

APPLICATION OF COMPOSITIONAL FINGERPRINTING TO AN ITALIAN SITE CONTAMINATED BY HYDROCARBONS

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EXTENDED ABSTRACT

L'analisi della composizione di una miscela inquinante, costituita da petrolio o dai suoi prodotti di raffinazione, può dare utili informazioni circa l'origine della contaminazione e i processi da essa subiti, attraverso l'identificazione di composti omologhi e di parametri di correlazione che consentono di tracciare il percorso e la storia della contaminazione stessa. Questo risulta particolarmente importante qualora esistano più potenziali sorgenti di inquinamento e si voglia individuare il responsabile, come ad esempio nel caso di due stazioni di servizio adiacenti o quando su una stessa area si succedono diversi proprietari.

In questo articolo viene presentato un caso di applicazione di tecniche di fingerprinting composizionale per la caratterizzazione di un sito contaminato da idrocarburi, collocato nell'Italia settentrionale. Nell'area di studio sorge una stazione di servizio con un distributore di carburante distaccato, ma in passato il sito, ora sede del solo punto di ristoro, era suddiviso in due zone che includevano un punto ristoro di dimensioni inferiori all'attuale e un distributore di carburante, proprietà di un'altra società. Durante lo scavo per l'espansione di un edificio, è stata riscontrata una contaminazione da idrocarburi, fatto che ha determinato la necessità di attribuire la responsabilità della contaminazione e quindi l'onere della bonifica a una delle due società interessate. A tale scopo sono stati prelevati dagli scavi 7 campioni di terreno e sottoposti ad analisi di fingerprinting composizionale per determinare la sorgente di contaminazione degli idrocarburi e la loro età di rilascio nell'ambiente. Sebbene le tecniche di fingerprinting siano ben note nella letteratura scientifica, la loro applicazione in Italia risulta essere ancora scarsamente diffusa. Quando si parla di contaminazione da idrocarburi in realtà si indica una contaminazione costituita da una miscela di alcune centinaia di composti. Il fingerprinting composizionale, attraverso lo studio di classi contaminanti omologhi presenti, permette di identificare tali composti e conseguentemente di distinguere la tipologia di contaminazione (es. benzina, gasolio, cherosene) e l'età di rilascio. In particolare attraverso la valutazione dei rapporti tra specifici composti della miscela indici del livello di degradazione subito dalla contaminazione, nel caso di studio sono state condotte analisi mediante GC-MS sia su idrocarburi volatili (composti leggeri quali benzene, toluene, etilbenzene e xileni_BTEX e gli additivi utilizzati come antidetonanti utilizzati nelle benzine quali metil *ter*-butilene MTBE, dibromoetano_1,2-EDB e dicloroetano_1,2-EDC) che semivolatili e/o non volatili (famiglie omologhe di idrocarburi) presumibilmente presenti nell'area. Nei 6 campioni prelevati a 4 e a 5 m dal piano campagna, è stata riscontrata la presenza di idrocarburi semivolatili e/o non volatili, la miscela era infatti caratterizzata dall'assenza di BTEX e antidetonanti. Questo ha consentito di escludere che potesse trattarsi di un prodotto leggero, quale la benzina.

I composti omologhi rilevati hanno invece permesso di affermare che per 2 campioni (F5_1 e F5_2, prelevati a fondo scavo) la contaminazione è legata esclusivamente a gasolio. In particolare la concomitante presenza degli isoprenoidi pristano (i-C₁₉) e fitano (i-C₂₀) e l'alta abbondanza degli idrocarburi policiclici aromatici (IPA) fenantrene, dibenzotiofene e di C₄-naftalene, supportano la conclusione che si tratti di un gasolio altamente degradato. Anche nel campione F2 (prelevato lungo la parte meridionale dello scavo) non sono stati trovati prodotti idrocarburi leggeri, ma sono stati complessivamente riscontrati composti attribuibili a un prodotto più pesante del gasolio (olio lubrificante). In particolare l'assenza di isoprenoidi e la relativa abbondanza di C₄-fenantrene e C₄-dibenzotiofene supportano questa conclusione. Infine nell'ultimo gruppo di campioni (F1, F3 e F4_prelevati rispettivamente lungo la parete settentrionale, occidentale ed orientale) è stata riscontrata la presenza di un range di prodotti idrocarburi più ampio che oltre al gasolio comprende una frazione idrocarburi più leggera (probabilmente cherosene) e una più pesante (olio lubrificante).

I vari composti contenuti nei prodotti di raffinazione sono più o meno sensibili alla biodegradazione e per questo motivo è possibile definire una sequenza temporale con cui questo processo influisce sulle alterazioni dei prodotti, a partire dagli n-alcani (più suscettibili alla biodegradazione) sino ai terpani (più recalcitranti), permettendo valutazioni sulle variazioni della composizione dell'intera miscela contaminante nel tempo. Nel caso in esame è possibile riscontrare una generale deplezione degli n-alcani a catena più corta e degli IPA con il minor numero di gruppi metile. Al fine di stimare il tempo intercorso dal rilascio di un gasolio in ambiente naturale è possibile utilizzare il rapporto tra eptadecano (n-alcano con 17 atomi di carbonio) e pristano (isoprenoide con 19 atomi di carbonio) che per il caso in esame ha fornito un'età della contaminazione compresa tra 15 e 25 anni. L'assenza di contaminazione legata a benzine, oggi ancora utilizzate nel sito, e la forte degradazione dei prodotti ritrovati nel sottosuolo, hanno pertanto permesso di attribuire l'evento inquinante al proprietario precedente dell'area.

ABSTRACT

In this paper, a case study of compositional fingerprinting application to characterize an Italian site, with evidence of hydrocarbons contamination, is presented. Though the fingerprinting approach is not widely used, especially in Italy, this methodology permits to identify the type of contamination and its level of degradation by the study of the homologues classes of contaminants present in the mixtures. In characterization of contamination due to spillage of diesel, through the use of specific ratios between compounds of the mixture, it is possible to determine the contaminant grade of alteration and thus gives a prediction of the contamination age. In case study here presented, using the ratio heptadecane/pristane ($n\text{-C}_{17}/\text{pr}$), a prediction of the contamination age was carried out for the identified diesel contamination. These aspects are also fundamental for a correct characterization of the site and therefore to choose the most suitable site-specific remediation strategy. All these data, combined with the usual geochemical analysis, can give an added value in order to assess the responsibility of contamination and therefore the duty of reclamation, especially in case of different owners. In this way, a successful reclamation, from the point of view of both the expected results and the economic view, is possible.

KEY WORDS: hydrocarbons contamination, compositional fingerprinting, characterization, remediation

INTRODUCTION

Thousands of chemicals with different properties and toxicity are daily employed in our modern and industrialized world and many of them can be detected in all the compartments of the environment (e.g., water, sediment, soil, air and biota). Contaminants of particular interest are the refined products of crude oil since, nowadays, fossil fuels cover almost the totality of the amount of energy needed. In fact, refined products are used as fuels in cars (gasoline and diesel), aircrafts (jet fuels) and ships (heavy fuel oil); for heating and electricity generation, as lubricants in machinery; as asphalt for road building and in the production of chemicals and plastics. As consequence, the exploration, the production, the transportation and the widespread use of this family, inevitably result in contamination of the environment (ALIMI *et alii*, 2001).

Gasoline, diesel and lubricants, are the end products of the refining process of the petroleum. More in general, the term "petroleum" refers to the family naturally occurring (e.g. gases: natural gases; liquids: gas condensates and crude oils; solid: bitumen and oil shale/sand) that contain complex mixtures with ten thousands of hydrocarbons and non-hydrocarbons (nitrogen-, sulfur- oxygen- and metal containing compounds). The chemical, physical (i.e. API Gravity and sulfur content), and compositional (such as ratio pristane/phytane and percentage of benzothiophenes) properties of the petroleum vary with the different geographical origin. The refined products maintain these differences plus the

ones related to the refining processes actuated in the different refineries. Moreover, each refined products has its fingerprints that is due to its chemical composition, i.e. the typical hydrocarbon range of gasoline is $\text{C}_3\text{-C}_{12}$, while in diesel is $\text{C}_{15}\text{-C}_{25}$ and in the residual oils, carbons range from 14 to more than 40 (HEAT *et alii*, 1993; KAPLAN *et alii*, 2001; ODEBUNMI *et alii* 2002).

In addition, gasoline and diesel fuels have a variety of additives. Most of these are required for the purpose of lubricating and keeping engine parts clean; they consist of detergents and antioxidants and are considered proprietary by the various refineries that are using them and thus their composition is not available. For the purpose of assignment of source, most of the additives are not very useful because many of them have similar chemical compositions and may not be easily differentiated and furthermore they decompose relatively quickly in water and may be not strong adsorbed on soil particles. In this concern, the two organohalogenated, ethylene dibromide (1,2-EDB) and ethylene dichloride (1,2-EDC) are of particular importance; in fact, the search of these additives can give useful information to date gasoline because in Italy, until 1988, they were added as anti-knocking or post-combustion gas evacuating. Since the type and the amount of additives have changed with time, the identification and quantification of the two organic compounds in a free phase product is very useful even because, on the contrary of lead alkylates that hydrolyze in water, they tend to be more persistent and so more easily surveyed for a longer period (KAPLAN *et alii*, 1997). Another additive used in gasoline is the Methyl Tertiary-butyl Ether (MTBE) and its presence indicates a more recent pollution because it was introduced after the end of the Eighties, beginning of Nineties, in the lead-free gasoline as substitute of the lead additives (STERN & KNEISS, 1997; KAPLAN *et alii*, 1997).

Furthermore, once in the environment crude oils and refined products are subjected to physical (e.g., evaporation, emulsification, natural dispersion, dissolution and sorption), chemical (e.g., photodegradation) and biological (e.g., microbiological degradation or biodegradation) weathering processes that lead to the alteration of their chemical composition and thus of their fingerprints (or chromatograms). Specifically, the different compounds contained in the refined products are more or less susceptible to biodegradation due to their chemical structures. For this reason it is possible to define a temporal sequence starting from the n-alkanes (more susceptible to biodegradation) to the terpanes (less susceptible), leading to the possibility to evaluate compositional changes of the whole contaminant mixture during the time (DOUGLAS *et alii*, 1996; KAPLAN *et alii*, 1996; WANG *et alii*, 1998; U.S. EPA 1999; MURPHY & MORRISON, 2002). This is the core of the analytical methodology called "compositional fingerprinting", based on the use of a gas chromatography - mass spectrometry (GC-MS) and that allows to the identification of the type of contamination and of its source among different possible sources and, furthermore, permits the determination of degradative effects on it (NORDTEST METHOD,

1991; WANG *et alii*, 1997; WANG *et alii*, 1999; DALING *et alii*, 2002; BEKINS *et alii*, 2005; CHRISTENSEN & TOMASI, 2007, HOSTETTLER *et alii*, 2013). The compositional methodology pursues these aims by the analysis of the contaminants composition, evaluating the presence and the abundance of individual compounds and quantitatively determining several ratios useful to measure the biodegradation degree, such as, for diesel, $n\text{-C}_{17}$ /pristane and $n\text{-C}_{18}$ /phytane, whereas n-alkanes ($n\text{-C}_{17}$, or heptadecane and $n\text{-C}_{18}$, or octadecane) are correlated to the isoprenoids pristane and phytane. This because bacteria preferentially consume the n-alkanes leading to a relative enrichment in abundances of isoprenoids that are less susceptible to biodegradation (ALIMI *et alii*, 2003; STOUT, 2003; WANG *et alii*, 2003a; WANG *et alii*, 2003b, WANG *et alii*, 2003c).

The accurate characterization of polluted sites is still a challenge and the ongoing research is focused on the definition of valuable tools of analysis able to reduce the uncertainties that affect it. During this study, the compositional fingerprinting has been applied to identify the soil contamination and trying to define its relative age in order to assess the responsibility of the contamination. These two aspects are also fundamental to better characterize the site and then to choose the most suitable remediation strategy both from the point of view of the expected results and from the cost of remediation.

SITE CASE STUDY

The area of study covers almost 2,500 m² (Fig. 1a) and it is located in a region in the central Italy. At the present, in the studied site it is located a service area with a separated fuel station, but in the past the area of the market was divided into two zones including a smaller market than the actual and a fuel station owned by a different company. During the excavation for the construction of a basement, planned in the context of expansion of existing buildings

-of the market, organoleptic evidences of a potential contamination by hydrocarbons were found in the soil. Since the previous division of the area showed the presence of a fuel station, an analytical integration by the use of compositional fingerprinting has been carried out to determine the type of contamination and its possible age. A total of seven soil samples have been collected from the four walls and the bottom of the excavation in the following way (Fig. 1b):

- one sample for each wall of the excavation at a depth of about 4 meters from the ground level (sample F1-northern wall, F2 -southern wall, F3 western, and F4 - eastern wall),
- one sample on the eastern wall at a depth of about 1 meter from the ground level (F4_1), and
- two samples at the bottom of the excavation, at a depth of about 5 meters from the ground level (samples F5_1 and F5_2), in the surrounding of the area characterized by a strong smell of hydrocarbons.

MATERIALS AND METHODS

SAMPLING

The samples were collected in sampling containers of glass fully filled with sampled soils, in order to avoid headspace and thus the loss of volatile compounds according to the protocol U.S. EPA SW-846 (EPA, 2007, Chapter 4).

HEADSPACE ANALYSIS

All the samples were analyzed to determine the concentration of volatile aromatic hydrocarbons BTEX (benzene, toluene, ethylbenzene and xylenes), of the oxygenate compound MTBE and of the additives 1,2-EDB and 1,2-EDC. The vials for the headspace analyses, containing 6 mL of the water samples plus

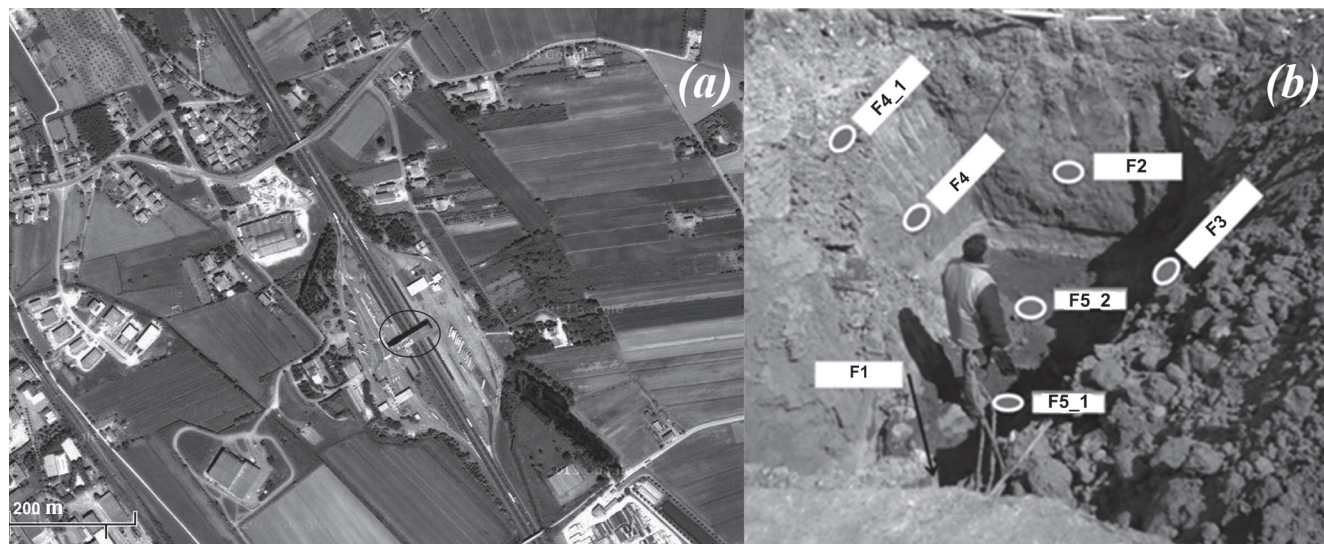


Fig. 1 - Geographical localization of the site of study: (a) map of the area; (b) excavation with samples location

7.2 g of carbonate potassium (K_2CO_3) were incubated at an incubation temperature of $85^\circ C$ for 50 min in a heating block in agitation (speed of 250 rpm). The syringe temperature of the autosampler was $90^\circ C$. The GC temperature was first held at $40^\circ C$ for 8 min, then increased to $180^\circ C$ at a rate of $5^\circ C/min$ and held for 2 min. Helium served as carrier gas.

The results of the GC-MS analyses showed the absence of these three classes of compounds allowing to suppose that these samples are not characterized by a contamination due to spillage of gasoline.

FULL SCAN ANALYSIS

The samples analyzed with the purpose to determine the semi-volatile and non-volatile fraction were extracted in two different ways, depending on the compounds researched. The Total Petroleum Hydrocarbons (TPH) have been extracted by ultrasonic extraction in acetone followed by clean up of the extract with a 6 mL column containing florisil and sodium sulfate (purchased from Thermo Scientific). Differently, the sample for the identification of the homologue compounds families have been treated extracting the contaminants in a soxhlet with a mixture of 50% methylene chloride and 50% acetone v/v (total volume 100 mL). The extracts were then analyzed as following; the temperature of the oven in the GC was first held at $40^\circ C$ for 5 min, then increased to $300^\circ C$ at a rate of $10^\circ C/min$ and held for 20 min. Helium served as carrier gas and the mass analysis range was m/z 40-1050.

RESULTS AND DISCUSSION

The results of GC-MS analyses showed the absence of the oxygenate compound MTBE and of the anti-knock additives 1,2-EDB and 1,2-EDC allowing to suppose that these samples are not characterized by a contamination due to a spillage of gasoline.

Contrarily, the analysis of the semivolatile compounds revealed that the only sample that does not appear to be contaminated by hydrocarbons is the F4_1 (eastern wall, take at about 1 meter of depth), while the chromatograms relative to n-alkanes (m/z 85) and isoprenoids (m/z 113) of the other samples show three different situations; the samples F5_1 and F5_2 can be grouped together, in the same way the samples F1, F3 and F4 can be grouped, whereas the sample F2 represents a group by itself.

SAMPLES F5_1 AND F5_2

Figure 2 shows the chromatograms of the samples collected from the bottom of the excavation. These chromatograms reveal that the samples F5_1 and F5_2 are contaminated by a diesel highly degraded, exposed to environmental processes of attenuation for a considerable period of time. In fact, the chromatograms, very similar among them, are characterized by the complete absence of n-alkanes and by the apparent abundance of the isoprenoids pristane ($i-C_{19}$) and phytane ($i-C_{20}$), which are characteristic of the diesel used for cars or as heating fuel.

Moreover, the analysis of the chromatogram relative to the

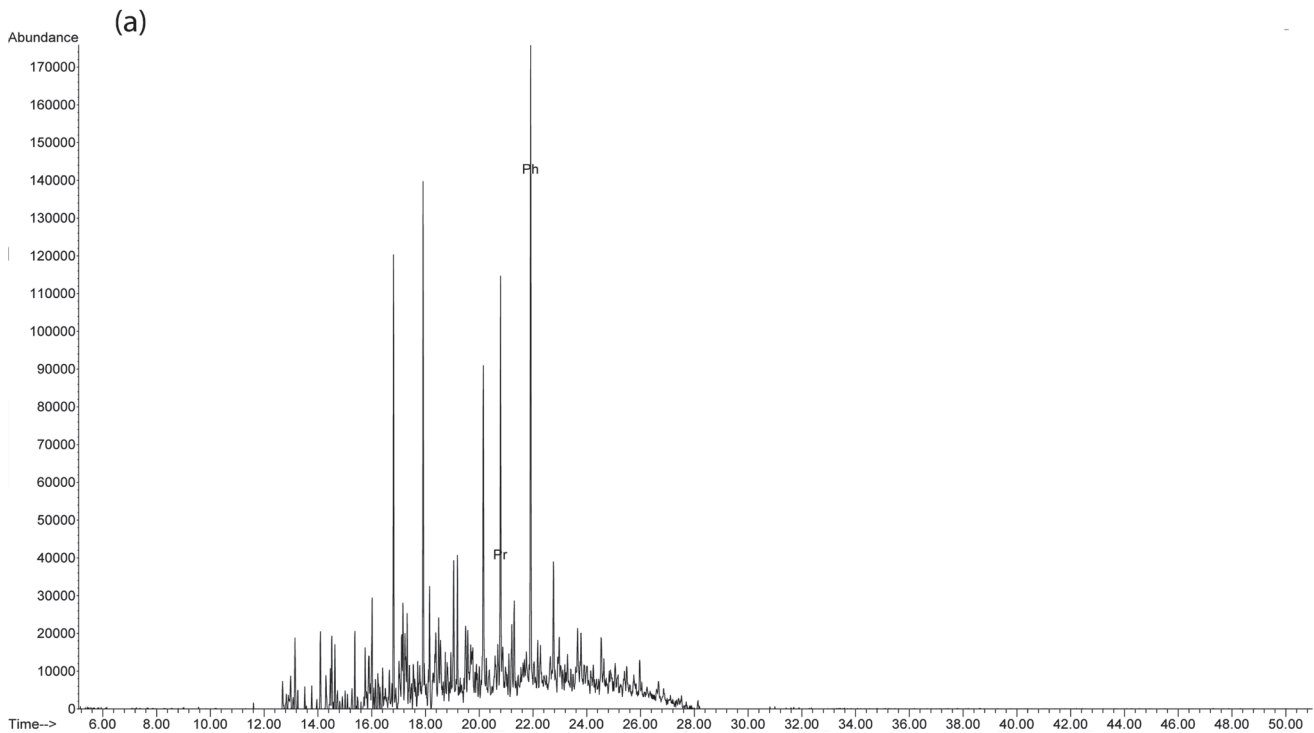


Fig. 2a - N-alkane chromatograms of the F5_1

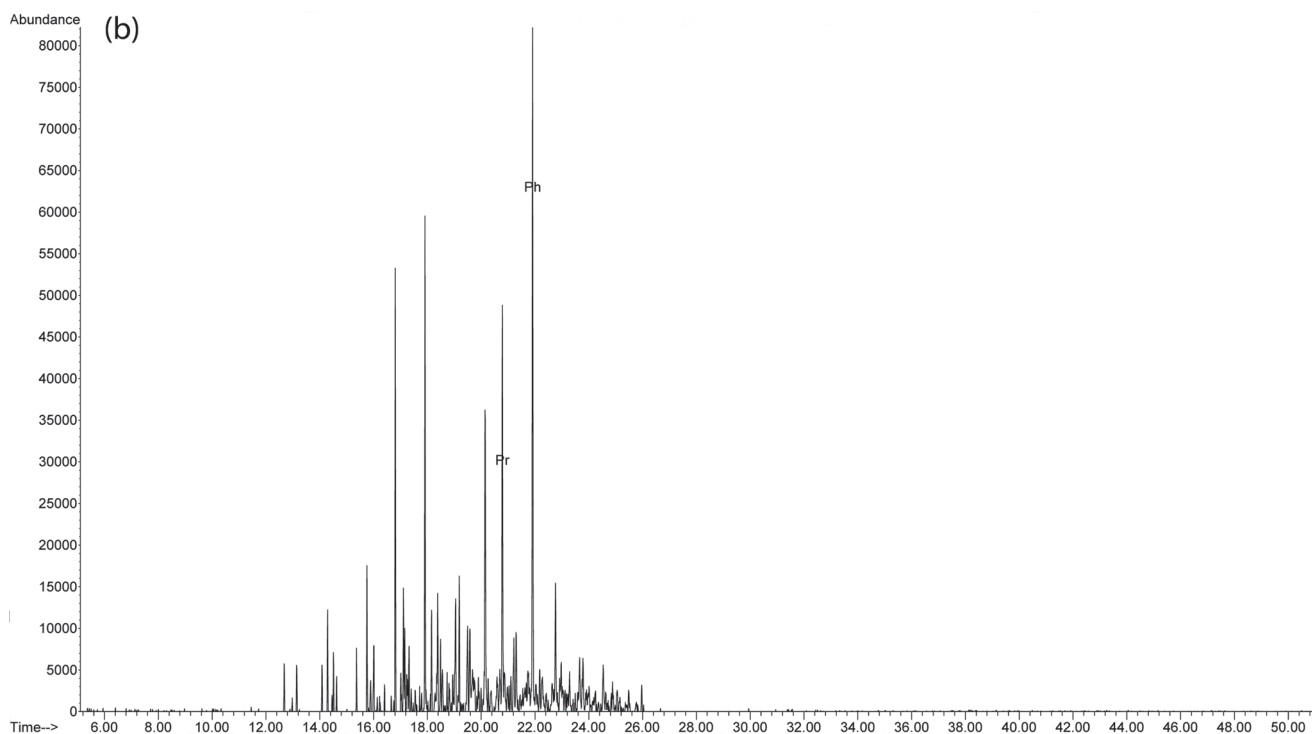


Fig. 2b - N-alkane chromatograms of the F5_2 samples

homologues family of the alkylated cyclohexanes (CHs) (Fig. 3a) and the pattern of distribution of the polycyclic aromatic hydrocarbons (PAHs Fig. 3b) provide additional support to the hypothesis that the contamination is due to spillage of diesel. In this case, due to the high similarity between the two samples, only the figures relative to the samples F5_1 are reported as example. The cited chromatogram (Fig. 3a) shows the higher abundances of CH-7 and CH-8, characteristic of the diesel fingerprint and no compounds with a chain shorter than CH-5, supporting the thesis of a contamination highly degraded (HOESTETTLER & KVENVOLDEN).

Furthermore, the histograms in Fig. 3b show a high abundance of phenanthrene and dibenzothiophenes, characteristic of the fingerprints of diesel and heavier fraction, and the presence of C₃ and C₄-naphthalene; the latter are not included in lighter fractions and this is a further confirmation of the absence of gasoline fuels. In addition, the removal of C₀ and C₁-naphthalene, C₀-phenanthrene, C₀-dibenzothiophene and the relative increase of C₃-naphthalene, C₂-phenanthrene and C₂-dibenzothiophene are other evidences of the high level of degradation of the contamination.

SAMPLES F1, F3 AND F4

In the chromatograms of the samples F1, F3 and F4 it is possible to determine the presence of three different ranges of distribution of hydrocarbons, identifiable as diesel highly degraded, as for the samples collected at the bottom of excavation, together with

a lighter fraction (probably kerosene) and a heavier one (Fig. 4).

The chromatograms for these samples are very similar among them and are characterized by the presence of the C₁₇ and C₁₈ n-alkanes in the typical region of middle distillates, n-alkanes between the n-C₁₂ and n-C₁₆ (range of light distillates) and between n-C₃₀ and n-C₃₆ (range of heavy distillates).

Another evidence of the presence of diesel fuel is done by the identification of the isoprenoids pristane and phytane. The light fraction may be composed by degraded kerosene, because the fresh product is characterized by a range of number of carbons between 9 and 16 with the n-alkanes decane (n-C₁₀), undecane (n-C₁₁) and dodecane (n-C₁₂) as main compounds (Fig. 5) and that are absent or are highly depleted in the sample analyzed, while are still identifiable the n-alkanes with a longer chain (from n-C₁₃ to n-C₁₆, Fig. 4).

Moreover, the pattern of distribution of the PAHs shows a high abundance of naphthalene and phenanthrene. Unlike the previous group, the isomers of the dibenzothiophene show a lower abundance than that of the other two PAHs (Fig. 6; the sample F3 is taken as example of this group). Dibenzothiophenes are not present in lighter refined products, as kerosene, while these products are rich of naphthalene. The pattern of distributions of the PAHs seems a snapshot of the mixed situation revealed by the chromatograms of the n-alkanes.

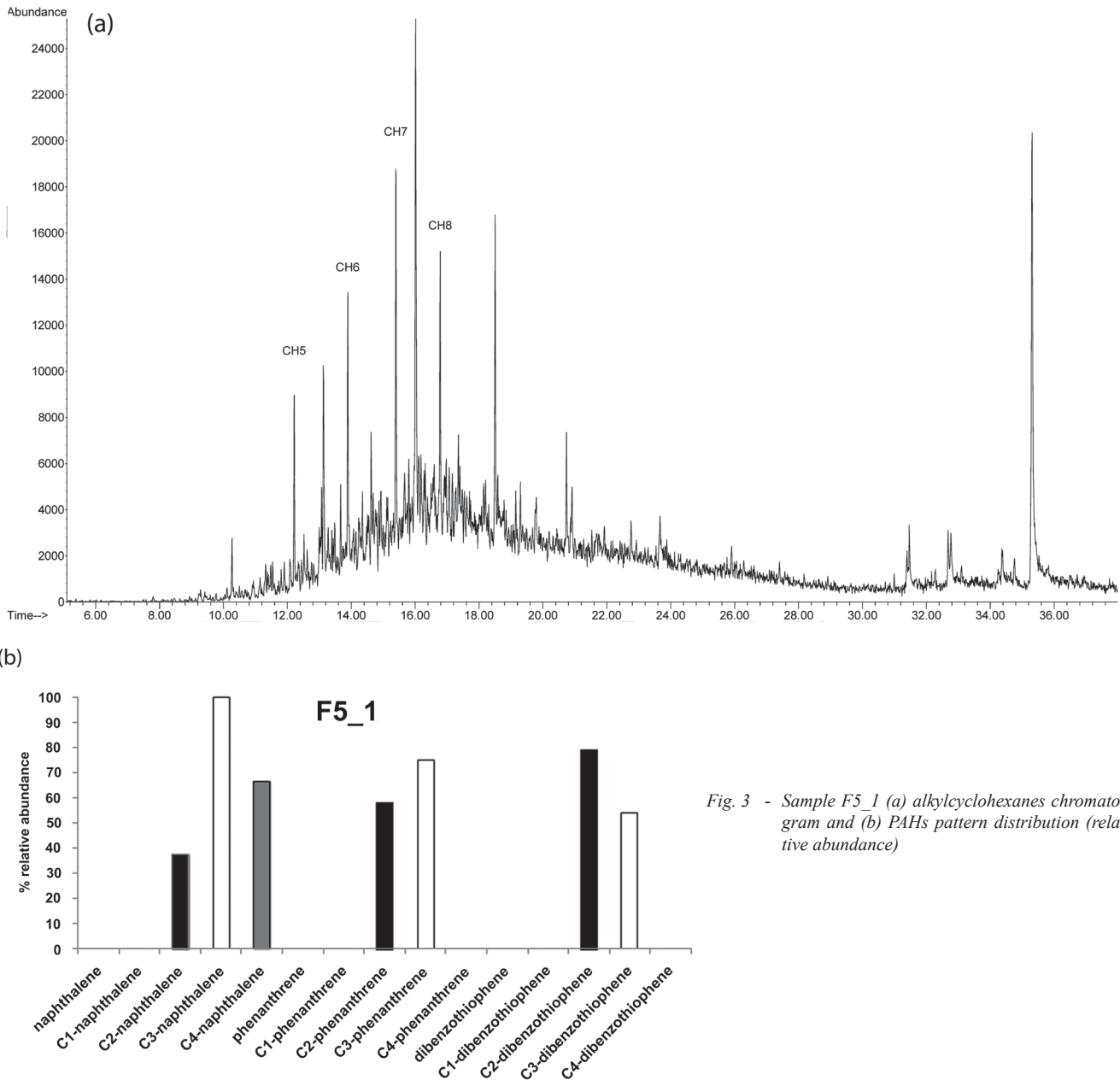


Fig. 3 - Sample F5_1 (a) alkylcyclohexanes chromatogram and (b) PAHs pattern distribution (relative abundance)

SAMPLE F2

Differently from all the other samples, the sample F2 shows a chromatogram relative to n-alkanes ranging from n-C₃₀ to n-C₃₆ (Fig. 7.a). In this sample isoprenoids were not identified. Also the pattern of distribution of the PAHs differs from the other because shows the presence of C₄-phenanthrene and the C₄-dibenzothiophene characteristic of the heavier fractions. Histograms reveal also a high abundance of naphthalene (mainly C₃ and C₄ that are not present in light products) and of phenanthrene and

dibenzothiophene in general. Also in this case the removal of C₀ and C₁-naphthalene, C₀-phenanthrene and the relative increase of C₃-naphthalene, C₂phenanthrene, C₂ and C₃-dibenzothiophene are evidences of the contaminant degradation (Fig. 7b).

CONCLUSIONS

A common element in all the samples analyzed is the heightened state of degradation to which seems to have been subjected the contaminant fuels (such as diesel and kerosene).

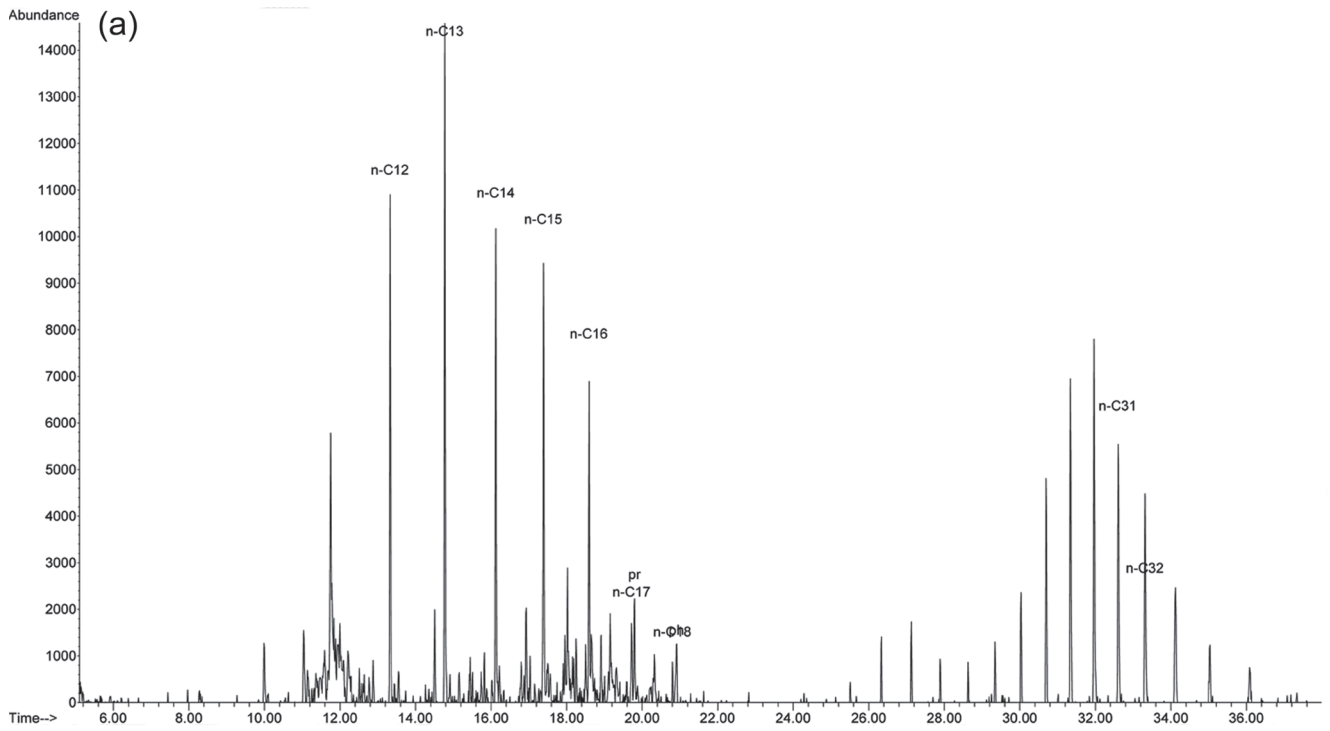


Fig. 4a - N-alkane chromatograms in F1

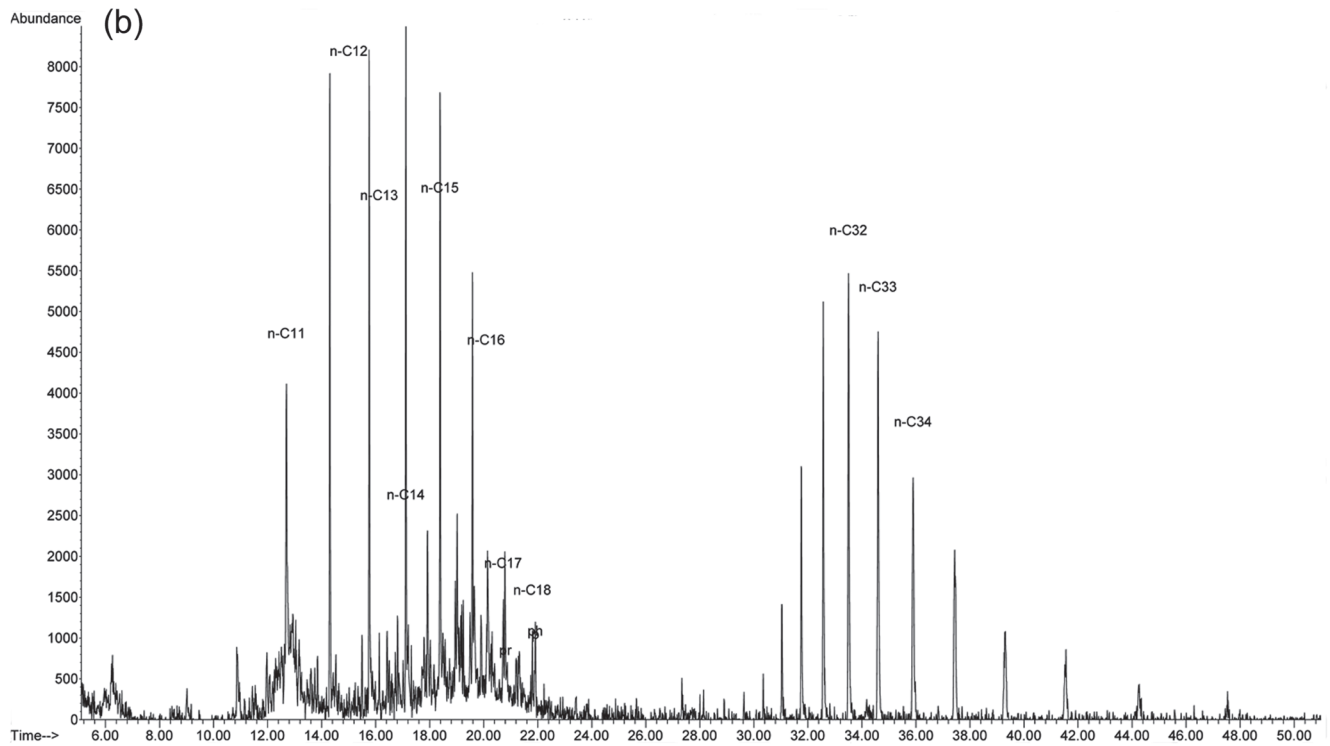


Fig. 4b - N-alkane chromatograms in F3

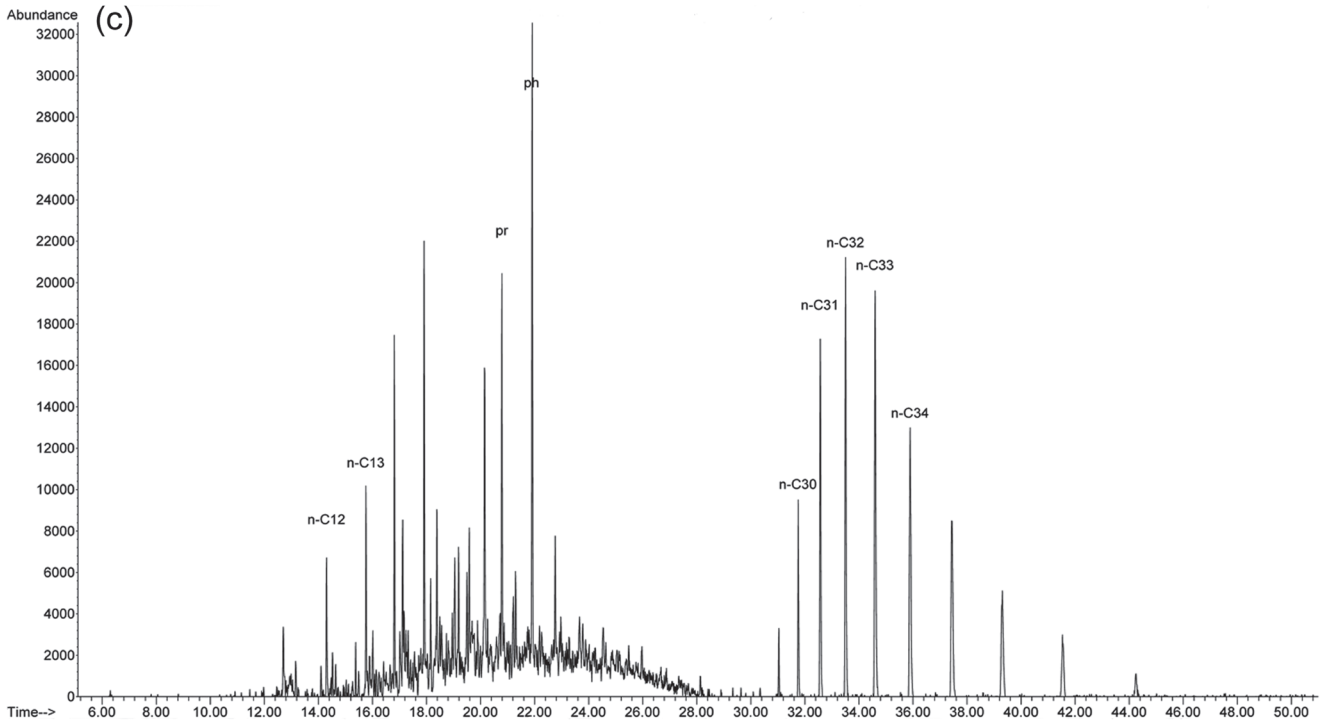


Fig. 4c - N-alkane chromatograms in F4 samples

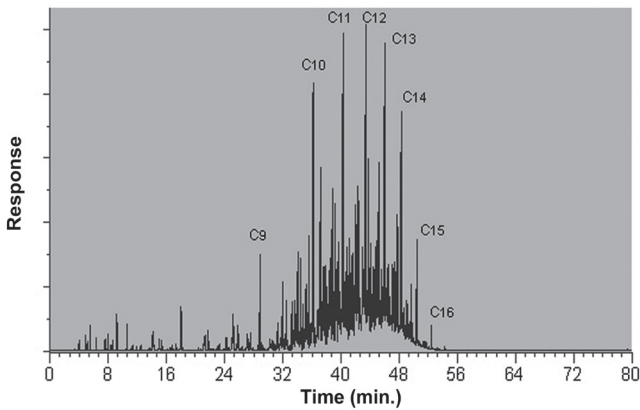


Fig. 5 - N-alkanes (C₉-C₁₆) pattern in the standard of kerosene

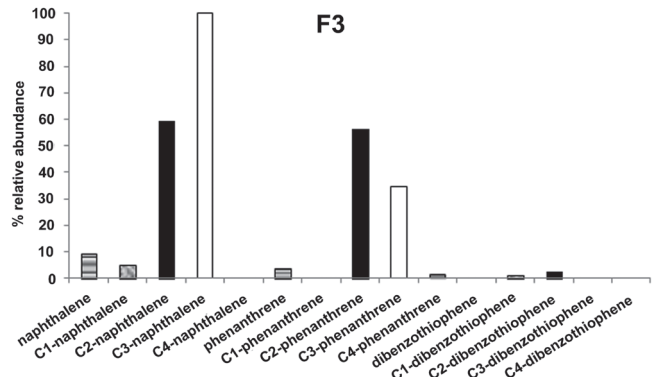


Fig. 6 - Pattern distribution (relative abundance) of the PAHs in the sample F3

This finding leads to suppose that is present an old contamination subjected to processes of biodegradation. In order to quantitatively estimate the time elapsed, from the spill of diesel, it is possible to determine the C₁₇/pristane and C₁₈/phytane ratios for diesel contamination (CHRISTENSEN & LARSEN, 1993; ALIMI *et alii*, 2003), as in the compounds unaltered, the n-alkanes C₁₇ and C₁₈ are much more abundant compared to isoprenoids while this situation is reversed in the compounds altered, since the microorganism present in the environment preferentially consume the n-alkanes. Christensen and Larsen (1993) shown that once

in the environment, the relationship n-C₁₇/pristane, typical of gas oils, decreases due to the biodegradation from the original value in the diesel unaltered to values close to 0 in approximately 20-25 years. This situation occurs in the samples taken from the bottom of the excavation F5_1, F5_2 and F3 where the n-alkanes appear to be completely removed while in samples F2 and F4 the relationship C₁₇/pristane assumes the value of 0.8 which leads to a date of approximately 13 years.

Furthermore, the n-alkanes are not the only compounds to be reduced; in fact there is evidence of degradation at the level

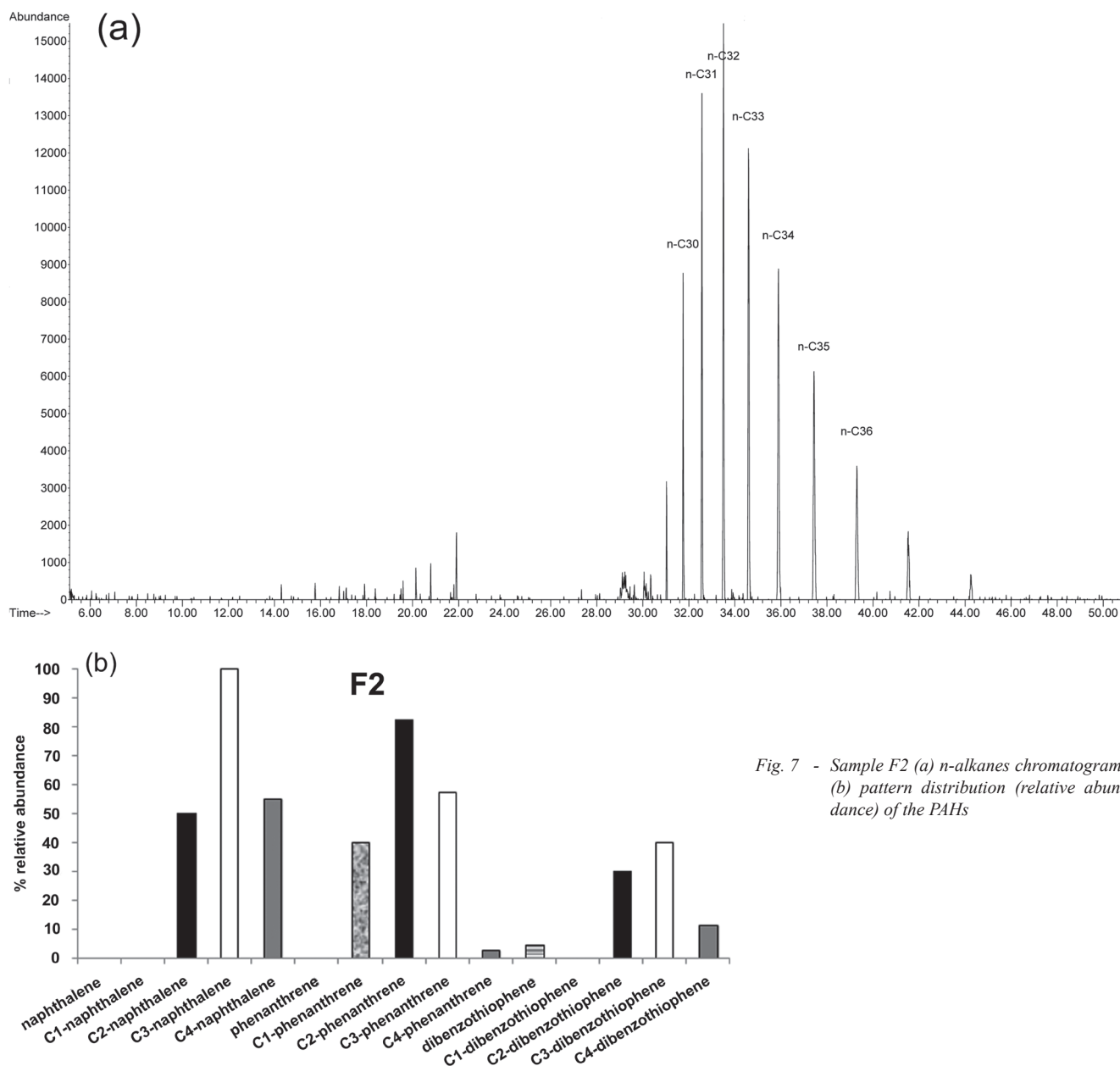


Fig. 7 - Sample F2 (a) n-alkanes chromatogram, (b) pattern distribution (relative abundance) of the PAHs

of PAHs (less susceptible than the n-alkanes to biodegradation) and alkylcyclohexanes leading to the conclusion that the diesel contamination is highly altered (level of alteration 6/7), as showed by ALIMI *et alii* (2003).

Considering all these factors, it can be concluded that the fingerprinting methodology was useful to identify the type of contamination, constituted mainly by degraded diesel (the refined product was not present only in the sample F2, among the contaminated samples) with also the presence of higher and lighter fractions. Since all these contaminants are amenable to refined products, normally used by

fuel station, and the proposed dating for diesel contamination ranges from 13 to 25 years, the data suggests that the responsibility of the contamination and therefore the duty of the reclamation can be attributable to the fuel station previously located in the site.

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