

FINGERPRINTING COMPOSIZIONALE E MODELLAZIONE NUMERICA DEL TRASPORTO DI NAPL IN FALDA PER L'APPLICAZIONE DEL POLLUTER PAYS PRINCIPLE

Trefiletti, Rigamonti, Renoldi



Environmental Forensic:

nell'accezione comune comprende quell'insieme di metodologie e tecniche in grado di rispondere alle questioni concernenti **la responsabilità di una contaminazione** o, più in generale, in grado di individuare la sorgente e tracciare la storia di una contaminazione.

Approccio classico

Dati storici

- tipo di attività attuale pregressa, destinazione d'uso dell'area, tipologia ed elenco delle sostanze usate nelle lavorazioni, stoccaggi, descrizione e mappatura di eventuali accumuli di rifiuti.

- rilievi aereofotogrammetrici

Dati ambientali

- caratterizzazione geologico-stratigrafica e idrogeologica del sito e dell'area circostante

- Campionamento e analisi chimico- fisiche dei parametri di interesse.



**Fingerprinting
composizionale
e isotopico**

Modellazione
matematica di flusso
e trasporto

Modellazione del
prodotto libero?

Linea di sviluppo

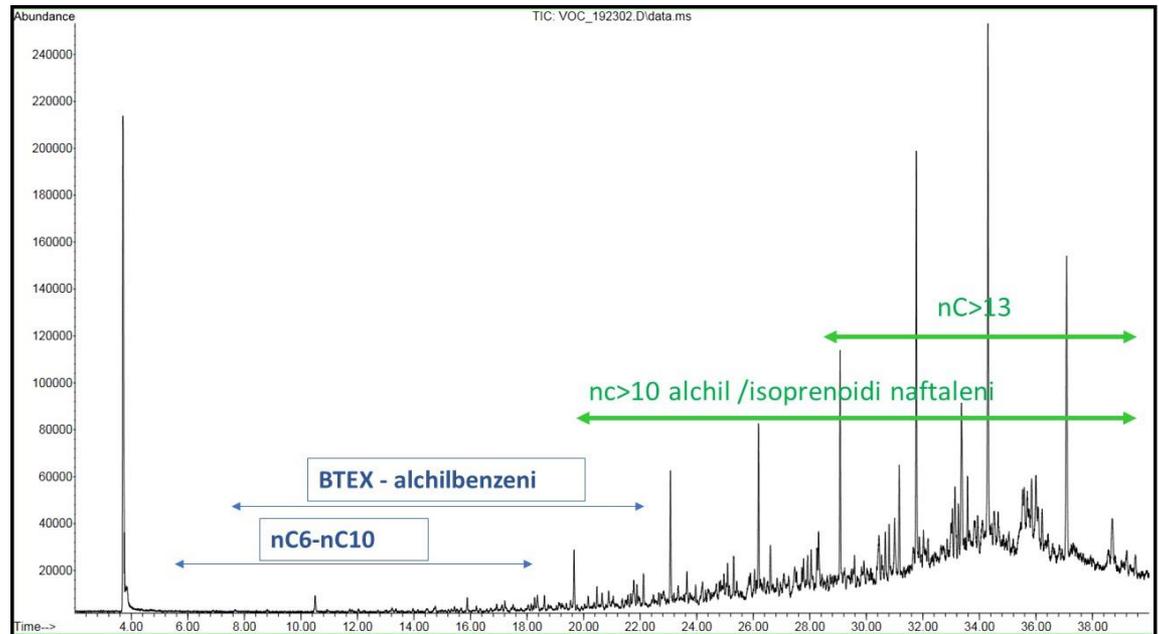
CENNI SUL FINGERPRINTING COMPOSIZIONALE

distribuzione relativa dei composti e dei biomarker dipende dalla materia prima di origine e dal processo di produzione.



- Caratterizzazione miscela (diesel, benzina, etc.)
- Individuazione sorgente

si basa sulla conoscenza delle proprietà geochimiche dei composti organici e del loro comportamento nell'ambiente

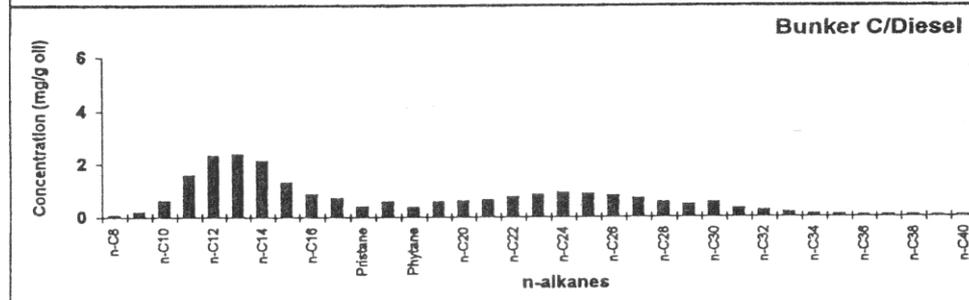
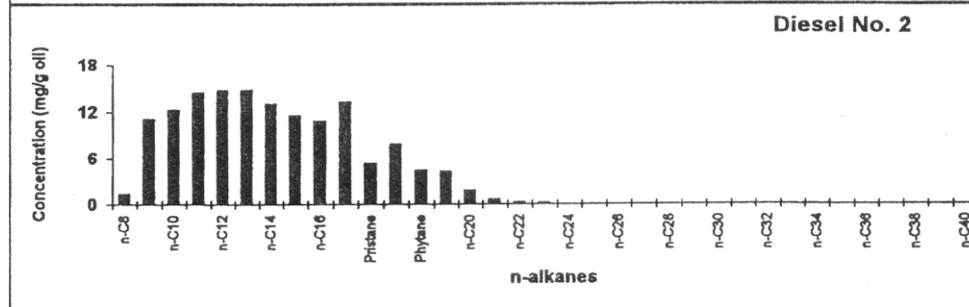
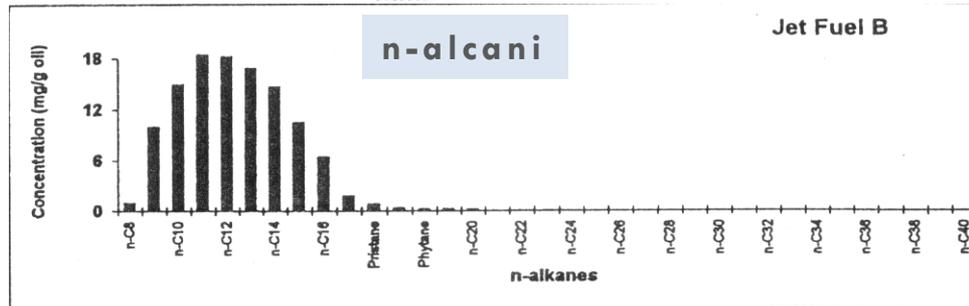
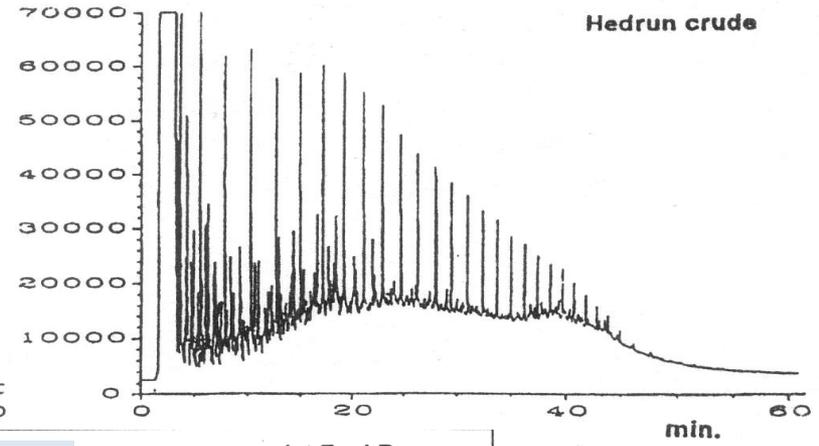
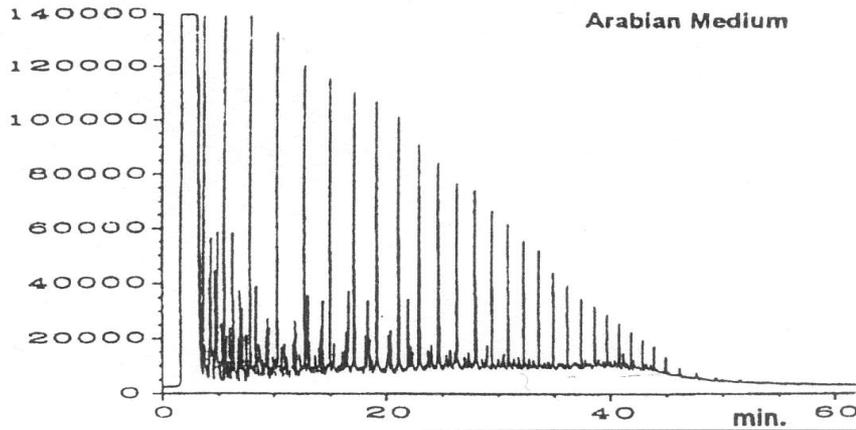


le miscele subiscono processi di alterazione che interessano «selettivamente» le diverse famiglie omologhe e, al loro interno, i singoli composti.



Stima tempi di rilascio
Identificazione e
caratterizzazione processi

Caratterizzazione- Identificazione Sorgente



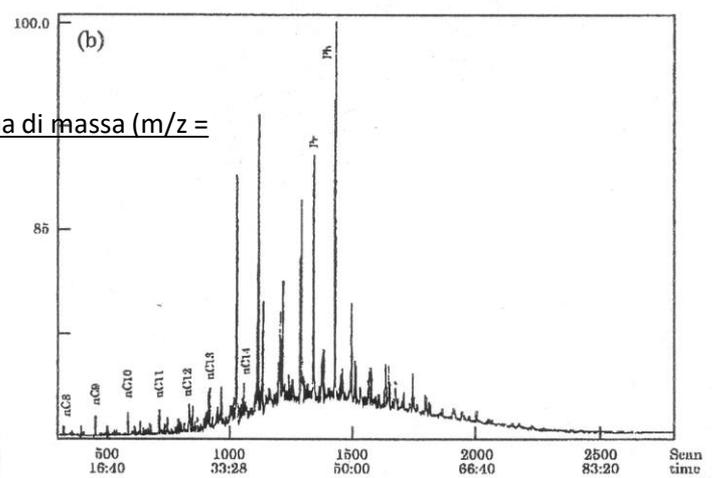
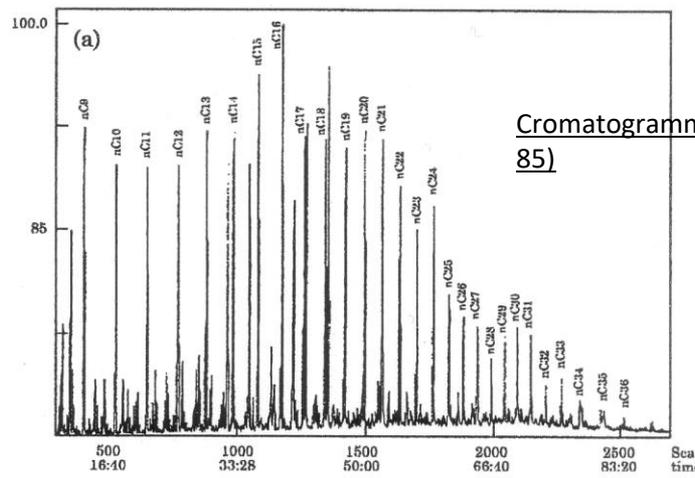
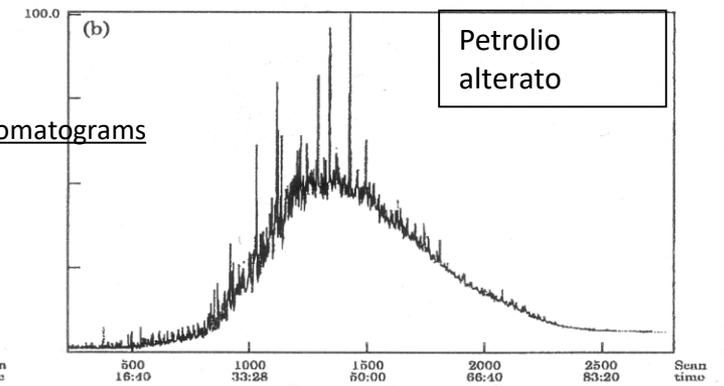
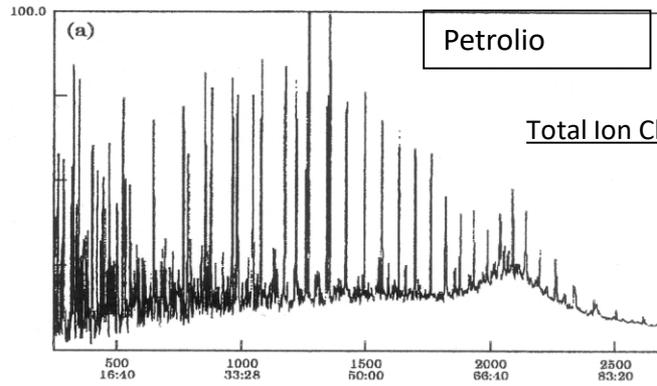
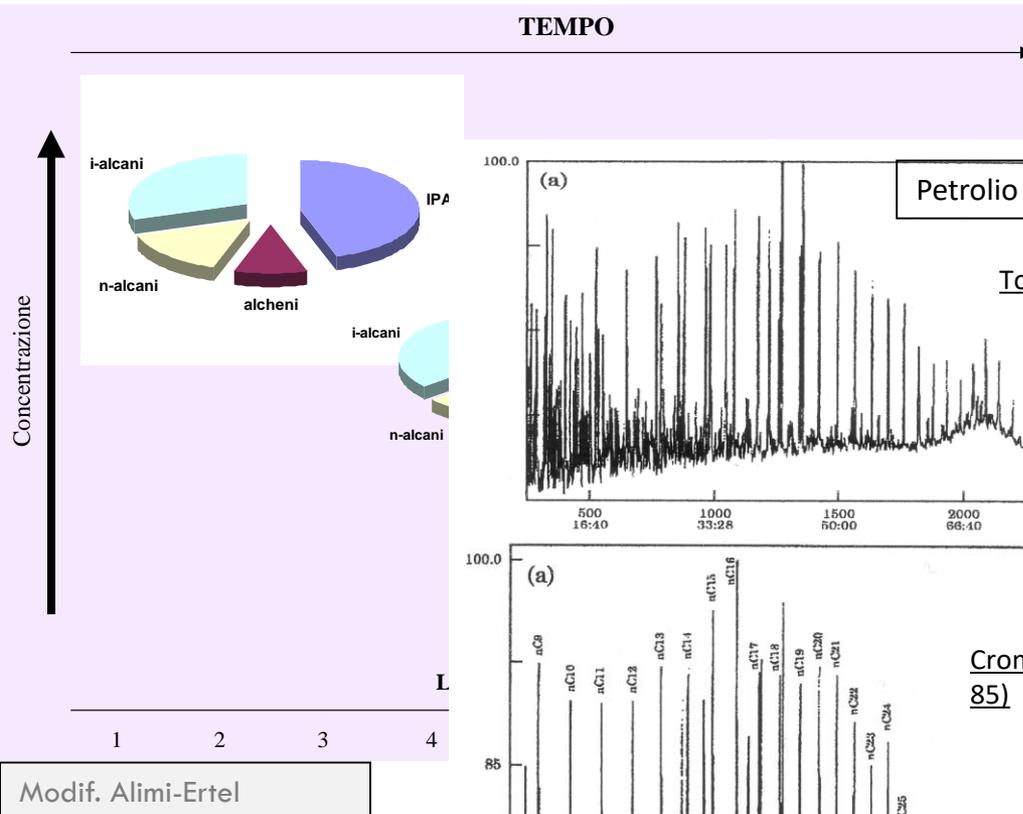
"Analytical Methods for Petroleum Hydrocarbons"
 - Washington State
 Department of Ecology

Wang et al. 1999

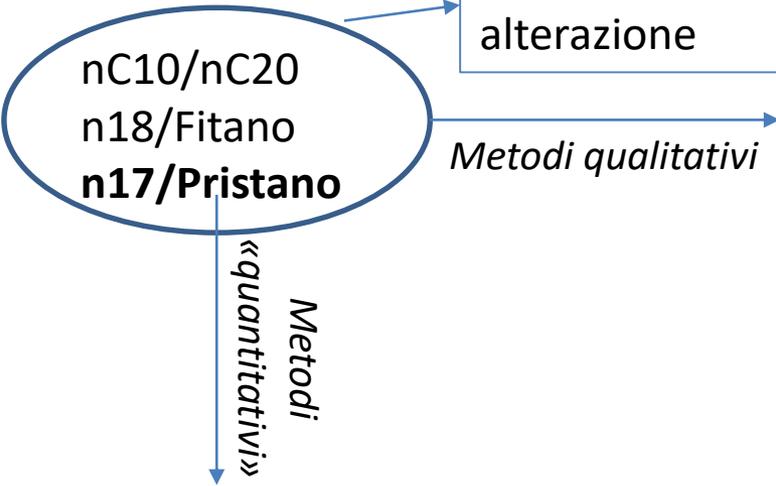
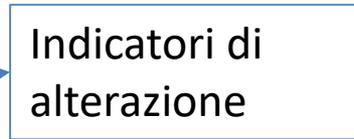


Alterazione - «Datazione»

N-alcani >> alcani monociclici >> alchilbenzeni >> isoprenoidi >>



Alimi, 2003



fuel type			degradation level	chemical composition	increasing level of biodegradation
Bunker C fuel	Diesel	Gasoline	1	abundant n-alkanes	
			2	light-end n-alkanes removed	
			3	middle range n-alkanes, olefins, benzene and toluene removed	
			4	more than 90% of n-alkanes removed	
			5	alkylcyclohexanes and alkylbenzenes removed; isoprenoids and C0-naphthalene reduced	
			6	isoprenoids, C1-naphthalenes, benzothiophene and alkylbenzothiophenes removed, C2-naphthalenes selectively reduced	
			7	phenantrenes, dibenzothiophenes and other polynuclear aromatic hydrocarbons reduced	
			8	tricyclic terpanes enriched, regular steranes selectively removed C31-to C35-homohopanes reduced	
			9	tricyclic terpanes, diasteranes and aromatic steranes abundant	
			10	aromatic steranes and demethylated hopanes* predominant	

* only present under special conditions

Change in gasoline, diesel fuel, and Bunker C composition during biodegradation

$$T = -9,47(n-C_{17}/Pr) + 20,5$$

Christensen&Larsen (C&L) - Kaplan

Insaturo, aerobico, evento repentino

Possibile funzione di n-C17/Pr
prodotto iniziale

Weathering regime:	Very aggressive	Aggressive	Moderate	Weak	Very Weak
Fresh fuel	0	0	0	0	0
<i>Kaplan Stages:</i>					
1. Abundant n-alkanes	<0.25	0-2	0-4	0-8	0-10
2. Light n-alkanes removed, benzene & toluene removed	<0.5	2-4	4-8	8-16	10-20
3. Middle-range n-alkanes removed, ethylbenzene & xylenes removed	<1	4-6	8-12	16-24	20-30
4. More than 50% of the n-alkanes	<2	6-8	12-16	24-32	30-40

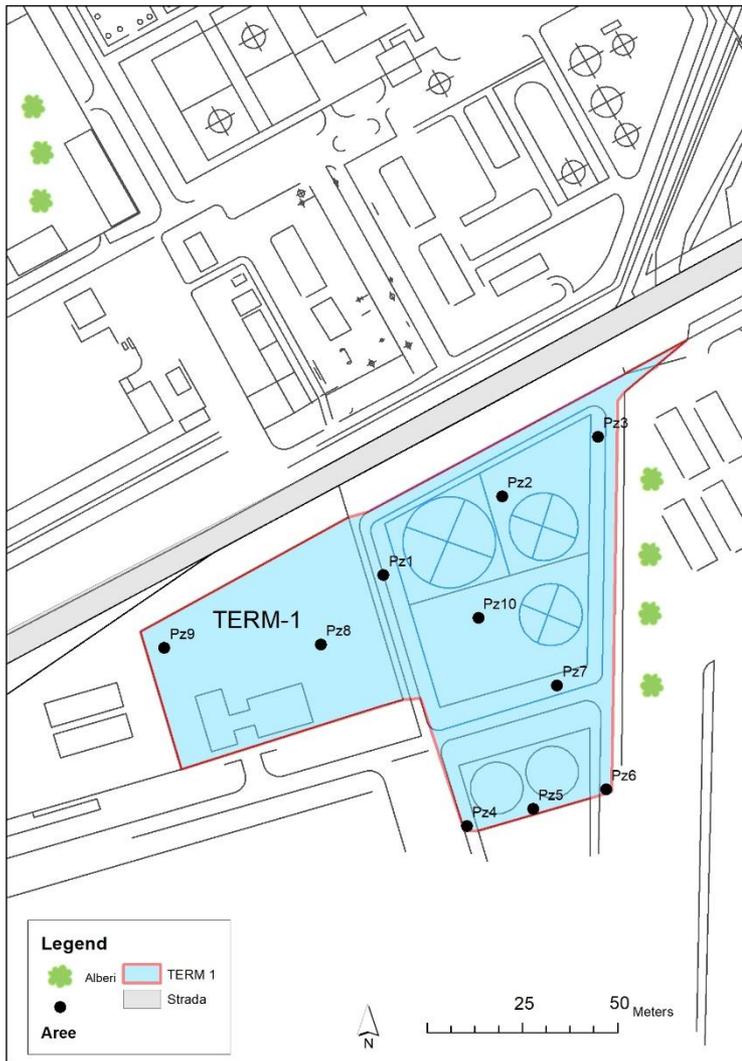
Stralcio da Oudijk, 2009



CENNI SUL FINGERPRINTING ISOTOPICO

Il rapporto tra isotopi stabili (quali $^{13}\text{C}/^{12}\text{C}$, $^{37}\text{Cl}/^{35}\text{Cl}$) essendo funzione della materia prima di origine, dei processi di produzione così come dei fenomeni chimici e biologici che un composto subisce nell'ambiente, determina un "fingerprinting" intrinseco di una sostanza (es. Benzene, Cloroformio, etc.)

IL CASO: INQUADRAMENTO DEL SITO

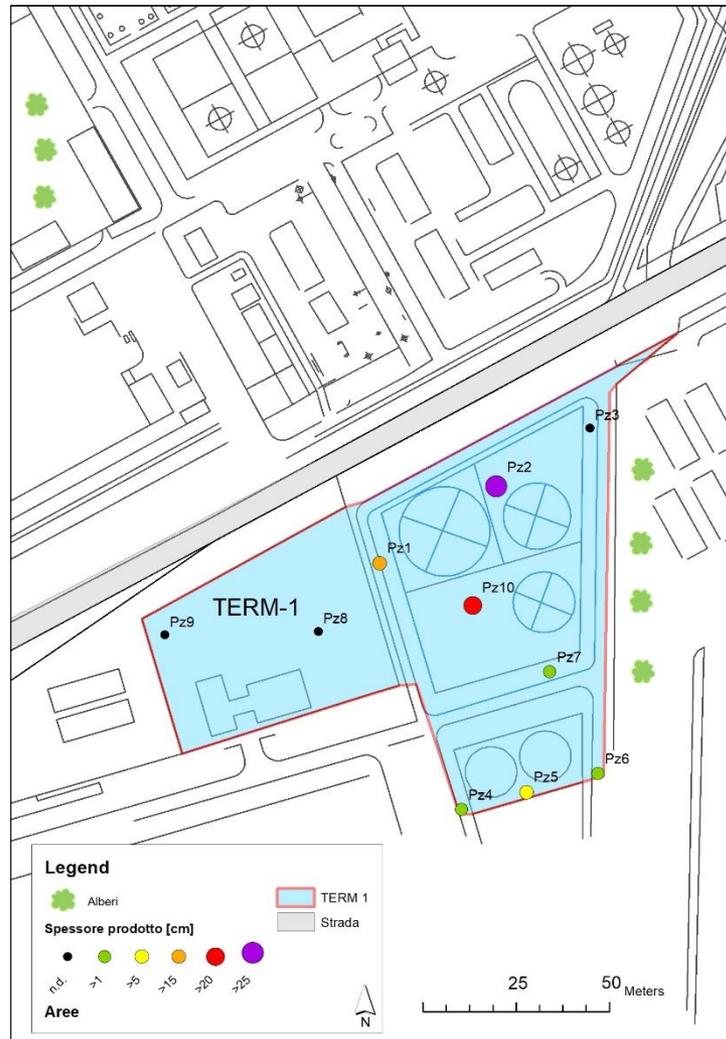


Term-1: azienda attiva in area industriale a ridosso di una superstrada.

Fino al 2002 stoccaggio prodotti idrocarburici, soprattutto riscaldamento domestico.

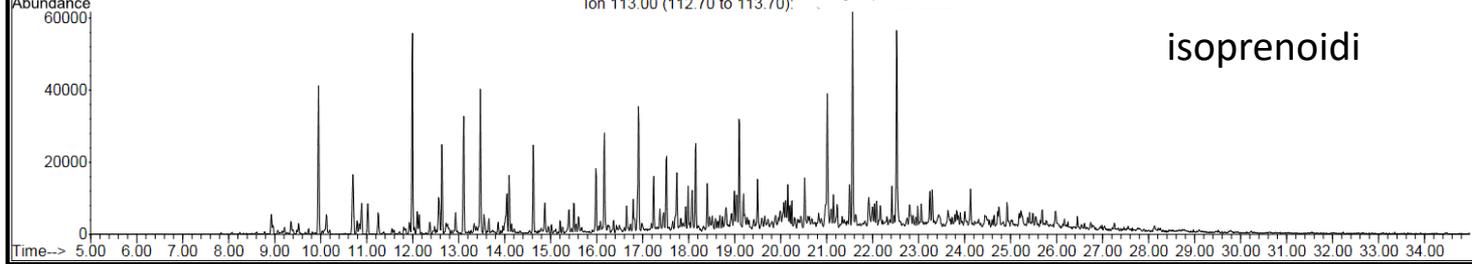
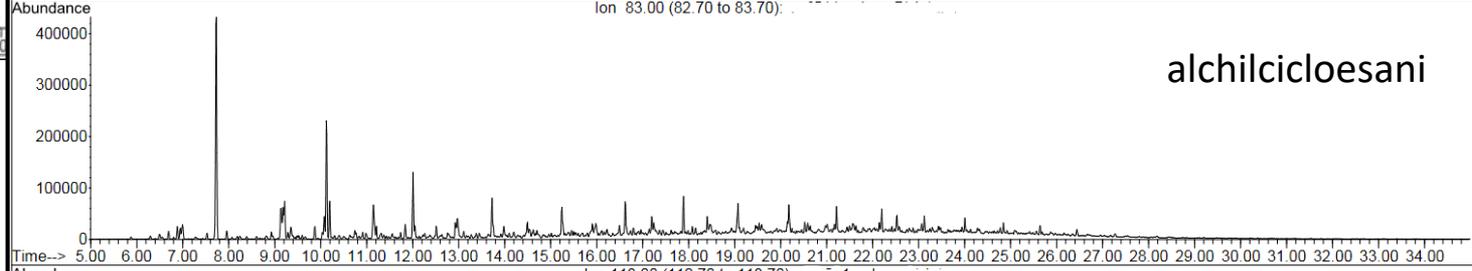
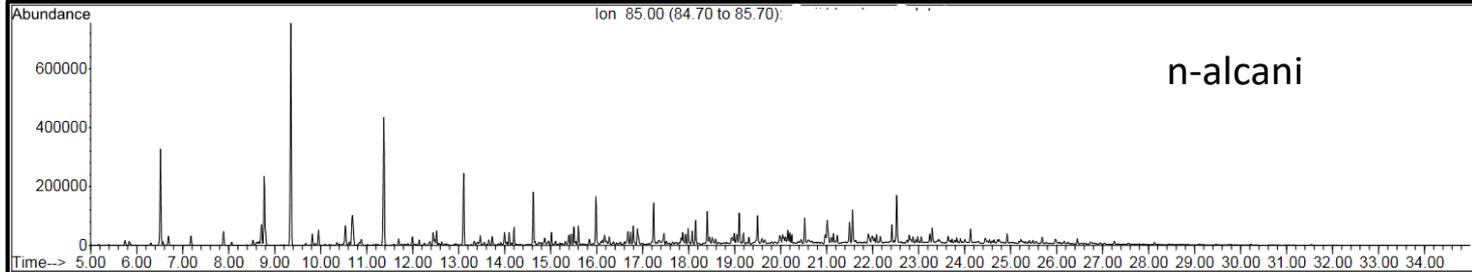
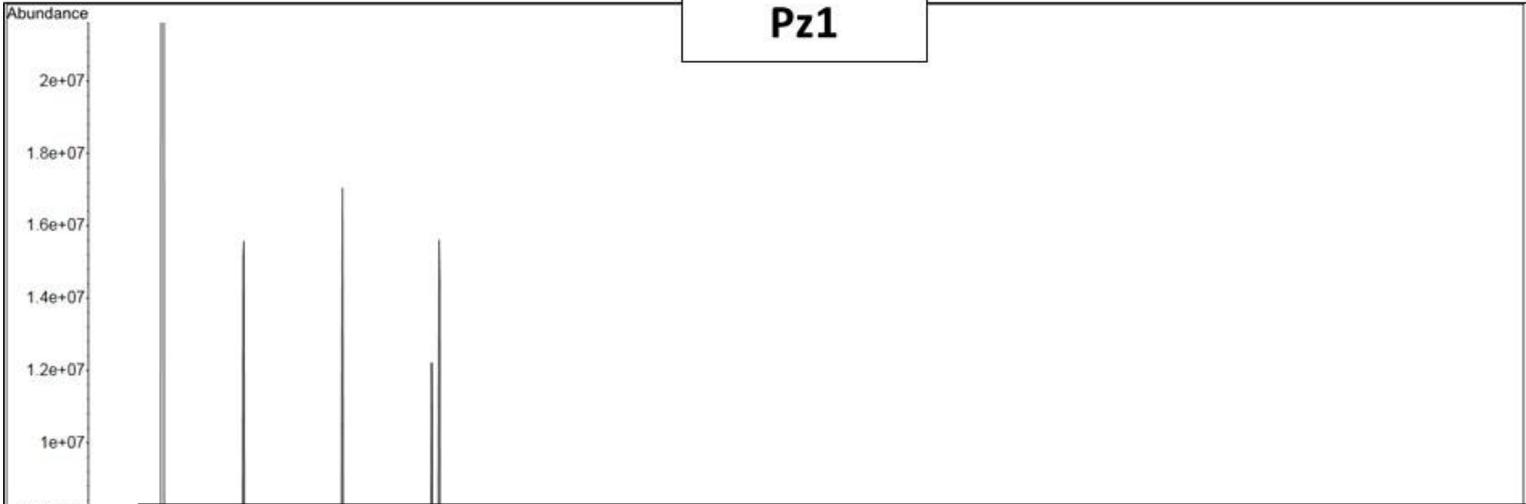
Dal 2002 procedimento di caratterizzazione/bonifica.

SITUAZIONE PRODOTTO NEL 2012

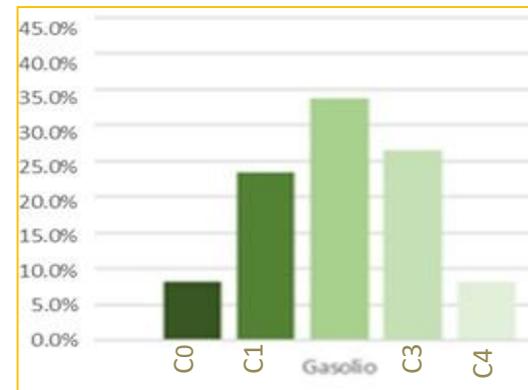
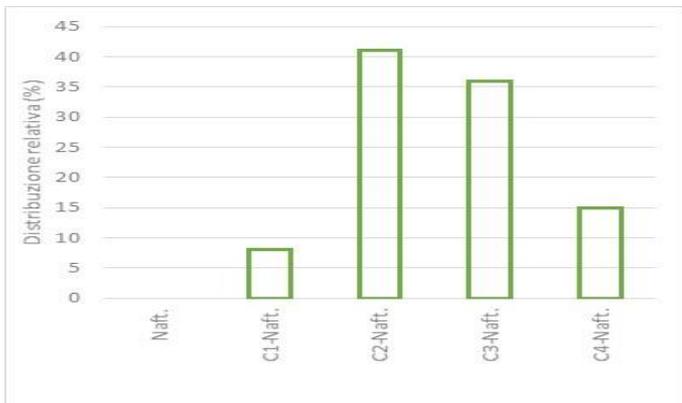
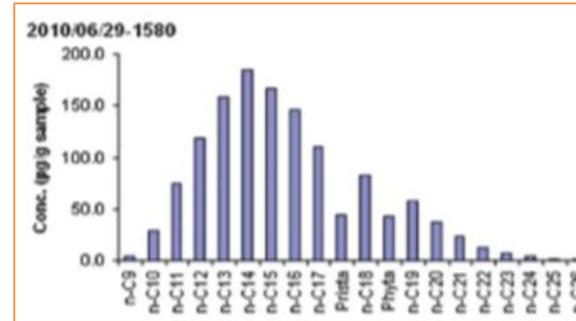
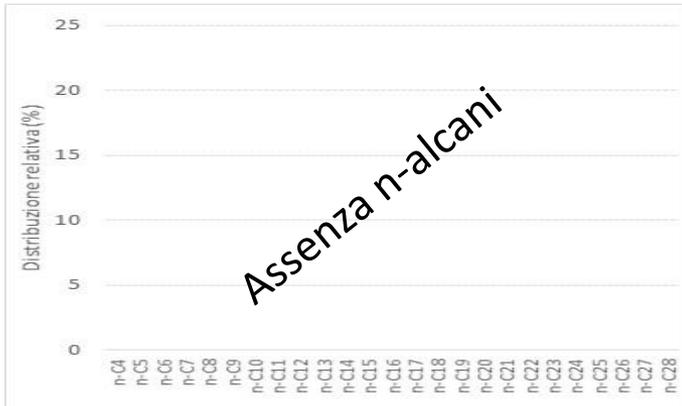


Realizzazione di una indagine di fingerprinting per ottenere la baseline

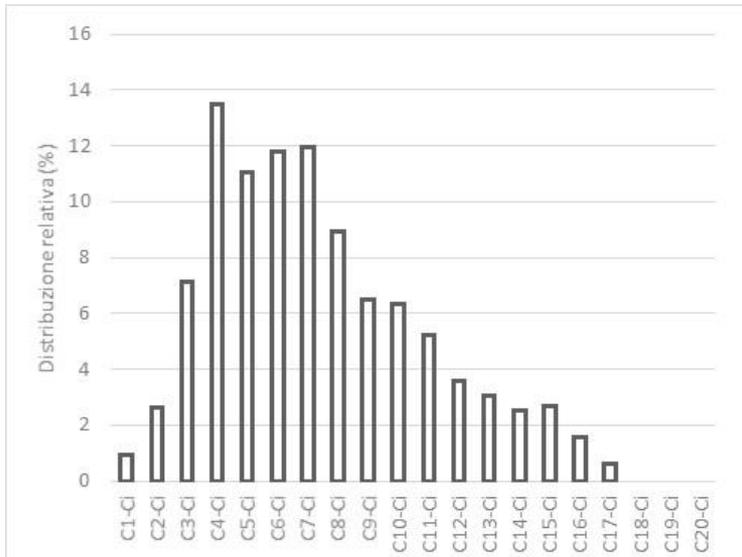
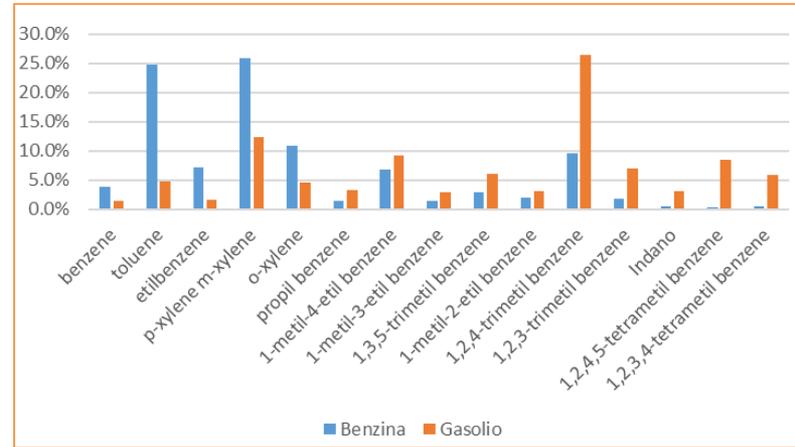
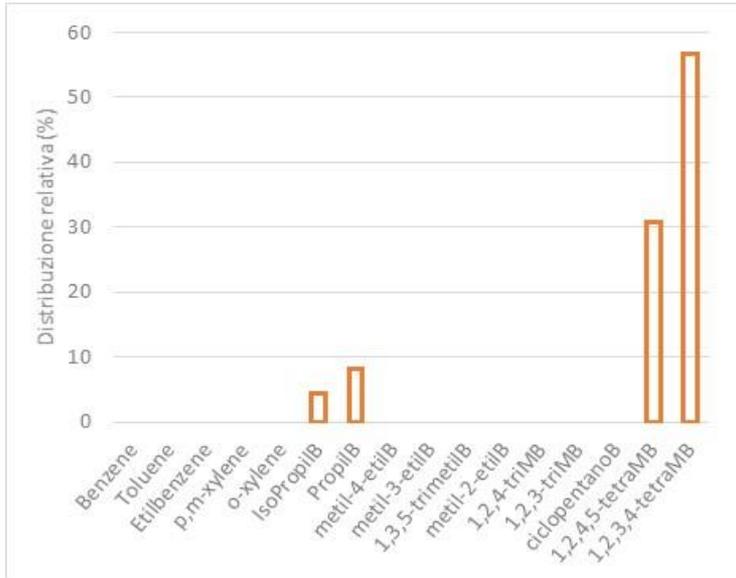
Pz1



INDAGINE FINGERPRINTING 2012: LA BASELINE



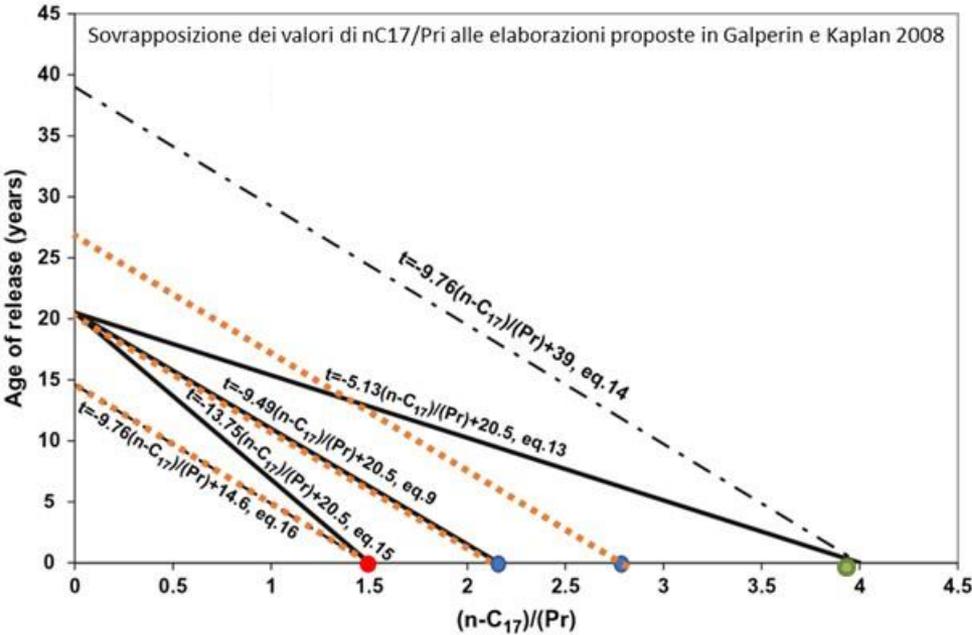
INDAGINE FINGERPRINTING 2012: LA BASELINE



	n-C17/Pr	n-C18/Ph	Pr/Ph
Pz2	-	-	0,78

INDAGINE FINGERPRINTING 2012: LA BASELINE

Weathering regime:	Very aggressive	Aggressive	Moderate	Weak	Very Weak
Fresh fuel	0	0	0	0	0
<i>Kaplan Stages:</i>					
1. Abundant <i>n</i> -alkanes	<0.25	0-2	0-4	0-8	0-10
2. Light <i>n</i> -alkanes removed, benzene & toluene removed	<0.5	2-4	4-8	8-16	10-20
3. Middle-range <i>n</i> -alkanes removed, ethylbenzene & xylenes removed	<1	4-6	8-12	16-24	20-30
4. More than 50% of the <i>n</i> -alkanes removed	<2	6-8	12-16	24-32	30-40
5. More than 90% of <i>n</i> -alkanes removed, alkyl-benzenes and alkyl-cyclo-hexanes begin to degrade	<3	8-10	16-20	32-40	40-50
6. All <i>n</i> -alkanes removed, alkyl-benzenes	<4	10-12	20-24	40-48	50-60
7. Isoprenoid removal significant	<5	>12	>24	>48	>60



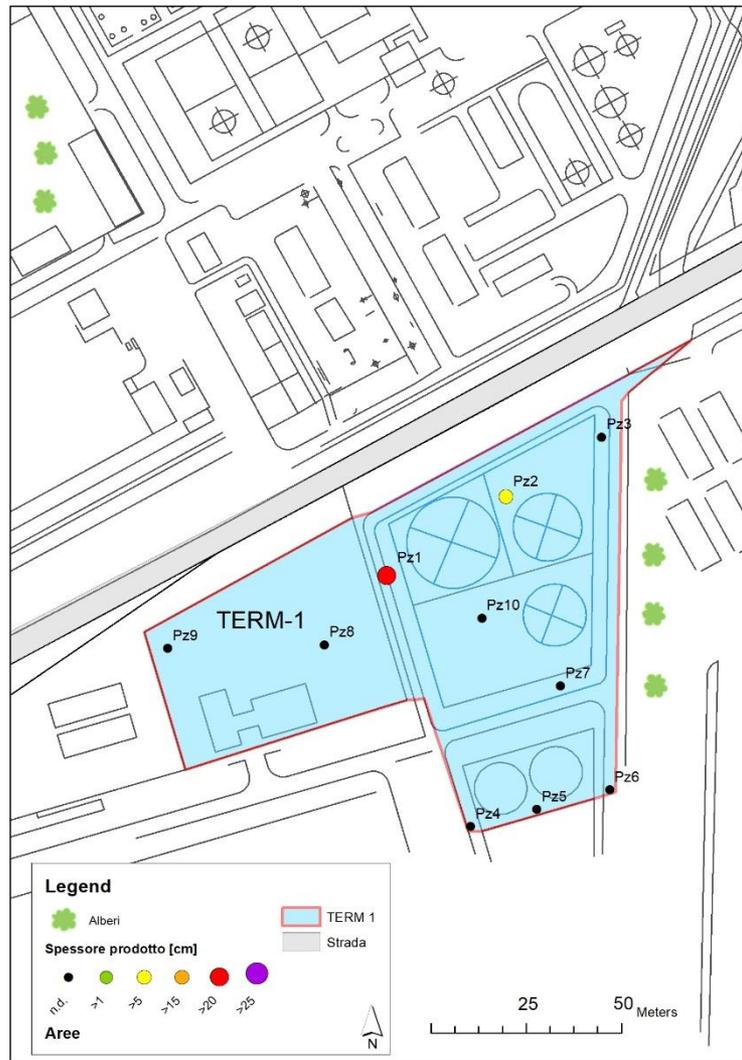
stima: tra i 10 e i 20 anni

fuel type	degradation level	chemical composition		
Bunker C fuel	Diesel	Gasoline	1	abundant <i>n</i> -alkanes
			2	light-end <i>n</i> -alkanes removed
			3	middle range <i>n</i> -alkanes, olefins, benzene and toluene removed
			4	more than 90% of <i>n</i> -alkanes removed
			5	alkylcyclohexanes and alkylbenzenes removed; isoprenoids and C0-naphthalene reduced
			6	isoprenoids, C1-naphthalenes, benzothiophene and alkylbenzothiophenes removed, C2-naphthalenes selectively reduced
			7	phenantrenes, dibenzothiophenes and other polynuclear aromatic hydrocarbons reduced
			8	tricyclic terpanes enriched, regular steranes selectively removed C31 to C35-homohopanes reduced
			9	tricyclic terpanes, diasteranes and aromatic steranes abundant
			10	aromatic steranes and demethylated hopanes* predominant

* only present under special conditions

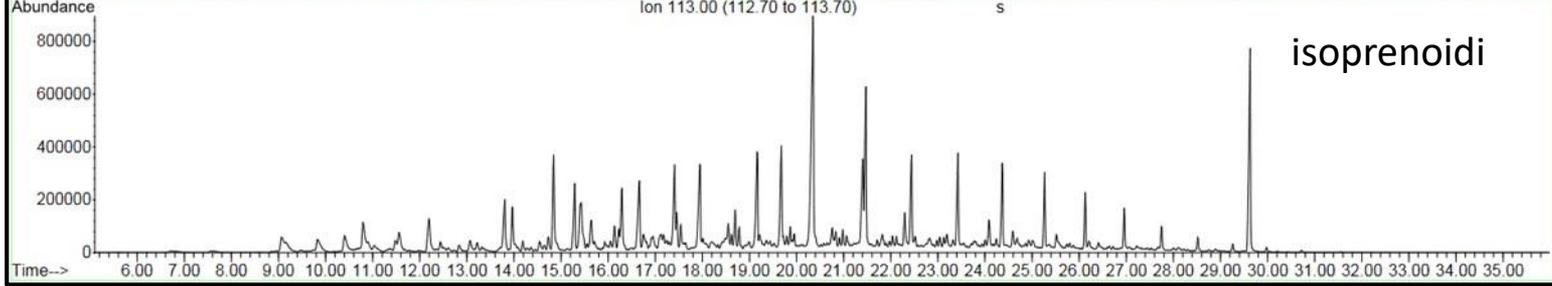
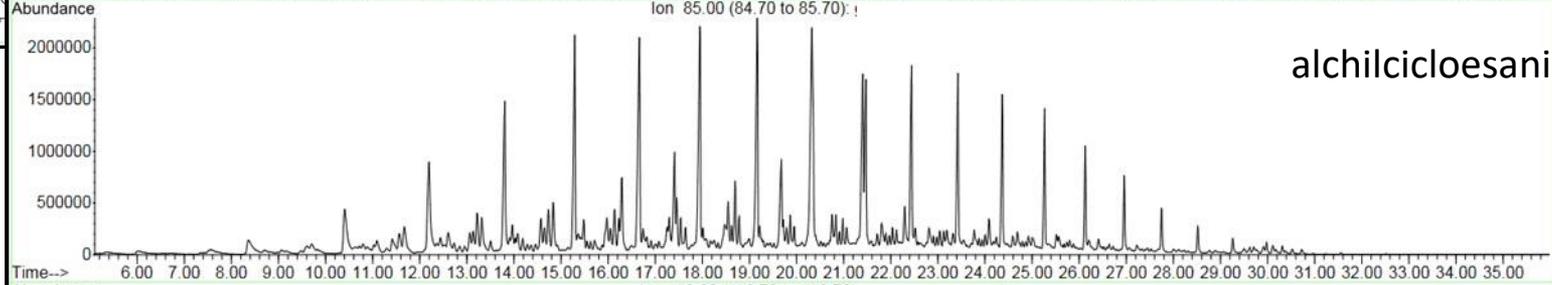
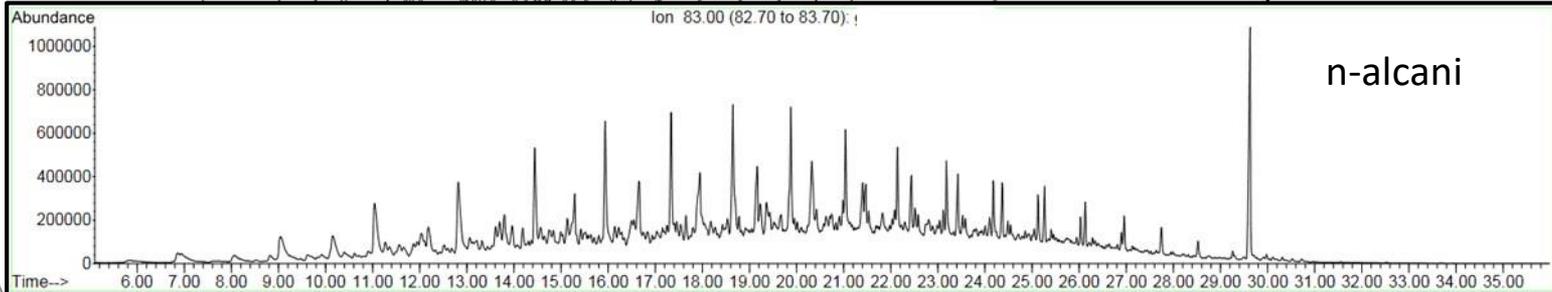
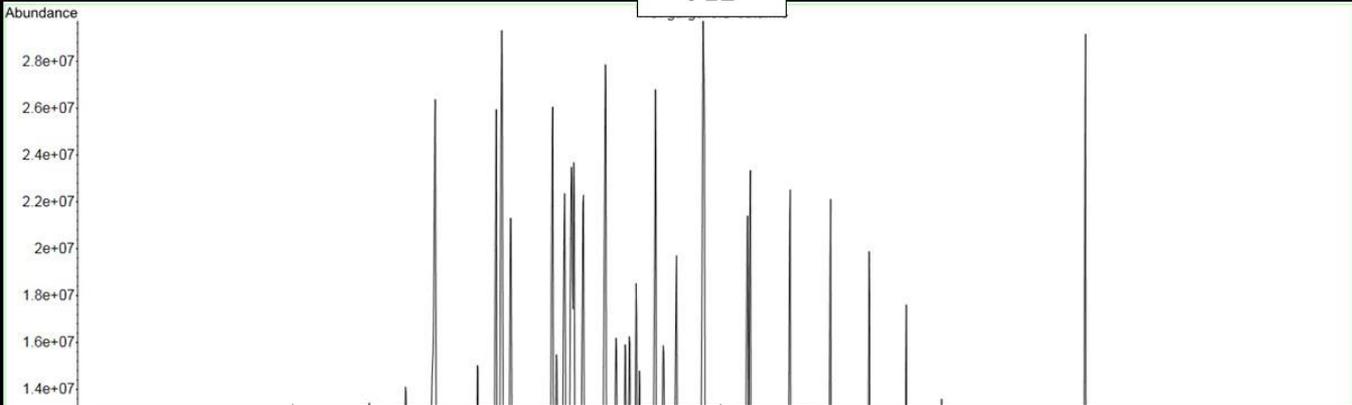
Change in gasoline, diesel fuel, and Bunker C composition during biodegradation

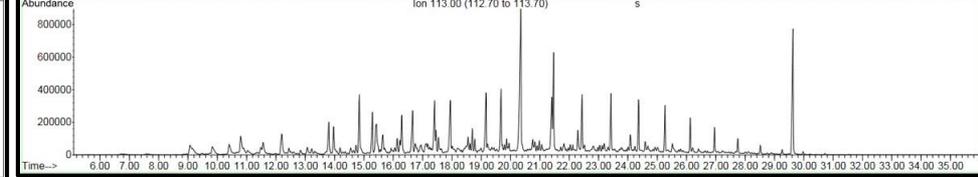
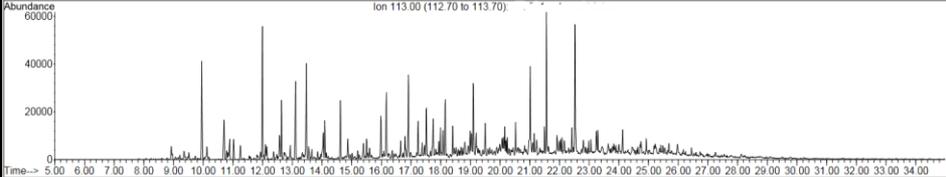
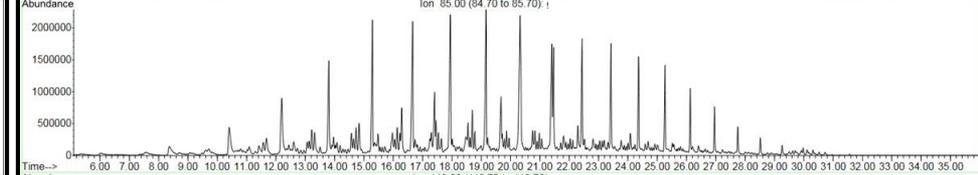
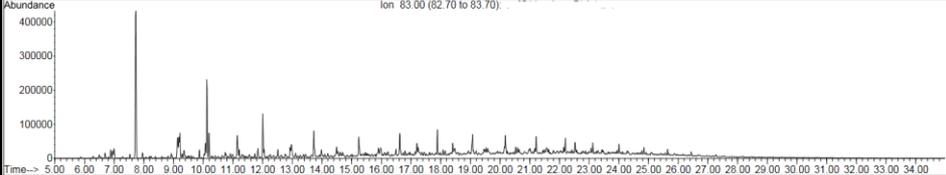
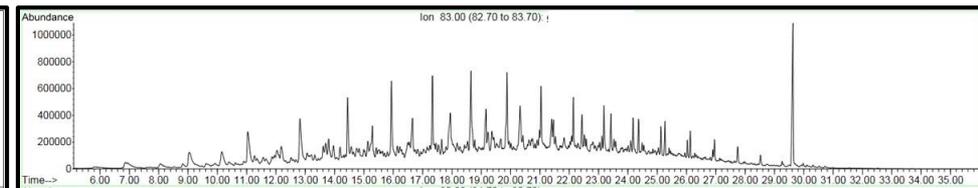
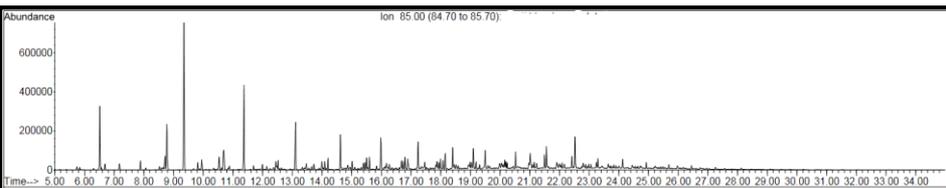
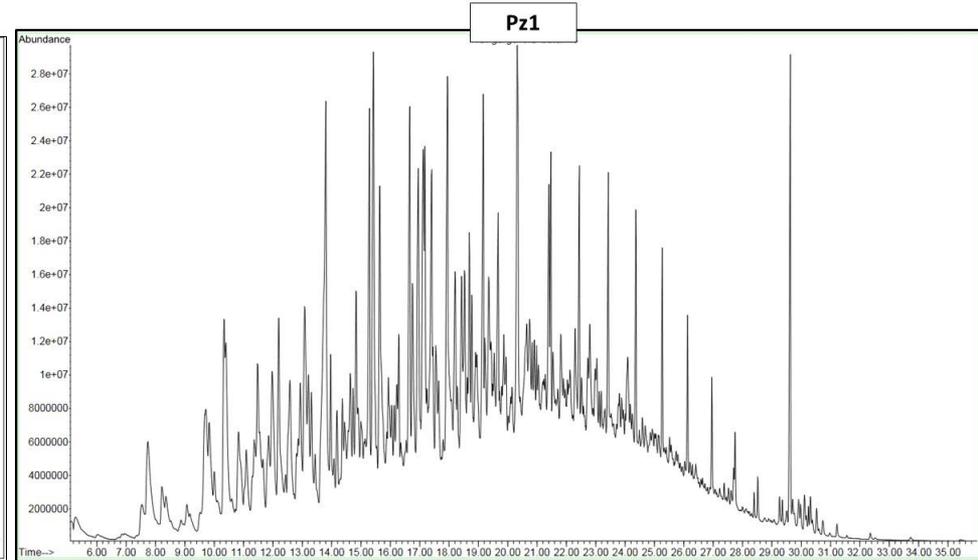
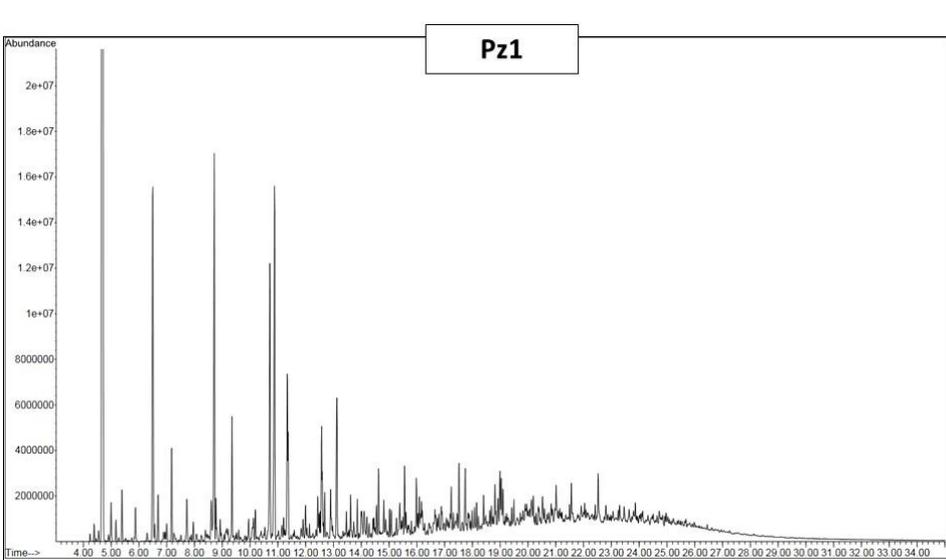




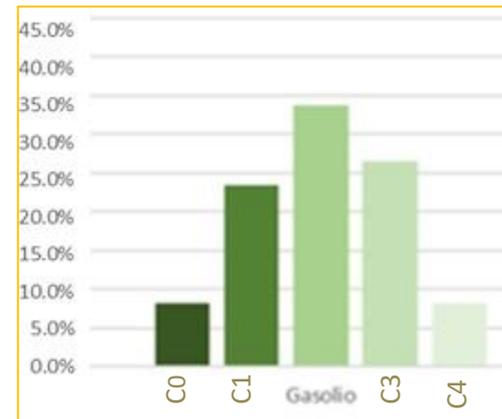
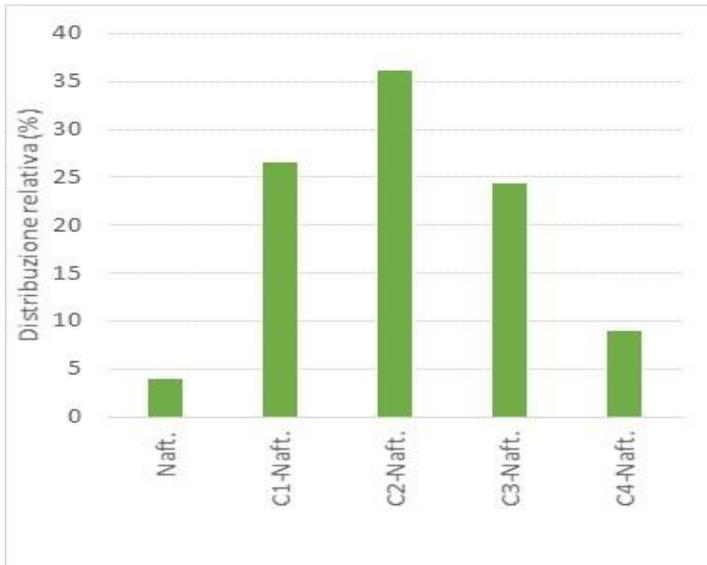
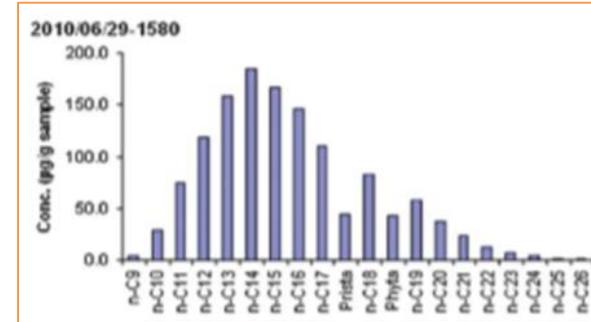
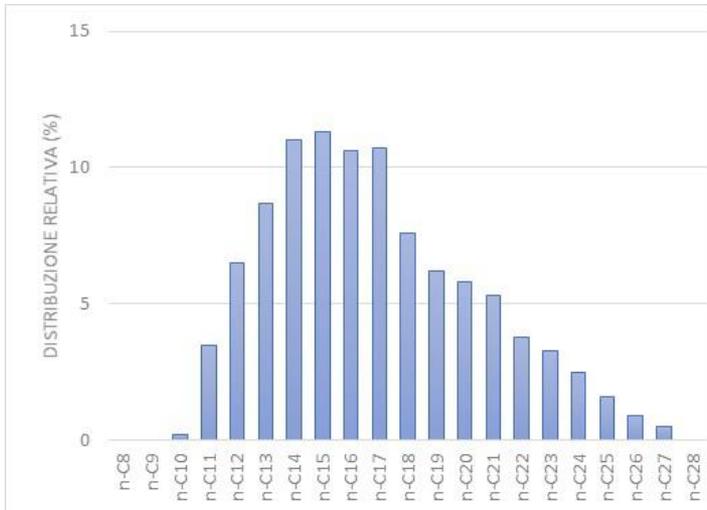
Nuova campagna di fingerprinting

Pz1



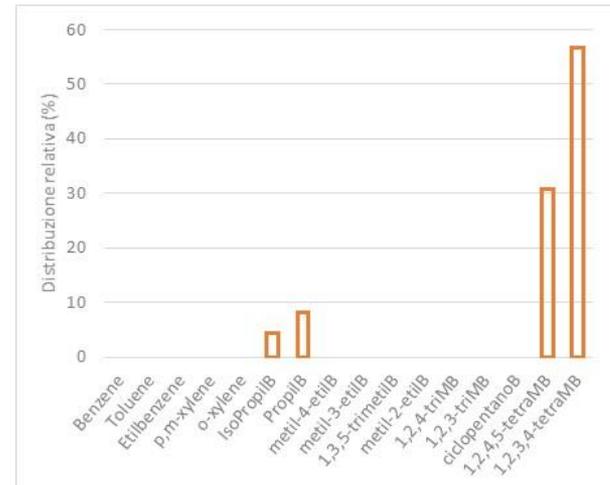
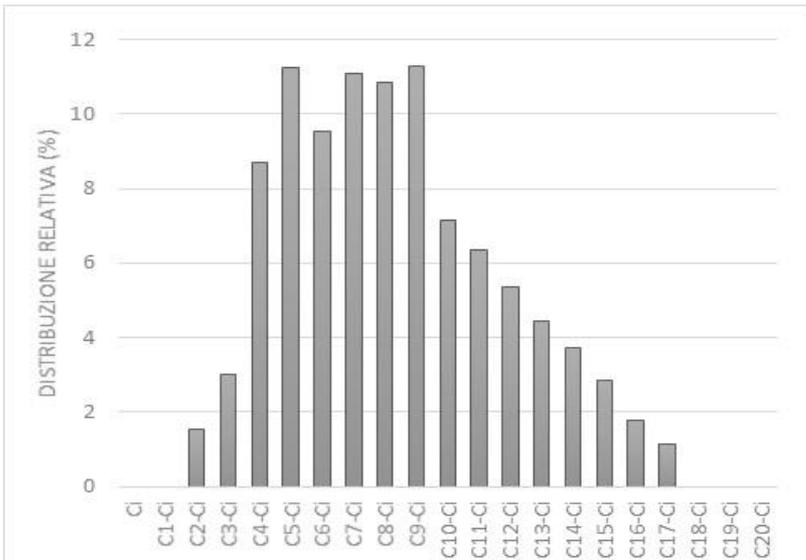
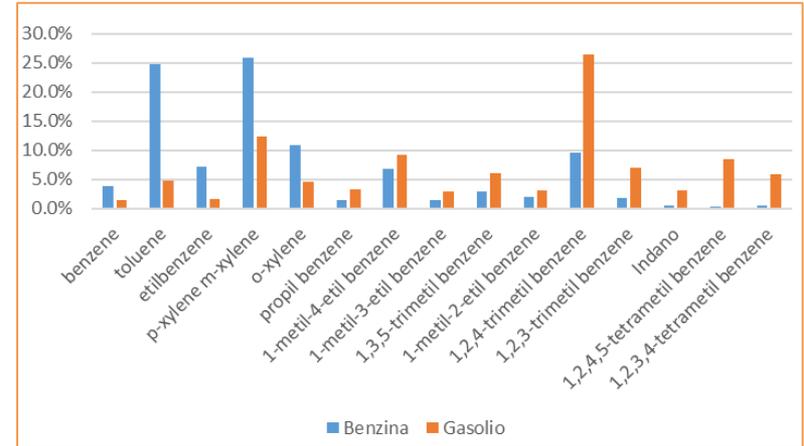
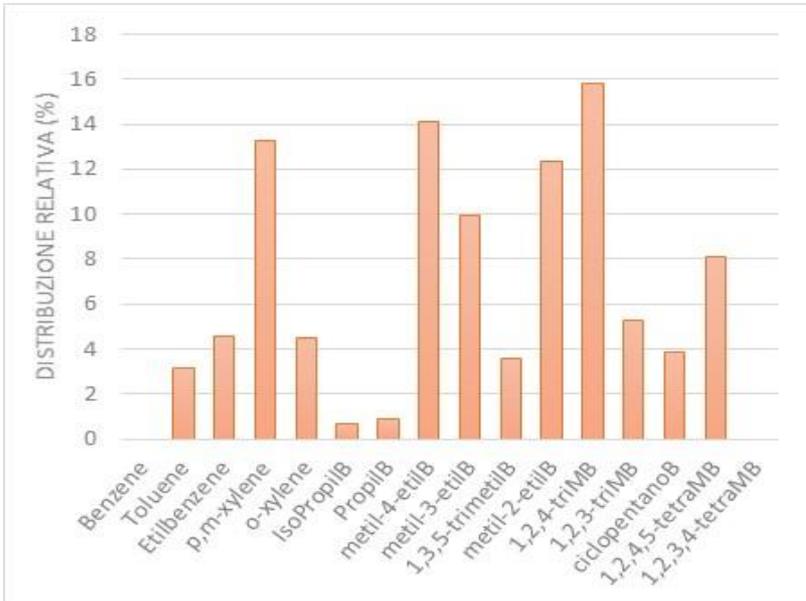


FINGERPRINTING 2018



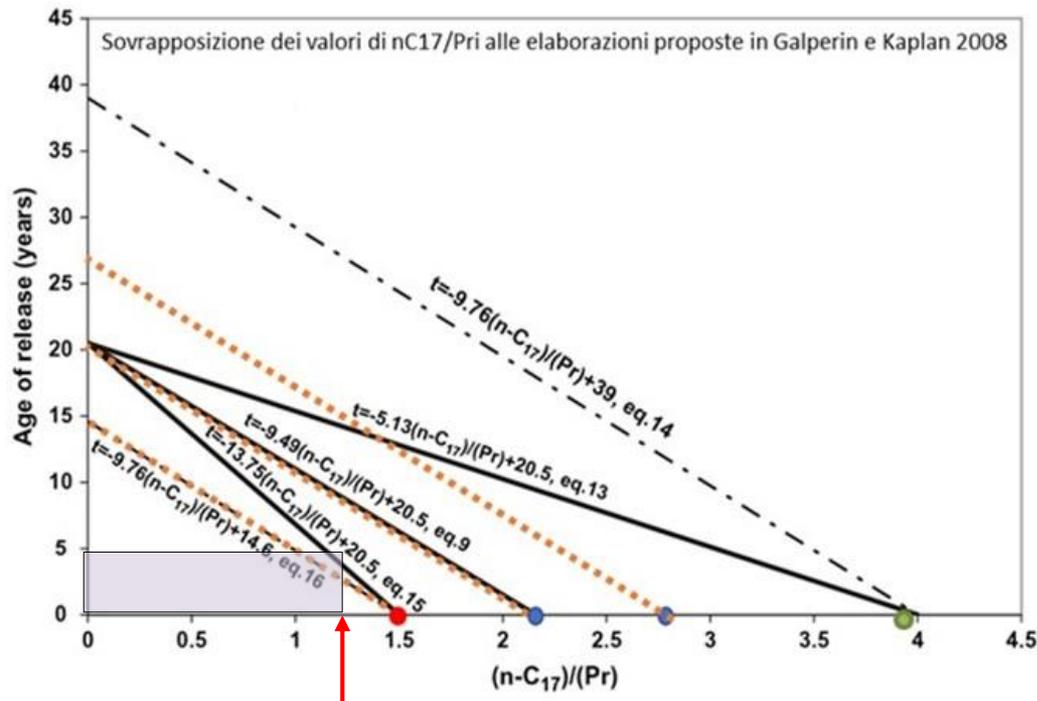
	n-C17/Pr	n-C18/Ph	Pr/Ph
Pz1	1,79	1,16	0,72

FINGERPRINTING 2018



	n-C17/Pr	n-C18/Ph	Pr/Ph
MON06	1,22	1,08	1,06

FINGERPRINTING 2018: DATAZIONE



Tempo di rilascio stimato < 5 anni

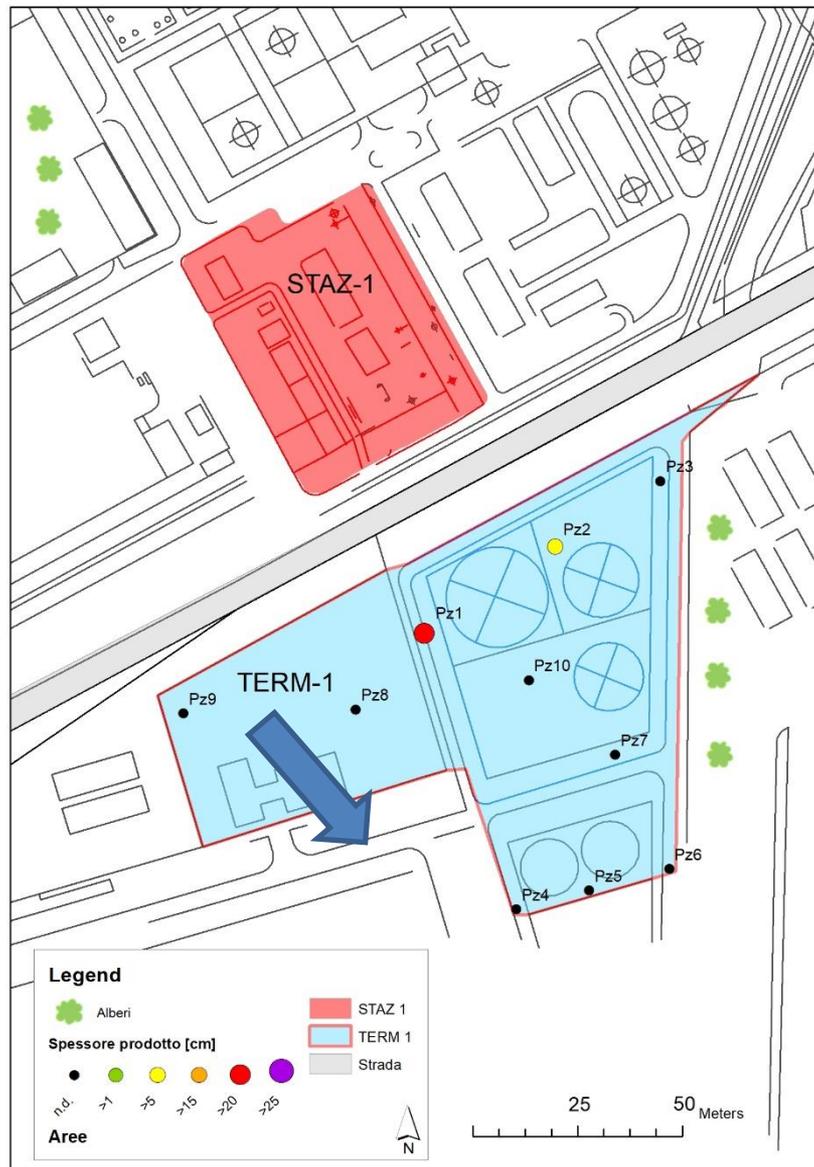
Weathering regime:	Very aggressive	Aggressive	Moderate	Weak	Very Weak
Fresh fuel	0	0	0	0	0
Kaplan Stages:					
1. Abundant <i>n</i> -alkanes	<0.25	0-2	0-4	0-8	0-10
2. Light <i>n</i> -alkanes removed, benzene & toluene removed	<0.5	2-4	4-8	8-16	10-20
3. Middle-range <i>n</i> -alkanes removed, ethylbenzene & xylenes removed	<1	4-6	8-12	16-24	20-30
4. More than 50% of the <i>n</i> -alkanes removed	<2	6-8	12-16	24-32	30-40
5. More than 90% of <i>n</i> -alkanes removed, alkyl-benzenes and alkyl-cyclo-hexanes begin to degrade	<3	8-10	16-20	32-40	40-50
6. All <i>n</i> -alkanes removed, alkyl-benzenes	<4	10-12	20-24	40-48	50-60
7. Isoprenoid removal significant	<5	>12	>24	>48	>60

fuel type	degradation level	chemical composition
Bunker C fuel	1	abundant n-alkanes
	2	light-end n-alkanes removed
	3	middle range n-alkanes, olefins, benzene and toluene removed
	4	more than 90% of n-alkanes removed
	5	alkylcyclohexanes and alkylbenzenes removed; isoprenoids and C0-naphthalene reduced
	6	isoprenoids, C1-naphthalenes, benzothiophene and alkylbenzothiophenes removed, C2-naphthalenes selectively reduced
	7	phenantrenes, dibenzothiophenes and other polynuclear aromatic hydrocarbons reduced
	8	tricyclic terpanes enriched, regular steranes selectively removed C31 to C35-homohopanes reduced
	9	tricyclic terpanes, diasteranes and aromatic steranes abundant
	10	aromatic steranes and demethylated hopanes* predominant

↑ increasing level of biodegradation

* only present under special conditions
Change in gasoline, diesel fuel, and Bunker C composition during biodegradation



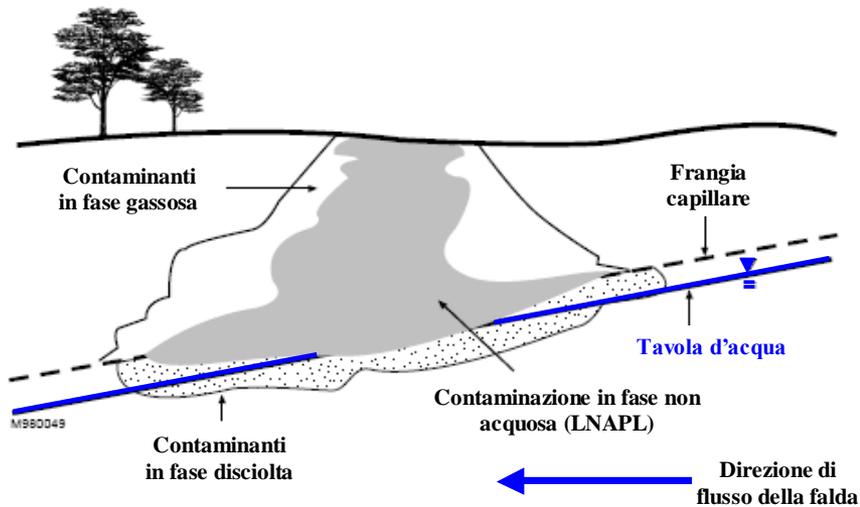


MODELLAZIONE TRIFASICA - TMVOC

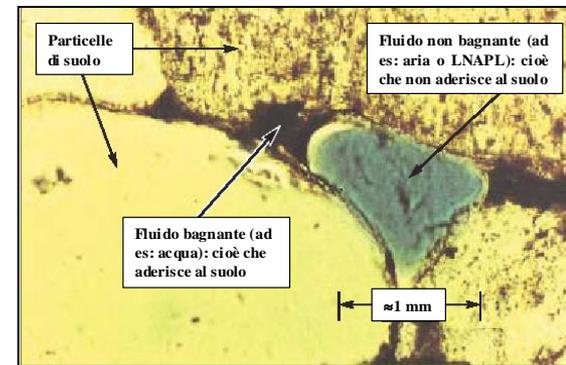
TMVOC (Lawrence Berkeley National Laboratory, 2002) è un simulatore numerico di flusso multidimensionale di tre fasi - acqua, gas interstiziale e una miscela di VOC (tra cui petrolio, benzina, gasolio), in mezzi eterogenei a vario grado di saturazione. Può considerare il trasporto di 20 componenti di cui, oltre l'acqua, gas non condensabili o VOC solubili in falda. E' in grado di simulare la biodegradazione.

Comprendere il comportamento di NAPL in mezzi saturi e insaturi in ambiente naturale in presenza di interventi (es. SVE, P&T)

Progettare/ottimizzare gli interventi di bonifica/rimozione NAPL



modificato da USACE, 1999



modificato da RTDF, 2005

MODELLAZIONE TRIFASICA: LIMITI E COMPLESSITÀ

A titolo esemplificativo per quanto riguarda lo spill:

- E' possibile simulare solo un numero limitato di parametri (6 con interfaccia Petrasim) → deve essere scelta una selezione rappresentativa quando si hanno miscele complesse. Le proprietà chimico-fisiche variano all'interno della stessa famiglia di composti (diffusione, solubilità, etc)
- I processi di trasporto richiedono un gran numero di parametri chimico-fisici per ogni composto e proprietà specifiche del terreno (es. grado di saturazione dei terreni, pressione capillare etc.) difficili da ottenere.

Parameter
Critical temperature [K] (Tc)
Critical pressure [bar] (Pc)
Critical compressibility (Zc)
Pitzer's acentric factor (omega)
Chemical dipole moment [debyes] (Dipm)
Chemical normal boiling point [K] (Tb)
Chemical vapor pressure constant VPAM (VP A)
Chemical vapor pressure constant VPBM (VP B)
Chemical vapor pressure constant VPCM (VP C)
Chemical vapor pressure constant VPDM (VP D)
Chemical molecular weight [g/mol] (MolWt)
Chemical ideal gas heat capacity constant CPAM (CPVAP A)
Chemical ideal gas heat capacity constant CPBM (CPVAP B)
Chemical ideal gas heat capacity constant CPCM (CPVAP C)
Chemical ideal gas heat capacity constant CPDM (CPVAP D)
Reference NAPL (liquid) density [kg/m3] (LDEN)
Reference temperature for NAPL density [K] (TDEN)
Reference binary diffusivity of VOC in air [m2/s]
Reference temperature for gas diffusivity [K]
Exponent for calculation of chemical diffusivity
Liquid NAPL viscosity constant VLOAM (A tab.9.8)
Liquid NAPL viscosity constant VLOBM (B tab.9.8)
Liquid NAPL viscosity constant VLOCM (C tab.9.8)
Liquid NAPL viscosity constant VLODM (D tab.9.8)
Chemical critical volume [cm3/mole] (Vc)
Constant for chemical solubility in water SOLAM [mole fraction]

Alcune
proprietà dei
VOCs richieste

TMVOC – ESEMPLIFICAZIONE DEL CASO DI STUDIO

Parametri di riferimento gasolio da «Standard Handbook Oil Spill Environmental Forensics” -2nd Edition.
Scott Stout Zhendi Wang

Identificazione delle famiglie (es. alcani -40%, cicloalcani 40% etc.) percentualmente più significative di un gasolio medio.

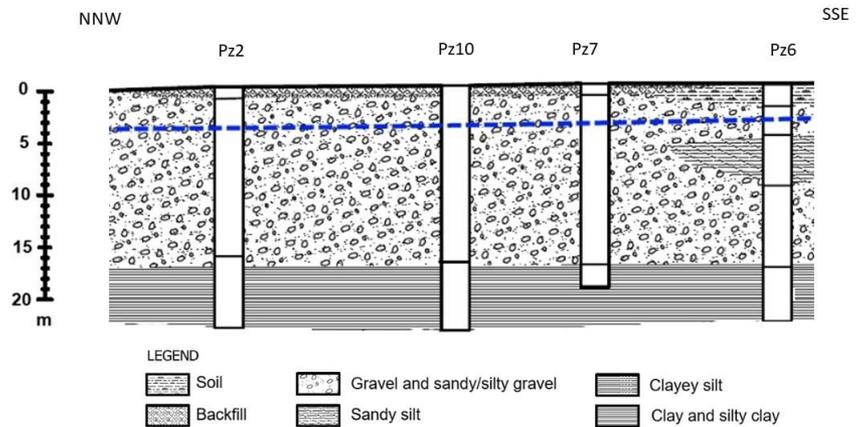
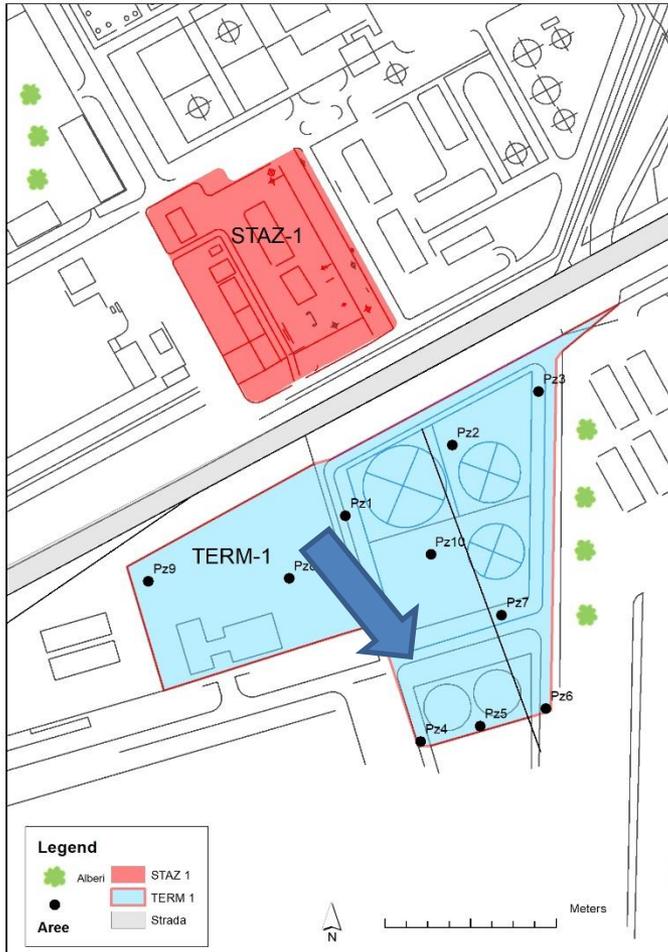
Scelta delle famiglie più importanti e per le quali è stato possibile individuare le caratteristiche di input del modello – riparametrizzazione a 100 della composizione.

Alcani (47,5%): pentadecano
Cicloalcani (47,5%): n-epitilciclopentano
IPA (3%): bifenile
BTEX (2%): Toluene

Group	Compound class	Gasoline	Diesel	Light crude	Heavy crude	IFO	Bunker C
Saturates		50-60	65-95	55-90	25-80	25-45	20-40
	Alkanes	45-55	35-45				
	Cyclo-alkanes	-5	30-50				
	Waxes		0-1	0-20	0-10	2-10	5-15
Olefins		5-10	0-10				
Aromatics		25-40	5-25	10-35	15-40	40-60	30-50
	BTEX	15-35	0.5-2	0.1-2.5	0.01-2	0.05-1	0-1
	PAHs		0.5-5	0.5-3	1-4	1-5	1-5
Polar compounds			0-2	1-15	5-40	15-25	10-30
	Resins		0-2	0-10	2-25	10-15	10-20
	Asphaltenes			0-10	0-20	5-10	5-20
Sulfur		<0.05	0.05-0.5	0-2	0-5	0.5-2	2-4
Metals (ppm)				30-250	100-500	100-1000	100-2000

Caratteristiche parametri: Reid R., Prausnitz J., Poling B. (1987) - The properties of gases & liquids – 4th Edition, McGraw-Hill, 1987

TMVOC – ESEMPLIFICAZIONE DEL CASO DI STUDIO



Distanza potenziale fonte: circa 42 metri

Spessore medio saturo: 15 metri

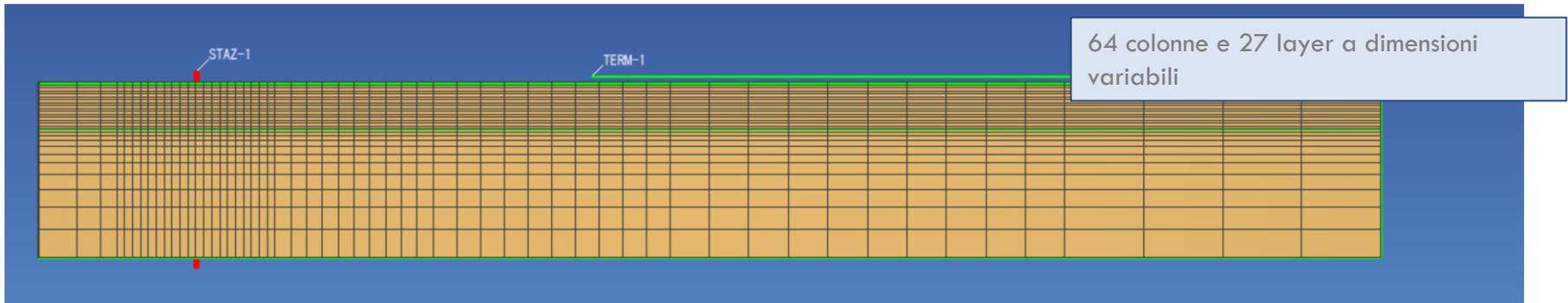
Gradiente: 7×10^{-3}

Permeabilità media: 3×10^{-4} m/s

Simulazione bidimensionale

Ipotizzate diverse condizioni di spill.

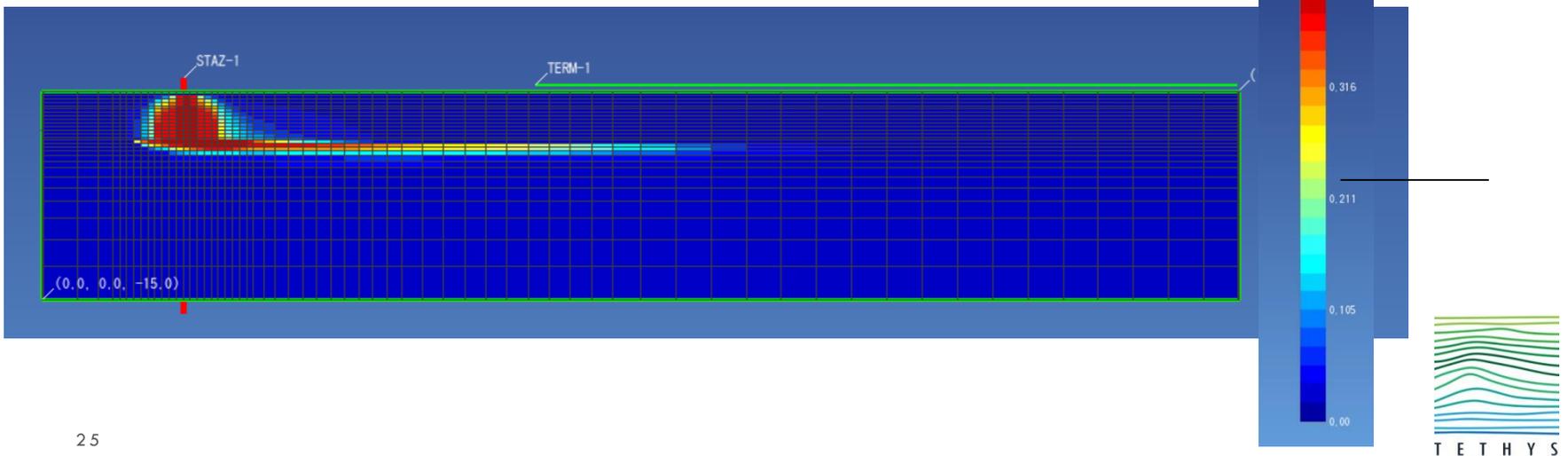
MODELLAZIONE



Simulazione bidimensionale.

Differenti condizioni di spill (durata e perdita).

Tempi di circa 3 anni potenzialmente compatibili con presenza di prodotto



CONCLUSIONI

Campagna di fingerprinting composizionale condotta nel 2012 per l'identificazione di una base-line caratteristica del sito: gasolio degradato compatibile con origine precedente a 2002.

L'indagine condotta nel 2018 su nuovo LNAPL rilevato ha identificato presenza di gasolio recente non compatibile con origine dal sito presente nell'ambiente da un periodo inferiore di 5 anni.

Ipotesi provenienza dalla stazione di servizio Staz-1, compatibile con la piezometria: applicazione della modellazione trifasica (TMVOC) in maniera esemplificativa per comprendere potenzialità tempi di propagazione. Prodotto riscontrato potenzialmente compatibile con un tempo di circa 3 anni.



Importanza di condurre una caratterizzazione preventiva tramite fingerprinting: la caratterizzazione specifica della contaminazione consente di individuare le **cause e la responsabilità di nuovi eventi**.

Utilità integrazione tecniche modellatorie. Possibili sviluppi di quella trifasica.

Grazie per l'attenzione

patrizia.trefiletti@tethys.srl

