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Identification of hydrocarbon sources in contaminated soils of three industrial areas

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HIGHLIGHTS

- ► Multi-criteria approach is required to characterize hydrocarbon sources in industrial sites.
- ► The results highlight multiple sources of hydrocarbons in soil samples.
- ► Both biogenic and anthropogenic hydrocarbons are detected in the three tank farms.
- ► Proposed methodology should be part integral of the environmental assessment studies.

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ABSTRACT

The present paper deals with identification of hydrocarbon sources in contaminated soil of three tank farms located in north, central and south Italy. Parent polycyclic aromatic hydrocarbons (naphthalene through benzo(g,h,i) perylene) and n-alkanes (n-C_{10} through n-C_{36}) were determined. The study of source assignments was carried out by their distribution patterns, their diagnostic ratios, and determination of less-commonly used markers. The data show anthropogenic and biogenic origin of n-alkanes and petrogenic and pyrolytic sources of PAHs. Multiple sources of hydrocarbons, that were not considered in the preliminary environmental assessments, are identified. The application of a multi-criteria approach allows to locate petroleum pollution sources that affect the study sites. The results demonstrate that the application of a multi-criteria approach for source identification is a key point to assess environmental damage and prove that an accurate study of source identification has to be performed. The suggested methodology is a useful tool to manage contaminated sites and to plan appropriate interventions of clean up.

1. Introduction

Petroleum chemical fingerprinting is a well-known and established methodology to investigate oil composition, to assess sources and fates, and to predict the long-term impact of spilled oils (Daling et al., 2002; Wang and Fingas, 2003; Stout et al., 2007; Guitart et al., 2008; Tobiszewski and Namiesnik, 2012). Detailed hydrocarbon fingerprinting can prove useful in site investigations where the sources of suspected leaked crude oil or petroleum products are both known and unknown (Stout, 2003). Nevertheless most of the studies to elucidate hydrocarbon sources are focused on sediments, suspended matter and aerosols, with limited research on soils in industrial areas (Iturbe et al., 2005; Pies et al., 2008; Agarwal et al., 2009; Ma and Zhou, 2011; Tobiszewski and Namiesnik, 2012). In these sites the heterogeneity of compounds and the complexity of the environmental matrix make source identification challenging and more than one source identification method is required to identify the origin of pollution.

Aliphatic alkanes and polycyclic aromatic hydrocarbons (PAHs) play an important role in characterization, differentiation, and source identification of oil spills in environmental forensic investigations (Wang et al., 1999a,b; Colombo et al., 2005a,b) since each source gives rise to distribution characteristic patterns of these compounds according to their production sources (Baumard et al., 1998). These hydrocarbons may have multiple origins such as spills from accidental or chronic leakages of land and marine pipelines, fuel tanks, domestic and industrial wastes, partial combustion of fuels, wood burning and diagenetic transformation of non-hydrocarbon natural products (Readman et al., 2002; Commendatore et al., 2012). However, other sources can contribute to their introduction into the environment such as superior plant wax, algae, plankton (Colombo et al., 1989; Kennicutt et al., 1994; Commendatore and Esteves, 2004). The study of PAH and n-alkane distribution allows to differentiate between anthropogenic and natural sources and their diagnostic ratios can be used to identify these sources (Asia et al., 2009). Particularly, the n-alkanes are commonly used to obtain a broad overview of hydrocarbon sources ranging from terrestrial vascular plant material to marine algae to petroleum (Harris et al., 2011) and the PAH molecular indices permit to discriminate between pyrolytic and petrogenic sources, since pyrogenic PAHs are generated by incomplete organic matter combustion at high temperature and petrogenic PAHs are related to crude oil and its refined products (Wang et al., 1999a,b;

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Page et al., 2002; Commendatore and Esteves, 2004; Maliszewska-Kordybach et al., 2009). In addition, some compounds, such as perylene, may have both natural and anthropogenic origin and their determination can give further information about contamination origin (Bakhtiari et al., 2009; Montuori and Triassi, 2012).

Consequently, a multi-criteria approach is required to distinguish biogenic compounds from petroleum hydrocarbons above all when corrective measures of pollution prevention have to be adopted. Therefore, the aim of the present study is to identify hydrocarbon sources in industrial sites by applying different source identification methods so that suitable actions can be performed for pollution prevention and risk management. Furthermore the paper stresses the necessity of carrying out an accurate study of source apportionment to perform a successful forensic investigation in sites where the impacts caused by multiple sources can provide cumulative effects on human health and environment.

For this purpose, the present paper deals with chemical characterization of soil samples collected in three tank farms located in north, central and south Italy. According to a previous chemical characterization, groundwater was contaminated by petroleum hydrocarbons and their concentrations were higher than the limits set by Italian regulatory authorities (Riccardi et al., 2008). In this paper EPA priority parent PAHs (naphthalene through benzo(g,h,i)perylene) and n-alkanes (n-C_{10} through n-C_{36}) were detected; the study of source assignments was carried out by their distribution patterns, their diagnostic ratios, and less-commonly used markers. According to the scientific literature many ratios of selected molecular species can be used (Colombo et al., 1989; Yunker et al., 1999; Daling et al., 2002; Yunker et al., 2002; Wang and Fingas, 2003; Commendatore and Esteves, 2004; De Luca et al., 2004). In this study the CPI ratio (Carbon Preference Index), defined as $2(\text{n-C27} + \text{n-C29})/(\text{n-C26} + 2\text{n-C28} + \text{n-C30})$ (Colombo et al., 1989), Phenanthrene/Anthracene (Phe/Ant), Fluoranthene/Pyrene (Flu/Pyr), Ant/(Ant + Phe), Flu/(Flu + Pyr) and Benzo(a)anthracene/ Chrysene + Triphelynene + Benzo(a)anthracene) (BaA/228) (De Luca et al., 2004) were adopted and calculated. The present paper wants to demonstrate that the application of a multi-criteria approach for source identification is a key point to characterize pollution levels and to locate contamination sources. This study suggests a methodology that aids the authorities to manage contaminated sites and to plan appropriate interventions of clean up.

2. Materials and methods

2.1. Site description

Soil samplings were carried out in three tank farms still in operation in order to verify soil quality and to identify the sources of pollution. The sites are located in three Italian cities, in the north, center and south of the country: Rho (MI), Rome (RM) and Palermo (PA). A detailed description of the sites is provided in Riccardi et al., 2008. Site plans are provided in Supplementary data (Fig. 1S, 2S and 3S).

In brief, the site MI is located in an industrial area characterized by several tank farms belonging to different oil companies that get petroleum products from the refinery 10 km far away by underground pipelines. The RM site is located on the outskirts of Rome in an industrial/semi-rural area where a petroleum refinery, a municipal landfill and a hospital waste incinerator lie within a short range. The PA shore site is located on the outskirts of Palermo in a heavily anthropized area.

Since a previous chemical characterization had shown petroleum hydrocarbon contamination of groundwater, a system of pumping wells was installed as a preliminary corrective measure in all the three sites.

2.2. Sampling

Soil samplings were carried out with a dry rotation drilling technique. Sampling points were chosen based on their location relative to the direction of groundwater flow: up-gradient area, tank area, that is the possible source of fuel leaks, and down-gradient area. The drillings were performed to a depth of 10 m. Sampling points were identified by site code and a progressive number: eight up-gradient points (MIS1, MIS2, MIS3, RMS1, RMS2, RMS3, PAS1 and PAS2), nine points close to fuel tanks and tank truck loading area, that are the possible sources of oil leaks (MIS4, MIS5, RMS4, RMS5, RMS6, PAS3, PAS4, PAS5 and PAS6) and six down-gradient points (MIS6, MIS7, RMS7, RMS8, PAS7 and PAS8). Soil samples were collected at each meter of depth and were air-dried, crushed and sieved (<2 mm) and stored at −20 °C in pre-cleaned amber glass bottles until further treatments.

2.3. Sample extraction

The extractions of soil samples were carried out in triplicate. Five grams of soil was mixed with 5 g of anhydrous sodium sulfate, spiked with 20 µl of PAH internal standard solution (0.5 ppm) and 2 µl of n-alkane internal standard solution (40 ppm) and extracted with Dionex ASE200 Accelerated Solvent Extractor (Dionex, Sunnyvale, CA). Operating conditions were: system pressure = 1500 psi; purge nitrogen pressure = 150 psi; purge nitrogen-time = 300 s; oven temperature = 100 °C; oven heat-up = 5 min; static time = 5 min; flush volume = 40% of extraction cell volume; dichloromethane 100%.

Internal standards were: naphthalene-d_8, acenaphthylene-d_8, acenaphthene-d_{10}, fluorene-d_{10}, phenanthrene-d_{10}, anthracene-d_{10}, fluoranthene-d_{10}, pyrene-d_{10}, benzo(a)anthracene-d_{12}, chrysene-d_{12}, benzo(b)fluoranthene-d_{12}, benzo(k)fluoranthene-d_{12}, benzo(a)pyrene-d_{12}, benzo[e]pyrene-d_{12}, perylene-d_{12}, indeno (1.2.3-c,d)pyrene-d_{12}, dibenzo(a,h)anthracene-d_{14}, benzo(g,h,i) perylene-d_{12}, n-decane-d_{22}, n-undecane-d_{24}, n-dodecane-d_{26}, n-tridecane-d_{28}, n-pentadecane-d_{32}, n-hexadecane-d_{34}, n-octadecane-d_{38}.

The extract was percolated through a column containing 30 g of anhydrous sodium sulfate and purified through a neutral alumina column that was eluted with 15 ml of dichloromethane. The collected eluates were dried under nitrogen stream and re-dissolved with 10 µl of toluene. The extract was stored at −20 °C in amber vial until analytical determination.

2.4. Chemical analysis

The detailed method is given in Riccardi et al., 2008. Briefly, PAH and n-alkanes were analyzed using a Hewlett-Packard 6890 gas chromatograph with a 5973A mass selective detector (Agilent Technologies, Palo Alto, CA). The MS was operated in selected ion monitoring (SIM) mode for quantitation of target compounds. PAHs from naphthalene through benzo(g,h,i)perylene and n-alkanes from n-decane (n-C_{10}) through n-triacontane (n-C_{36}) were detected. The compounds were identified on the basis of their mass spectra using the base peak and two qualifier ions for each compound and quantified by internal standard method. The detailed procedure of quality control, consisting of blank measures, calibration verifications and standard reference material analysis, was carried out routinely. The recovery efficiency was checked by analyzing standard reference materials (NIST2975, NIST1649b, NIST1941b) and soil samples spiked with known amount of standards. Compound recoveries ranged from 80% to 120%. The detailed procedure is described in Borsella et al. (2004). The concentrations were expressed as mean value ± uncertainty computed at the 95% level of confidence.

3. Results and discussion

3.1. Rho (MI)

Fig. 1 shows total PAH and n-alkane concentrations vs. depth in all the sampling points. At MIS6 sampling point total n-alkane and PAH