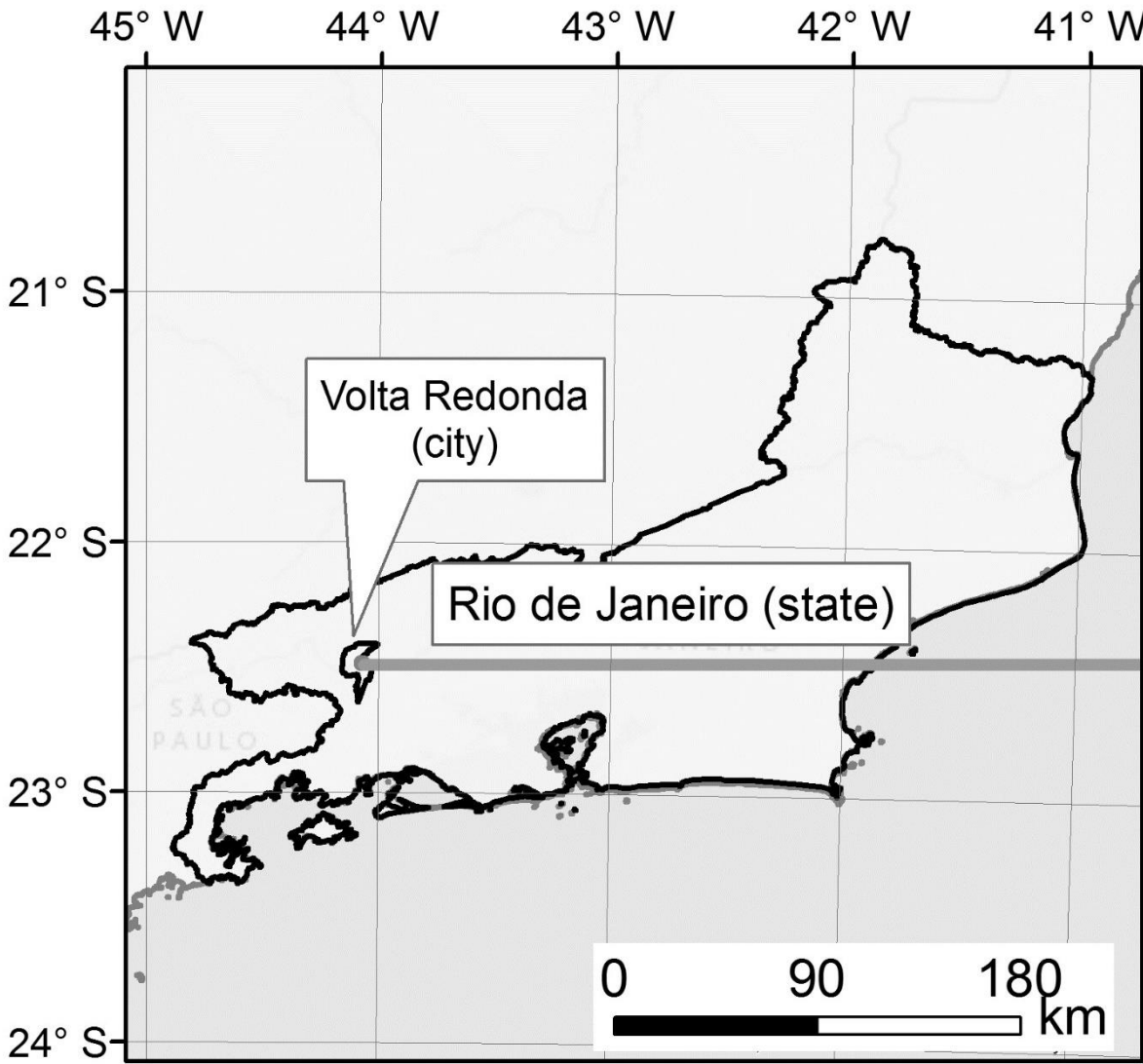
Main Objectives

Verify compatibility of hydrocarbons detected during previous investigations with steel mill wastes;

Determination of hydrocarbon chemical fingerprint in soils and soil vapors detected in all extension of the neighborhood;

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.

Legend:
Area of Interest

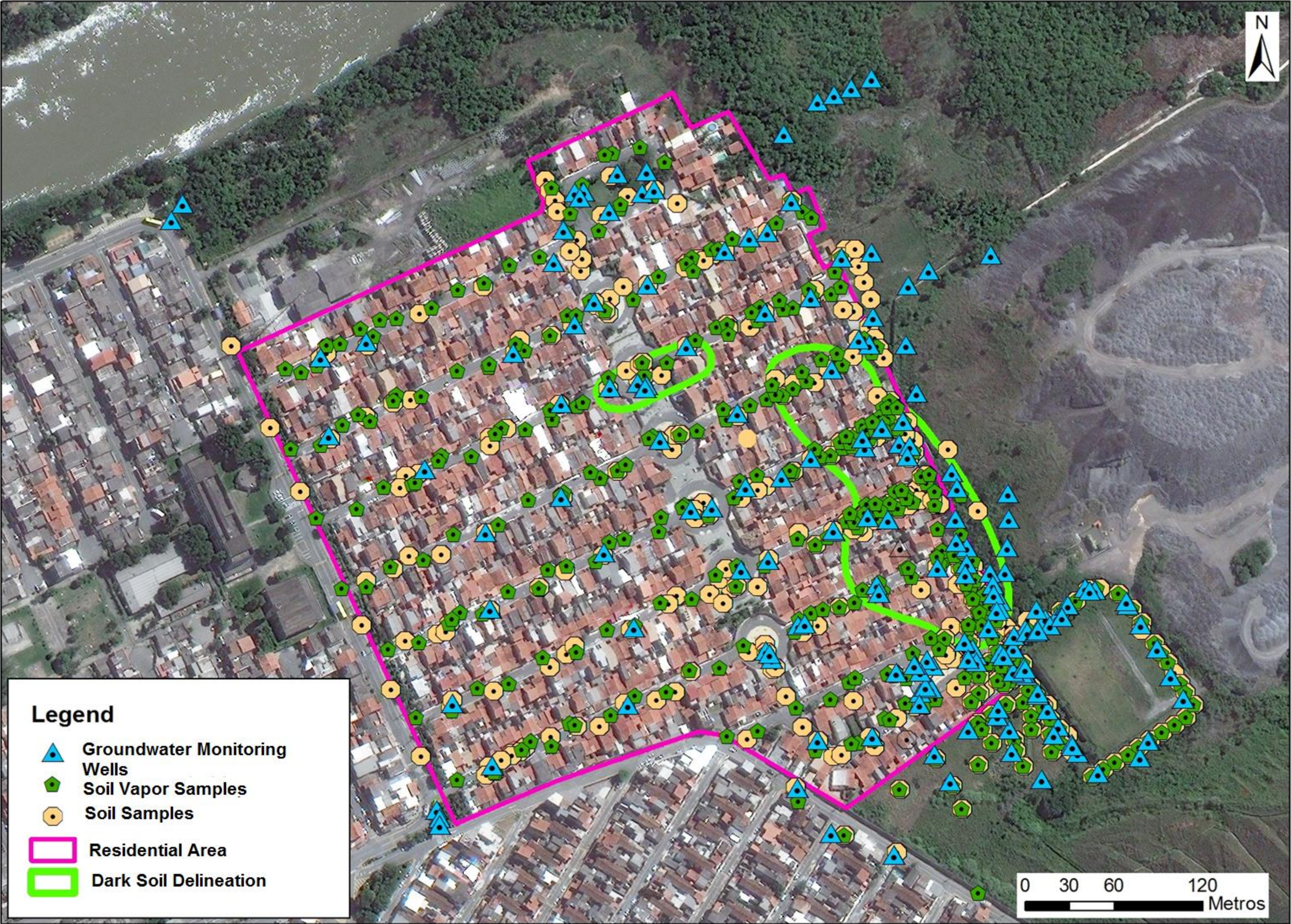# Steelworks wastes delineation, groundwater, soil and soil vapor samples

Legend

△ Groundwater Monitoring Wells
⬠ Soil Vapor Samples
⬤ Soil Samples
▭ Residential Area
▭ Dark Soil Delineation

Conceptual Site Model

Vapores relacionados a fontes urbanas difusas

Solo similar a qualquer área urbana

1m

Solo escuro
encontrado em apenas 10% do bairro e associado a subprodutos da siderurgia

2,5m

Água subterrânea

Hypotheses

1 - The superficial soil layer in the neighborhood (up to 1 meter deep) has the same composition and concentration detected in urban background areas in the municipality, probably associated with regional soot;

2 – The VOCs in the residential soil gas are associated with Gasoline and possibly Diesel fuel oil releases into the subsurface soils and sewers that are not associated with the steel mill waste;

Superficial — Residential

Subsurface — Residential

ENCOUNTERED @

Background

Steelworks wastes - "Dark Soil"

Soil and Soil Vapor Sampling

- 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.
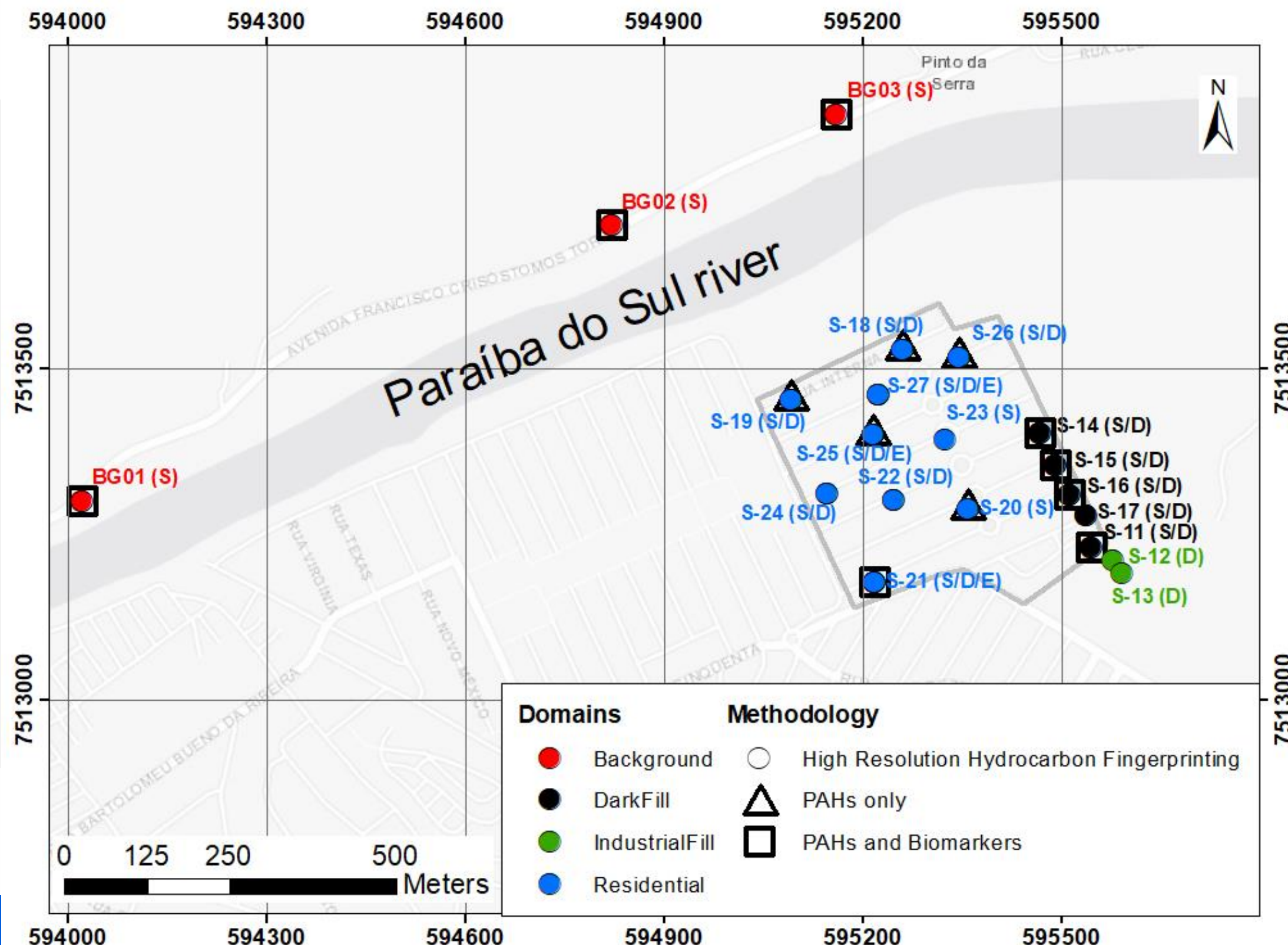
Methods

Forensics Hydrocarbon Fingerprinting

Analysis

Soil and Soil vapor samples were analyzed by Alpha Analytical, in Boston, USA;

Forensics Hydrocarbon Fingerprinting

The hydrocarbon analyses were conducted in accordance with EPA methods that were enhanced for forensic purposes:

> lower detection limits,
> additional quality control samples,
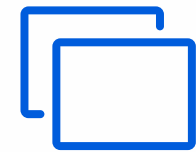> multilevel calibrations for diagnostic hydrocarbon analytes.

The methods meet or exceed the quality control provisions of comparable standard EPA methods.

Tiered Analytical Approach

VOCs: Regulatory EPA TO-15

Determined the concentrations of more than 80 VOC of traditional regulatory interest

VOCs PIANO Forense: Modified EPA TO-15

Determined the concentration of 1000 volatile hydrocarbons in 5 compound classes: **P**araffins, **I**soparaffins, **A**romatics, **N**aphthenes, and **O**lefins;

Various oxygenated compounds commonly found in oxygenated and reformulated gasoline are target analytes;

These results provide a basis to characterize and distinguish different types of gasoline, light petroleum distillates, and tar products.
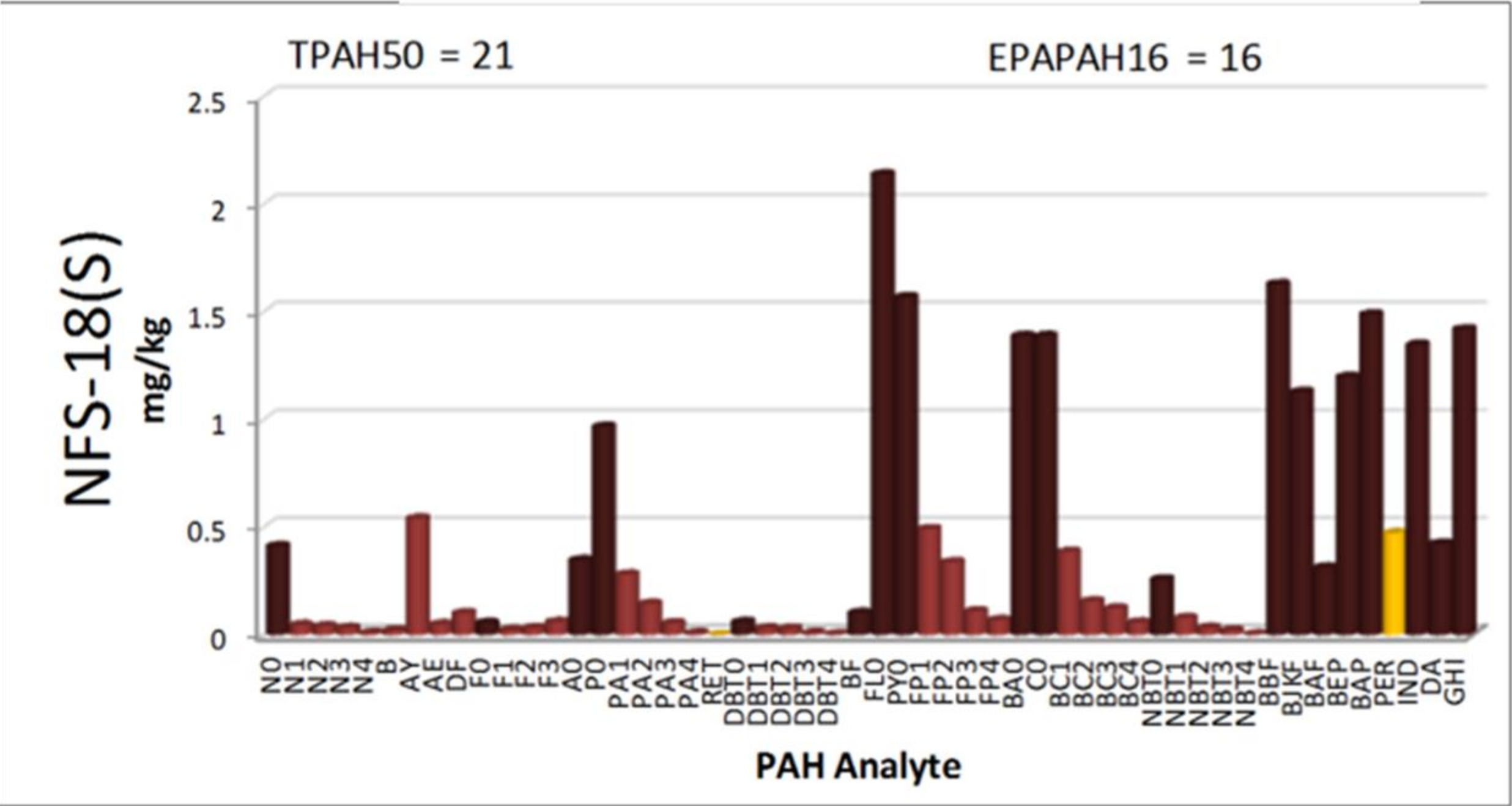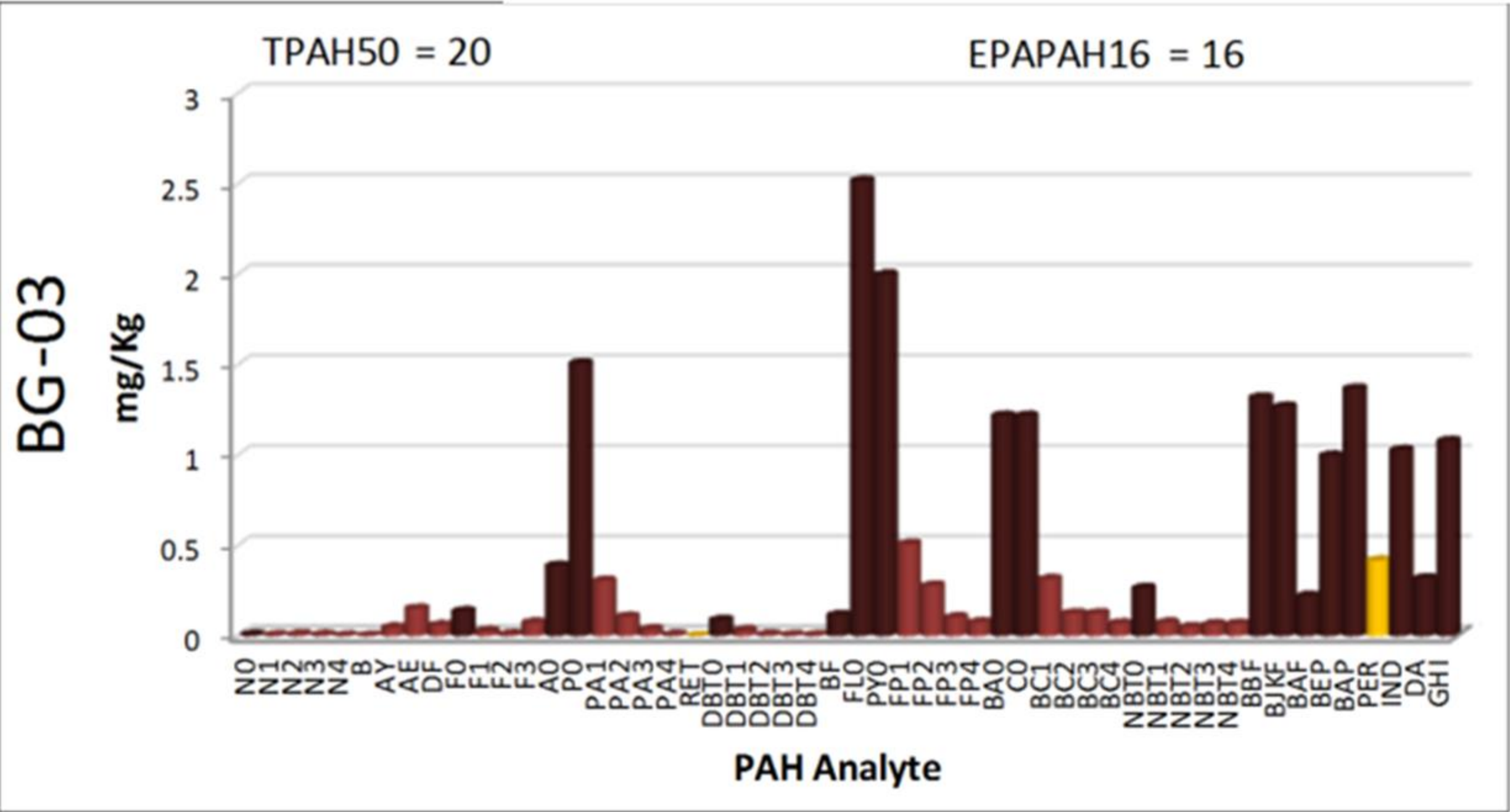
Tiered Approach – Detailement Level

Results - Soil

The residential soils match the background soil in terms of concentration and composition;

The PAH ratios indicate the background and residential soil samples are derived from similar high temperature combustion (soot) or carbonization (coke oven) sources
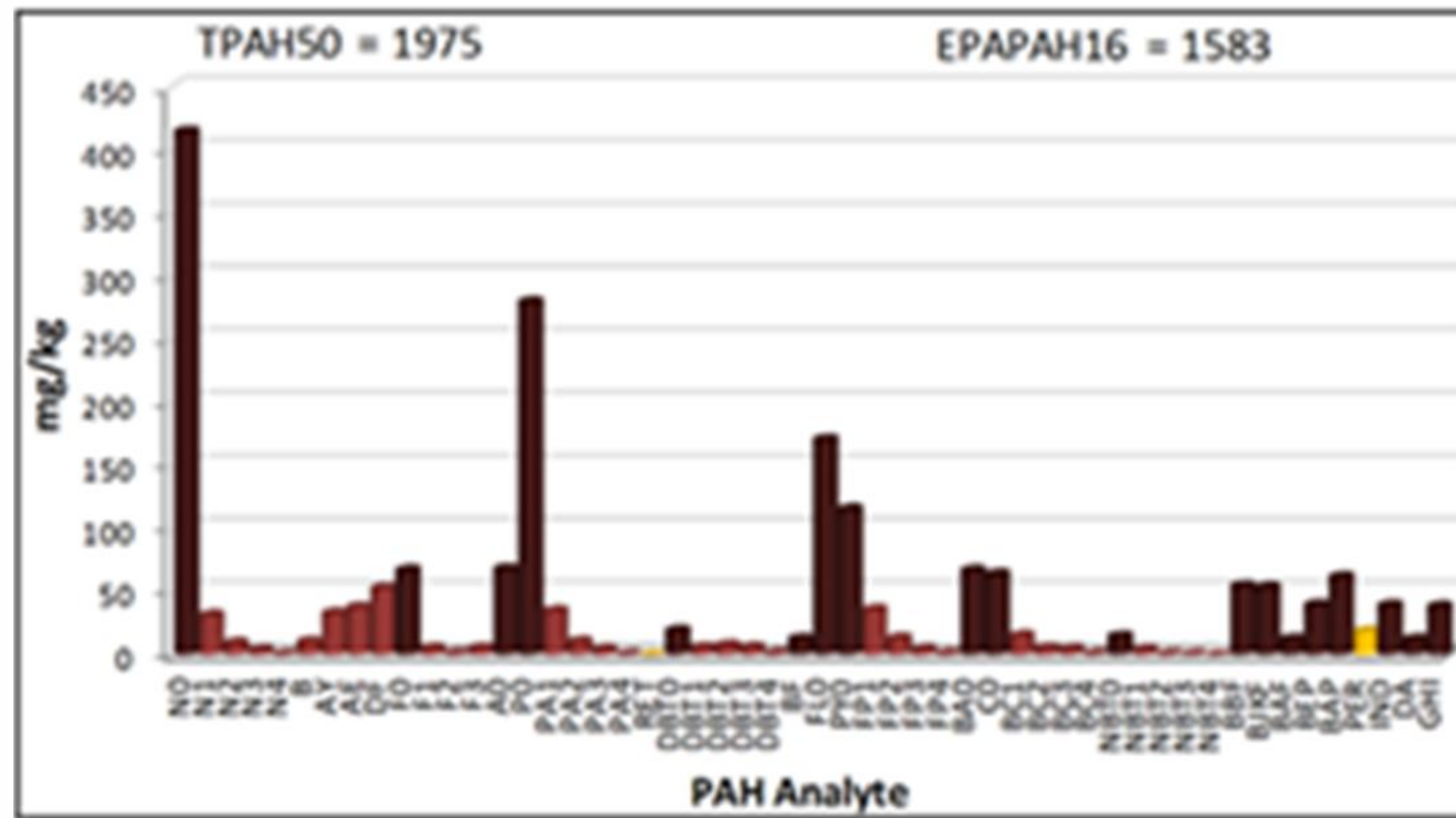
Results - Soil

EPAPAHs Totais - Solo Superficial

EPAPAHs Totais - Solo Subsuperficial

EPAPAH16 (mg/kg)
- Detecção até 1,0
- > 1,0 à 10
- > 10 à 100
- > 100 à 1.000
- > 1.000 à 10.000
- > 10.000

- The dark soil samples primarily contain mixtures of background soil; however, some are enriched by a second source of hydrocarbons;

- 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.

Hydrocarbon Fingerprint
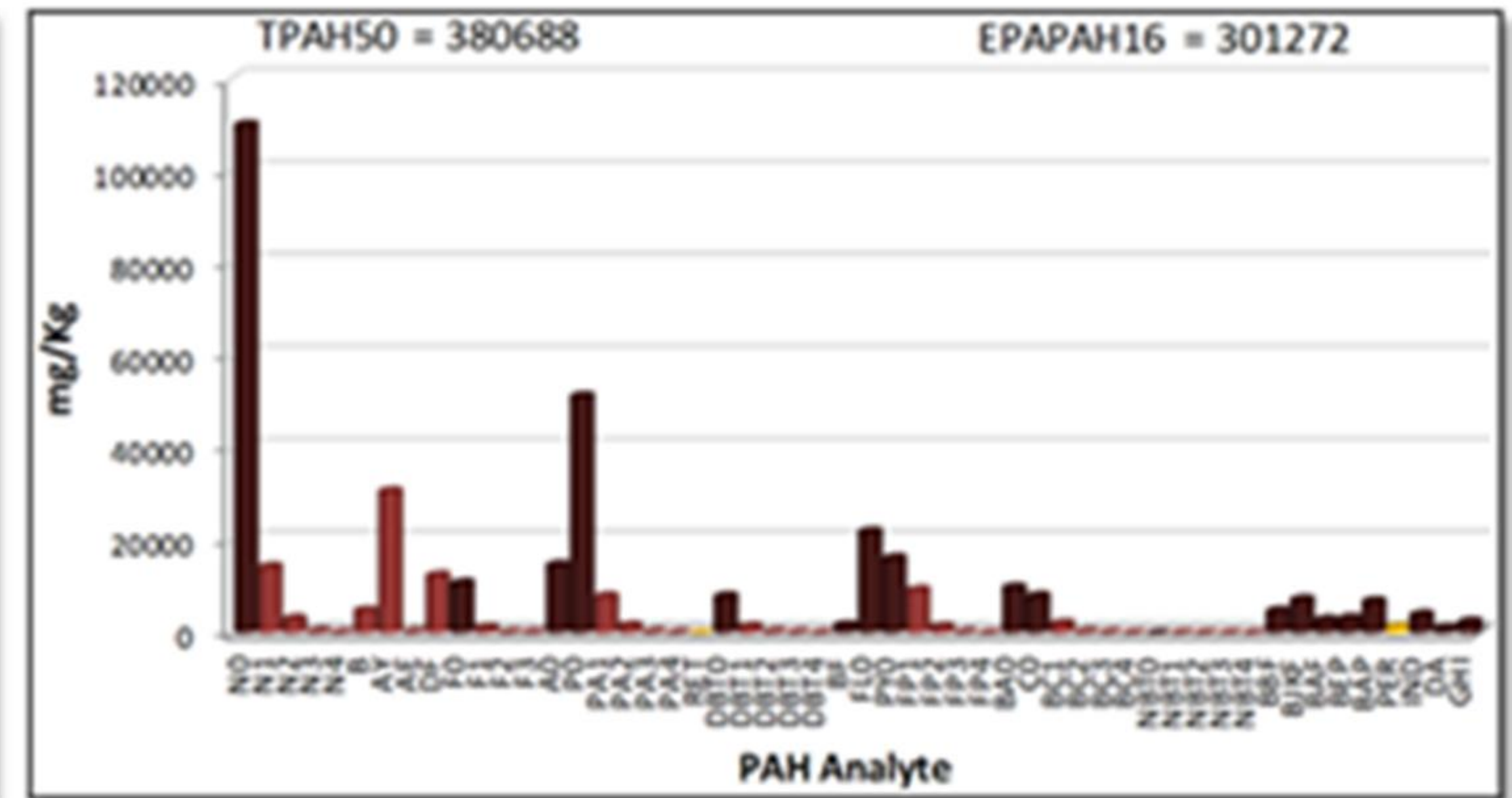
- In dark soil samples detected PAHs composition and concentrations are likely coal tar;
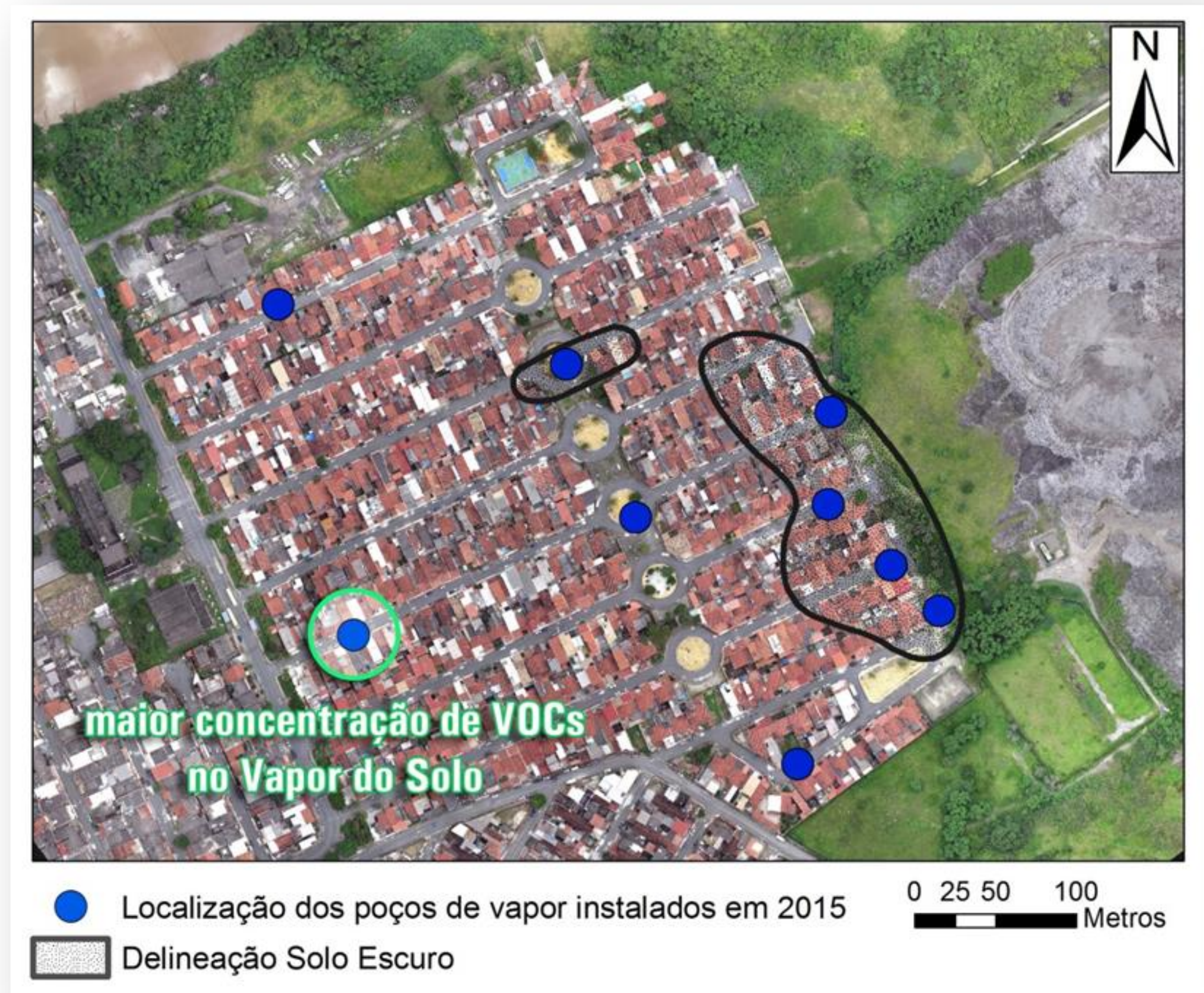- Naphtalene = tracer compound.

Resuls

Soil Vapor

The residential and dark soil vapor samples contain mixtures of **fresh and weathered gasoline** mixed with **VOC** from a variety of non-petroleum sources;

The sewer vapor samples contain relatively uniform mixtures of **fresh and weathered gasoline** mixed with **VOC** from a variety of non-petroleum sources.

There is no spacial relationship between higher VOC concentrations and dark soil delineation;

maior concentração de VOCs no Vapor do Solo

● Localização dos poços de vapor instalados em 2015

0 25 50 100 Metros

▨ Delineação Solo Escuro

Results

Soil Vapor hydrocarbon fingerprint

The residential and dark soil vapor samples contain mixtures of **fresh and weathered gasoline**
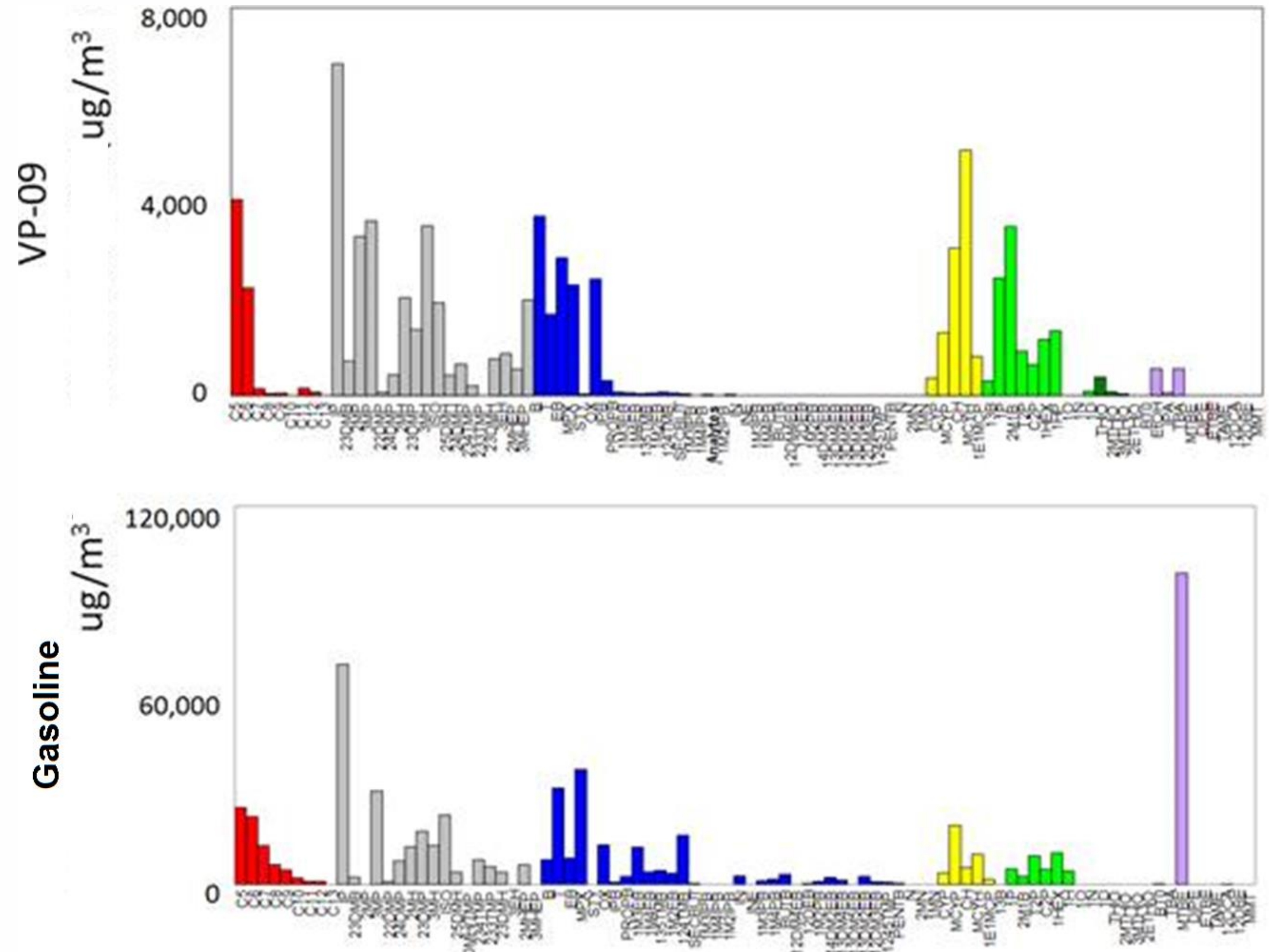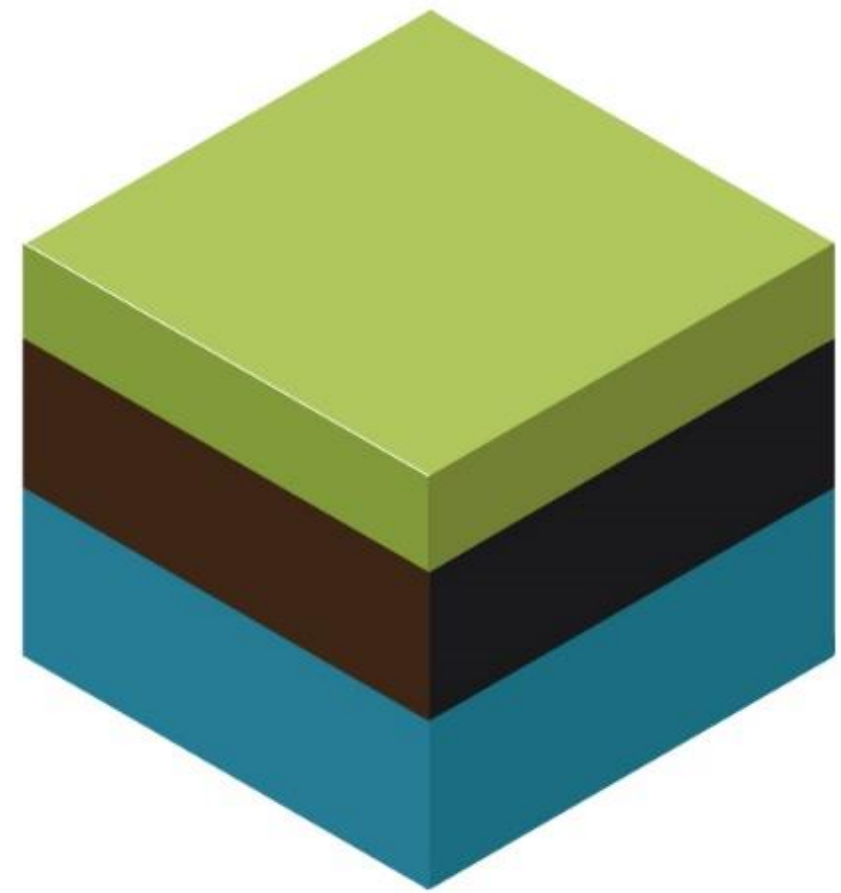
Conclusions

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.

Acknowledgments

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