Gas stations: characterization, dating and monitoring through compositional and isotopic fingerprinting analysis

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Isotope Tracer Technologies Europe SRL

Regulatory framework and Innovative Characterization
REGULATORY FRAMEWORK

RemTech Expo 2019 (18, 19, 20 September) FerraraFiere
www.remtechexpo.com

Why to apply compositional and isotopic fingerprinting?

COMPOSTI ORGANICI AROMATICI				
Benzene	< 0,05	µg/l	1	24
Etil benzene	< 0,05	µg/l	50	25
Stirene	< 0,05	µg/l	25	26
Toluene	1,78	µg/l	15	27
p-Xilene	0,52	µg/l	10	28
Xileni	0,65	µg/l	-	-
MTBE	32	µg/l	-	-
ETBE	46	µg/l	-	-
POLICICLICI AROMATICI				
Benzo[a]antracene	< 0,01	µg/l	0,1	29
Benzo[a]pirene	< 0,001	µg/l	0,01	30
Benzo[b]fluorantene	< 0,01	µg/l	0,1	31
Benzo[k]fluorantene	< 0,01	µg/l	0,05	32
Benzo[g,h,i]perilene	< 0,001	µg/l	0,01	33
Crisene	< 0,01	µg/l	5	34
Dibenzo[a,h]antracene	< 0,001	µg/l	0,01	35
Indeno(1,2,3-c,d)pirene	< 0,01	µg/l	0,1	36
Pirene	< 0,01	µg/l	50	37
Sommatoria IPA (31, 32, 33, 36)	< 0,01	µg/l	0,1	38
IDROCARBURI TOTALI (n-ESANO)	< 50	µg/l	350	90

Lots of analytical data but not very informative

Don't allow to undestand the type of release, when that happen, am I the responsible? What about other compounds such MTBE, ETBE…?

What about natural attenuation process? Which remediation strategy should I choose?

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Which analysis can be useful to get some answers?

Regular Analysis

COMPOSTI ORGANICI AROMATICI				
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Etil benzene	< 0,05	µg/l	50	25
Stirene	< 0,05	µg/l	25	26
Toluene	1,78	µg/l	15	27
p-Xilene	0,52	µg/l	10	28
Xileni	0,65	µg/l	-	-
MTBE	32	µg/l	-	-
ETBE	46	µg/l	-	-
POLICICLICI AROMATICI				
Benzo[a]antracene	< 0,01	µg/l	0,1	29
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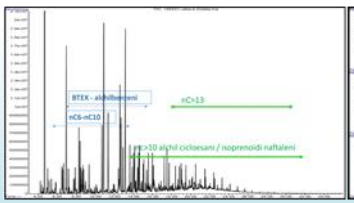
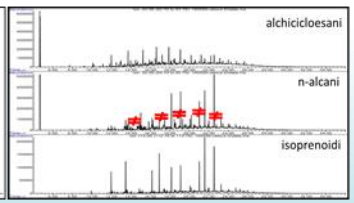
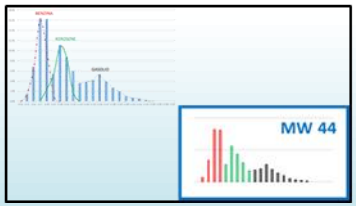
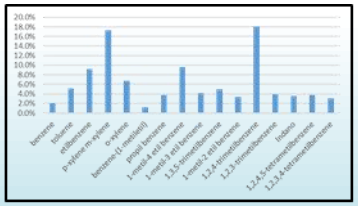
for enviromental regulatory porpuse

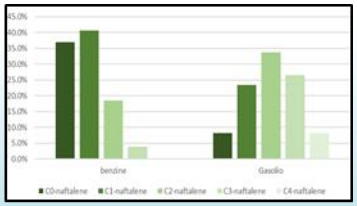
Fingerprinting analysis for conceptual model development











Can be once in while or Part of a monitoring plan

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Type of analysis

LEVEL	ANALYSIS	USE
I	phisical\chemical properties: density, viscosity, %S, distillation curves	Initial screening *(usually existing data)*
II	TIC (total ion cromatogram)	Type of product/degree of wheathering (low resolution - qualitative)
III	Compositional fingerprinting	Type of product/degree of wheathering (high resolution qualitative/quantitative)
VI	Biomarkers, Diagnostic indexes	Elapsed time from the release (high resolution qualitative/quantitative)
V	Stable Isotope Analysis	Several, very high resolution, sensitivity and source\responsability distinguishal

And more, for specific applications (GCxGC-FID, ecc)

Analysis on oil/product but also on water samples (dissolved phase)

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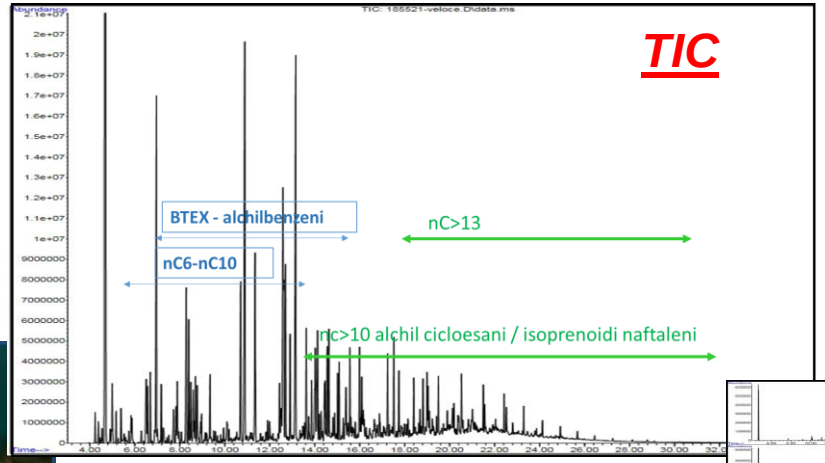
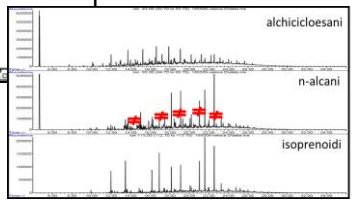
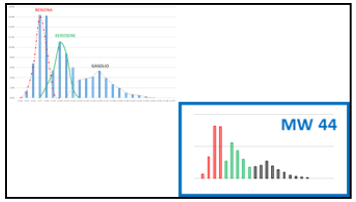
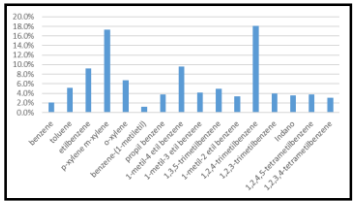
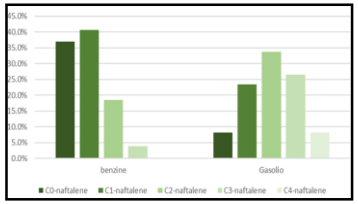
Rational behind?











fasi kaplan	degradazione				
	molto aggressiva	aggressiva	moderata	debole	molto debole
1. abbondanti *n* -alcani	<0,25	0–2	0–4	0–8	0–10
2. *n* -alcani leggeri, benzene e toluene rimossi	<0,5	2–4	4–8	8–16	10–20
3. *n* -alcani medi, etilbenzene e xileni rimossi	<1	4–6	8–12	16–24	20–30
4. *n* -alcani rimossi oltre il 50%	<2	6–8	12–16	24–32	30–40
5. *n* -alcani rimossi oltre il 90%, alchilbenzeni e alchilcicloesani iniziano a degradarsi	<3	8–10	16–20	32–40	40–50
6. *n* -alcani e alchilbenzeni rimossi completamente	<4	10–12	20–24	40–48	50–60
7. isoprenoidi rimossi significativamente	<5	>12	>24	>48	>60

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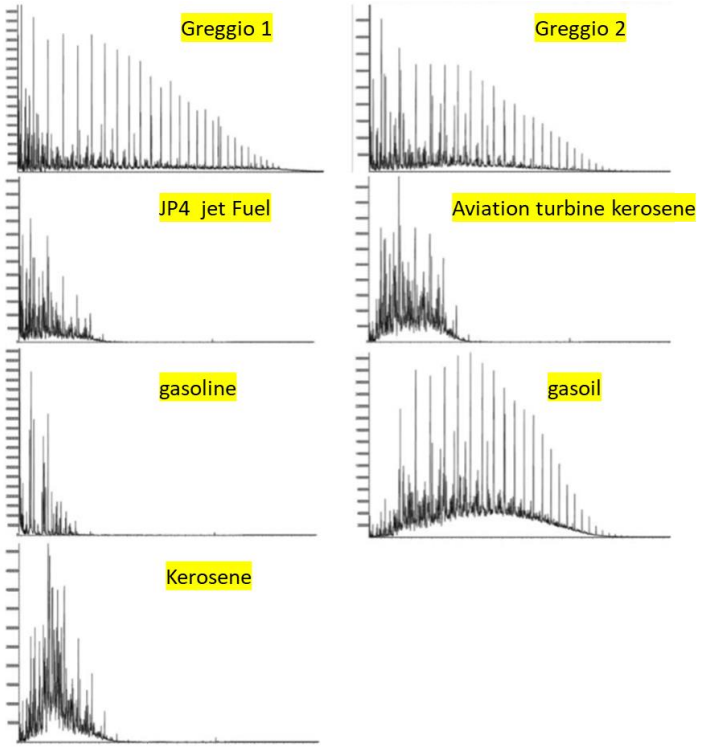
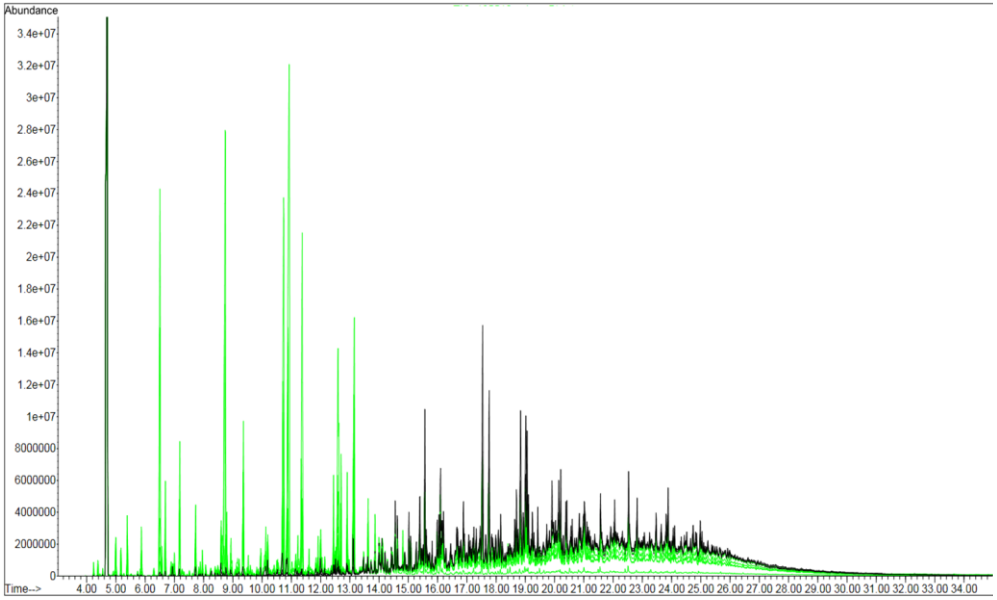
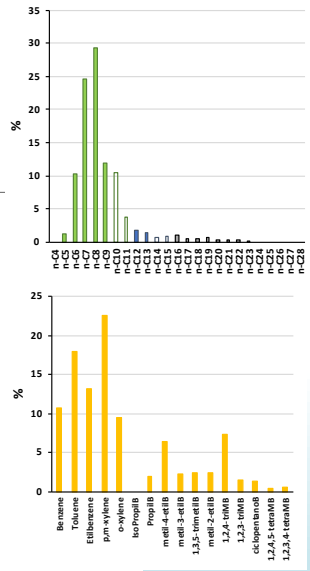
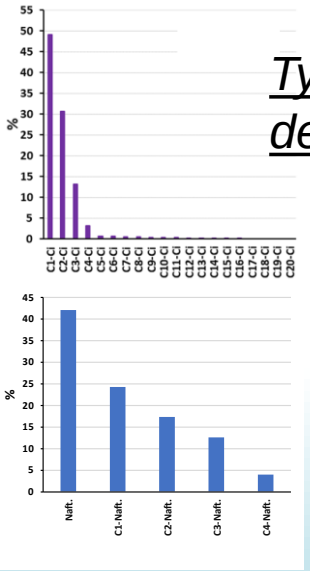
TIC + compositional fingerprinting

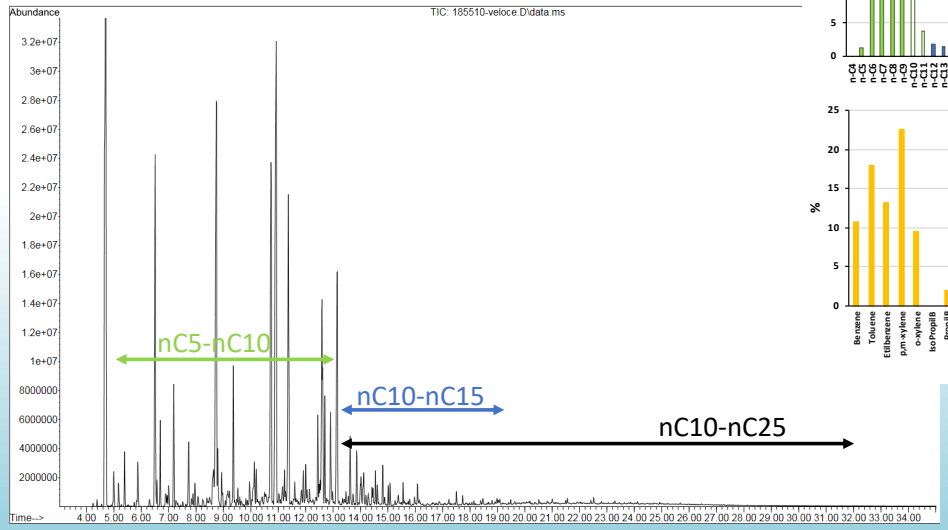








Type of product
degree of weathering



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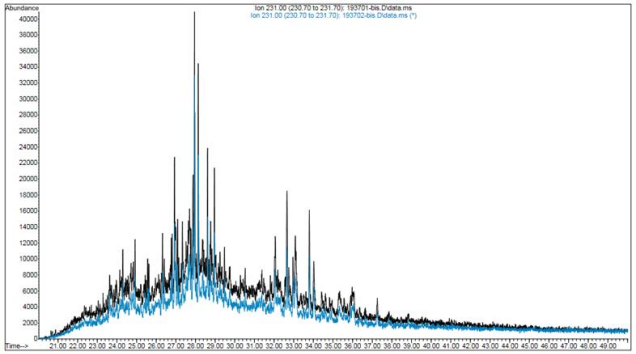
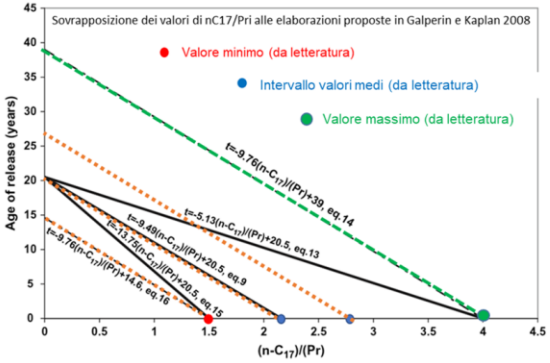
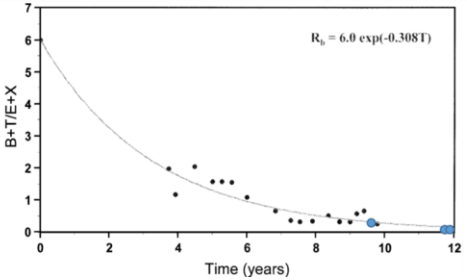
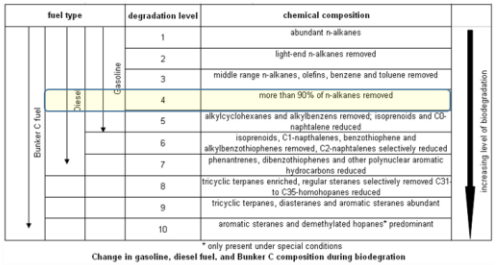
Biomarkers + diagnostic ratios



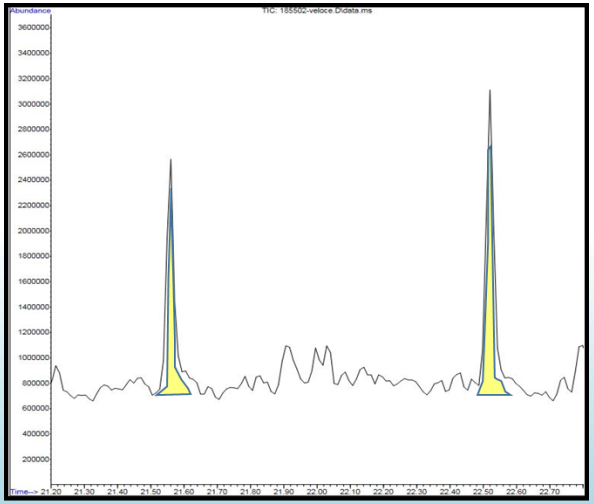




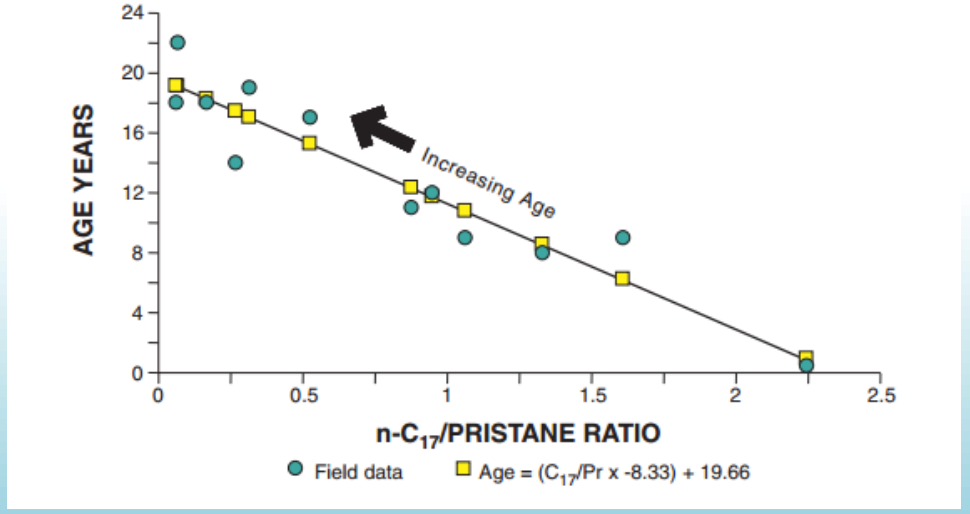
Weathering regime:	Very aggressive	Aggres-sive	Moderate	Weak	Very Weak
Fresh fuel	0	0	0	0	0
Kaplan Stages:					
1. Abundant *n*-alkanes	<0.25	0-2	0-4	0-8	0-10
2. Light *n*-alkanes removed, benzene & toluene removed	<0.5	2-4	4-8	8-16	10-20
3. Middle-range *n*-alkanes removed, ethylbenzene & xylenes removed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



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



	n-C17/pristano	n-C18/fitano	pristano/fitano
RW 6	-	-	0.76



CASE STUDY: conceptual model

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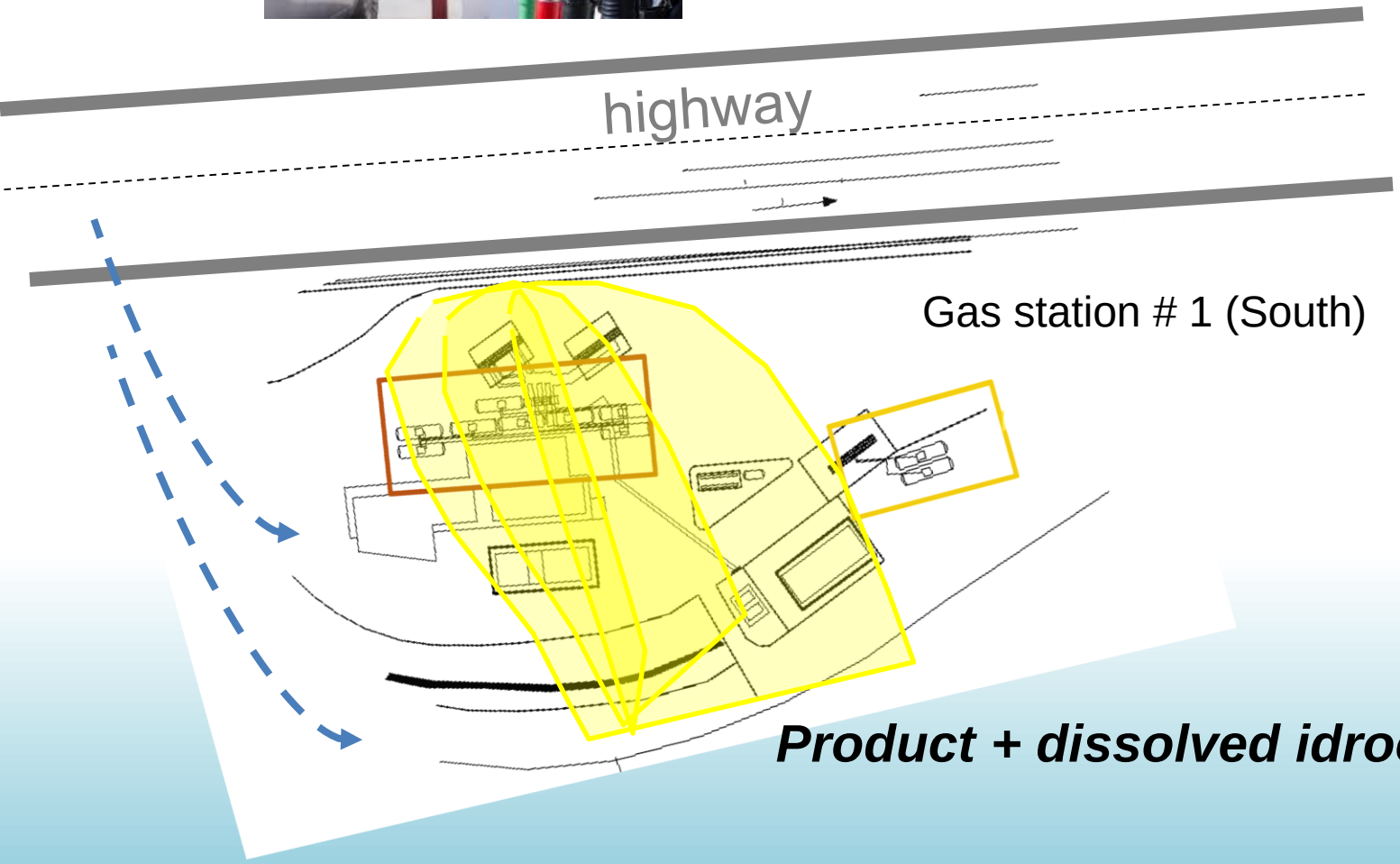
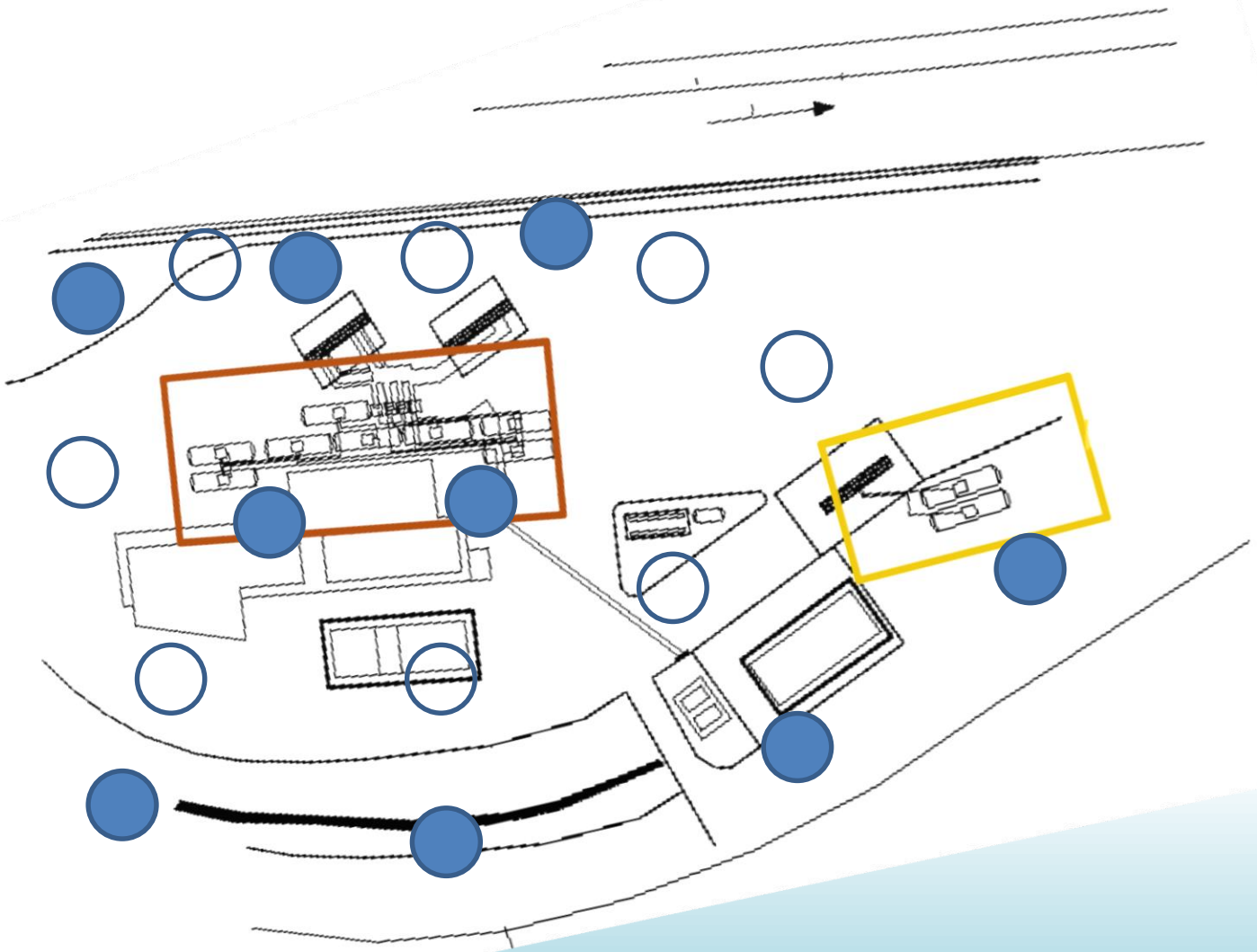
Gas station # 2 (North)



Product + dissolved idrocarbons

Monitoring wells for fingerprinting study



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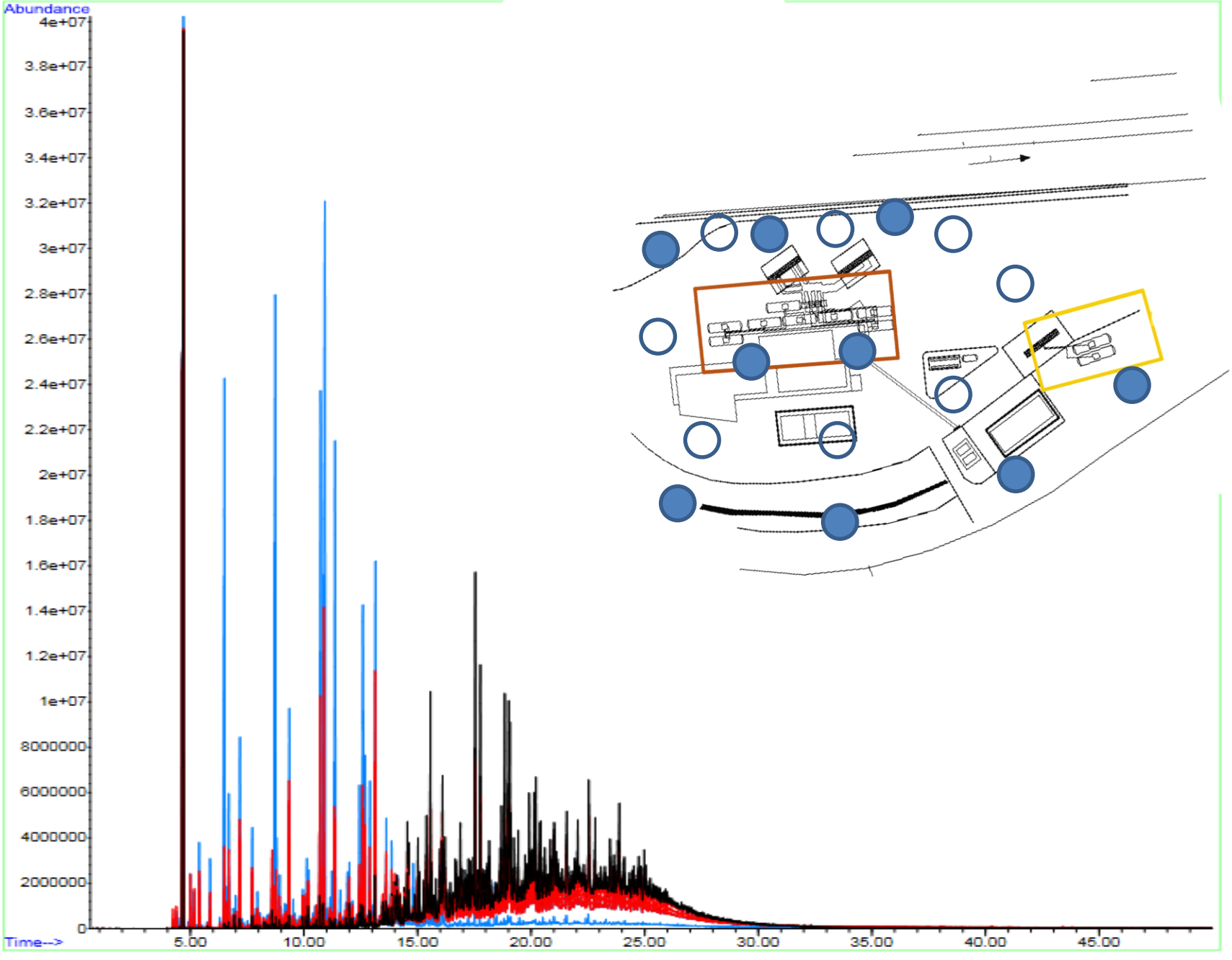
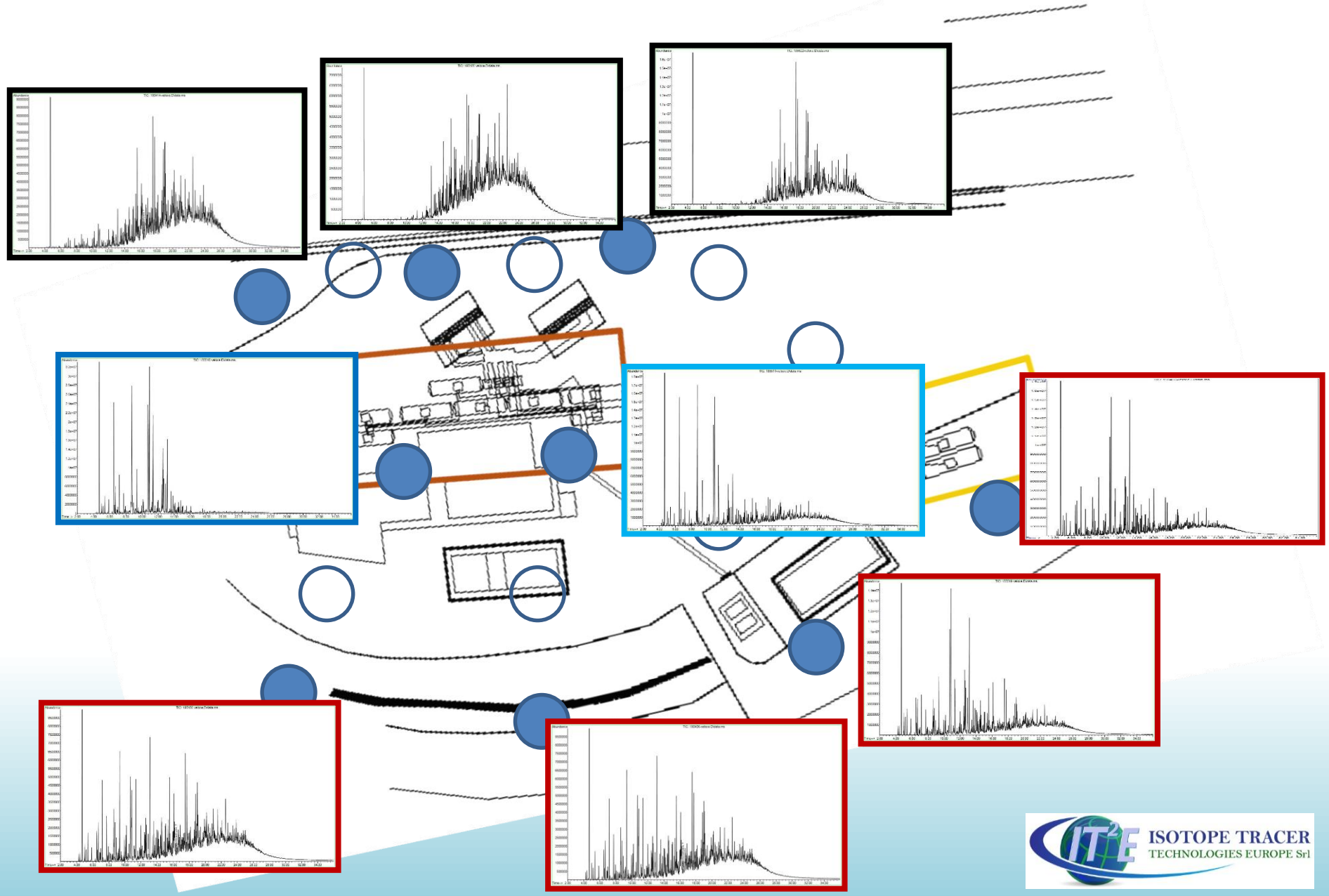

Abundance
4e+07
3.8e+07
3.6e+07
3.4e+07
3.2e+07
3e+07
2.8e+07
2.6e+07
2.4e+07
2.2e+07
2e+07
1.8e+07
1.6e+07
1.4e+07
1.2e+07
1e+07
8000000
6000000
4000000
2000000
0
Time-->
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
45.00

Monitoring wells for fingerprinting study



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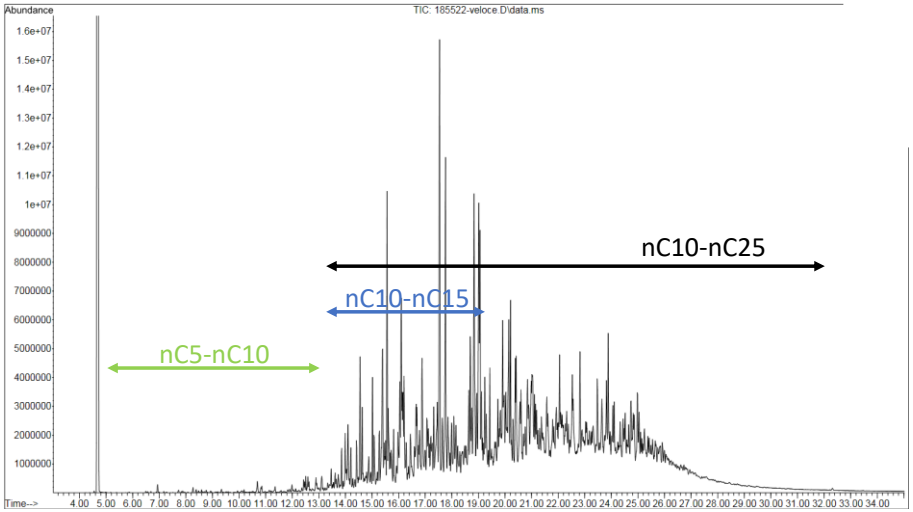
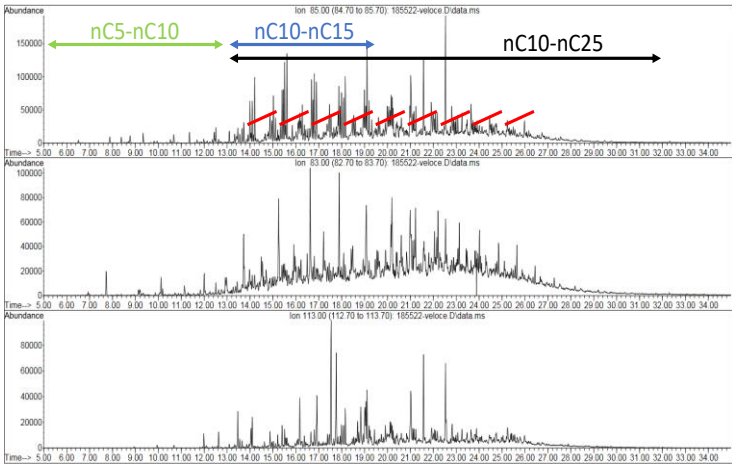
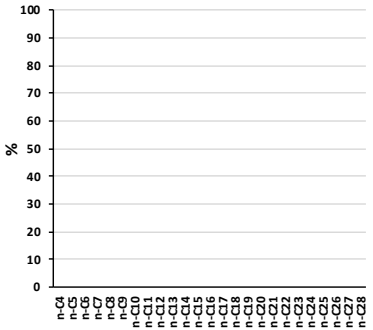
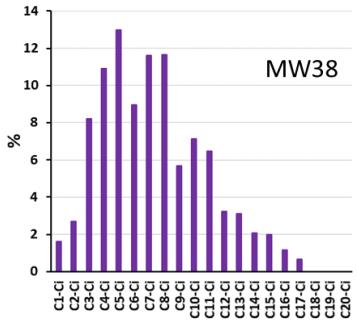
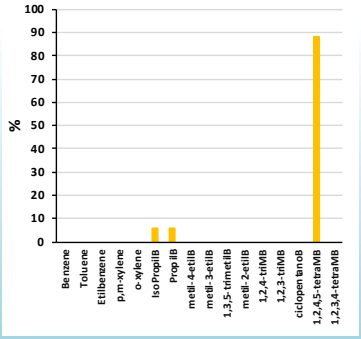
Upgradient Monitoring wells

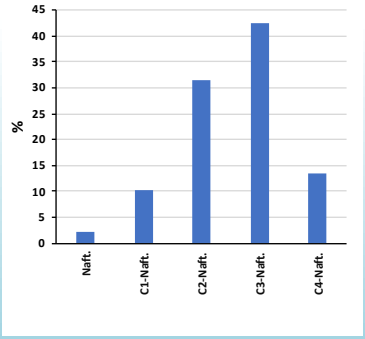












GASOIL profile

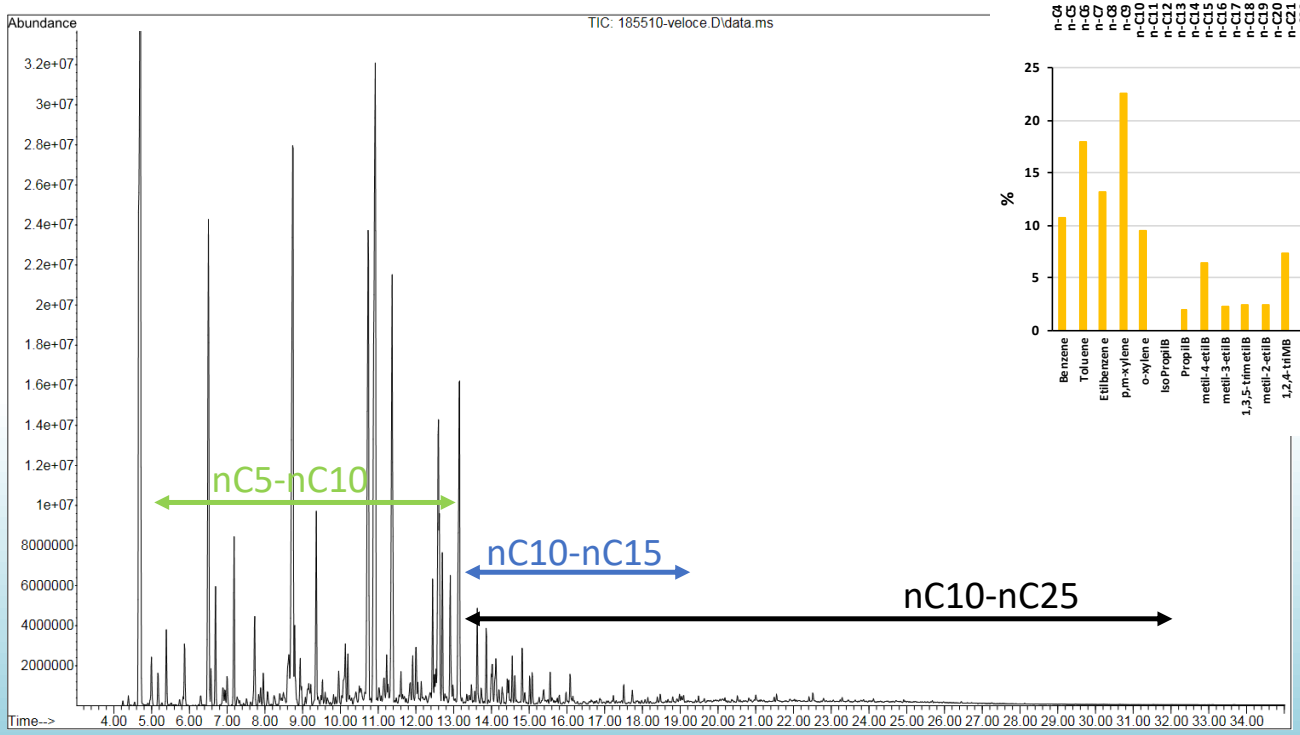
N-alkane not present
BTEX not present
Alchilbenzene highly reduced
Nafthalenes reduced

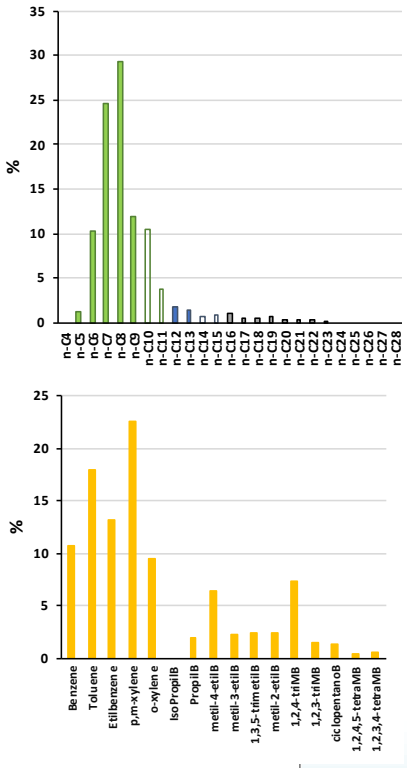
Severly degrada

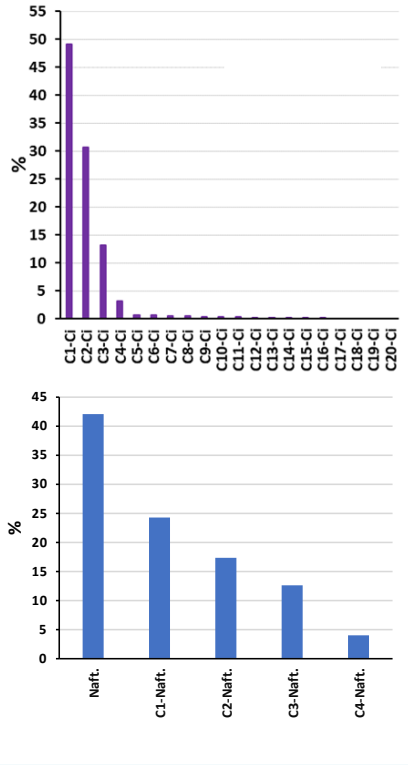
downgradient G.Station tank #1 (gasoline) and #2 (diesel) Monitoring wells

GASOLINE profile
N-alkanall present
BTEX Alchilbenzene high conc.

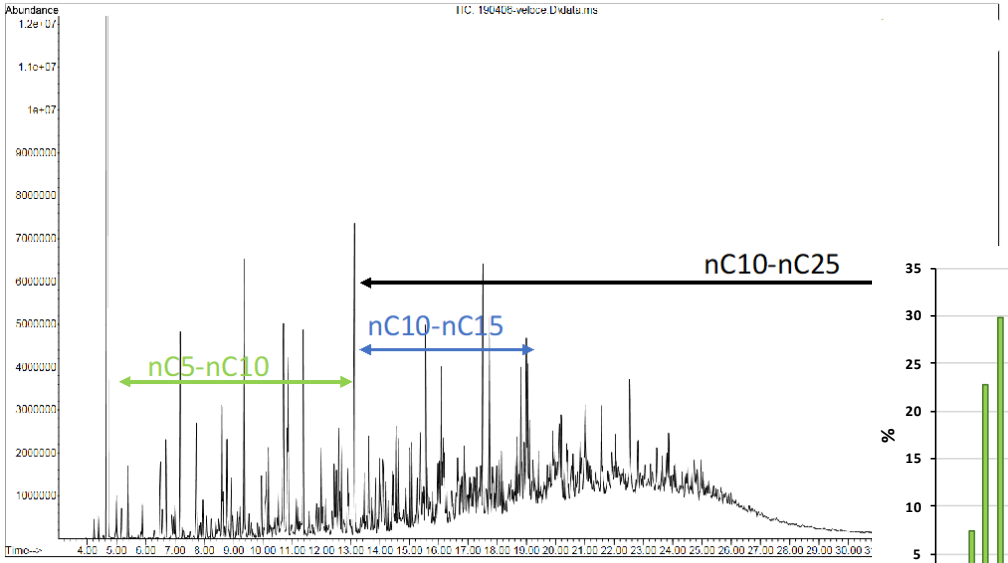
Fresh

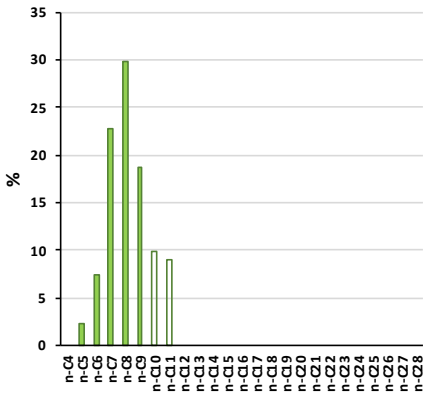


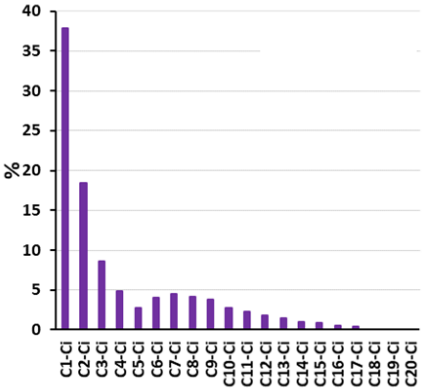




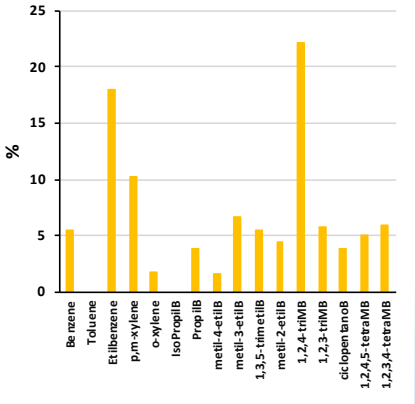
downgradient monitoring wells

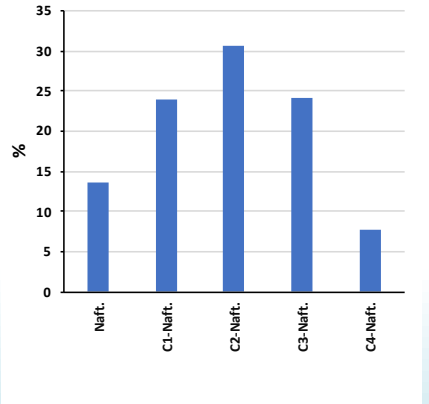




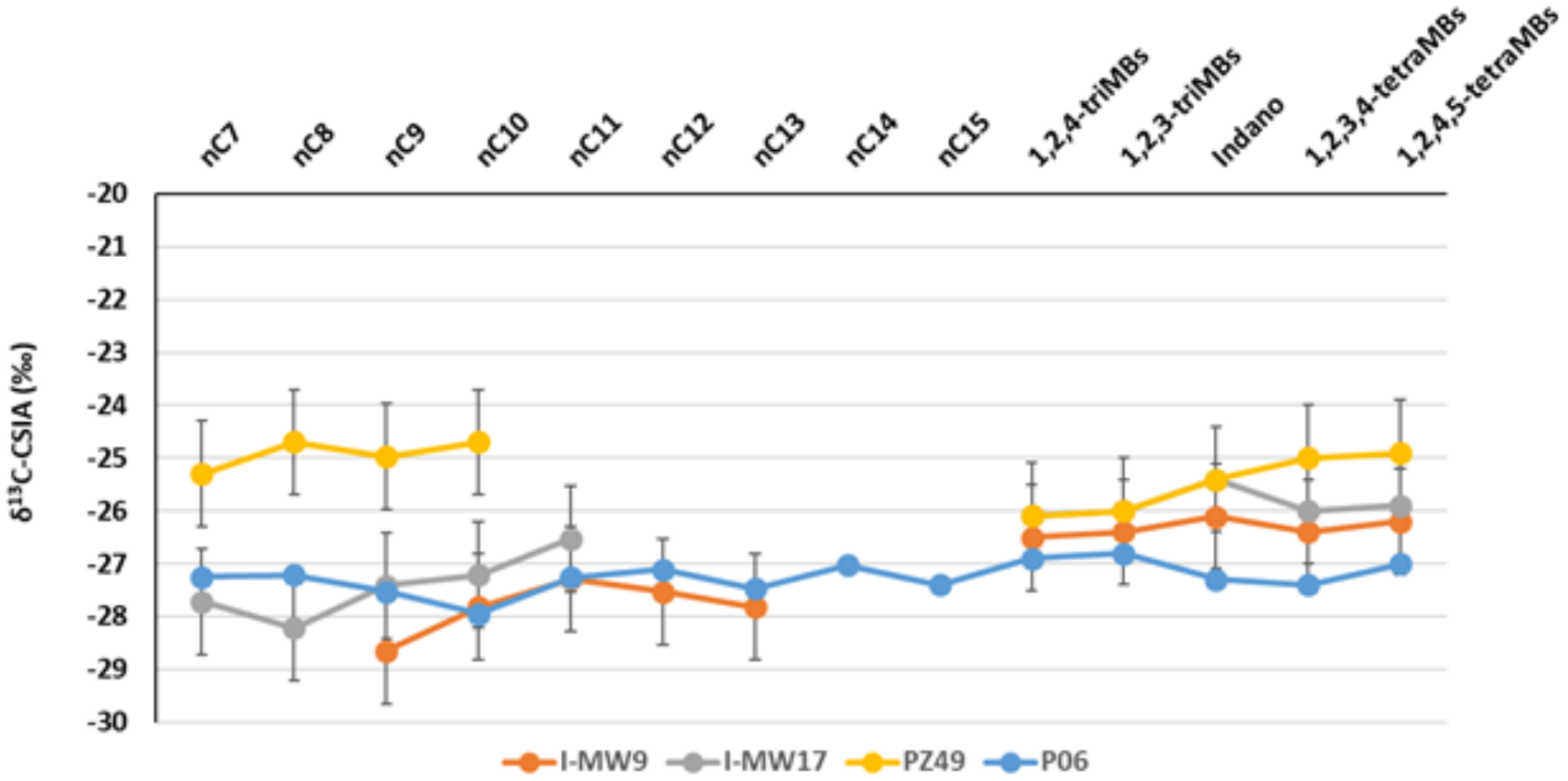


mix profile
N-alkanall present (TRACES)
BTEX Alchilbenzene reduced
Naphathalene gasoil profil dominated





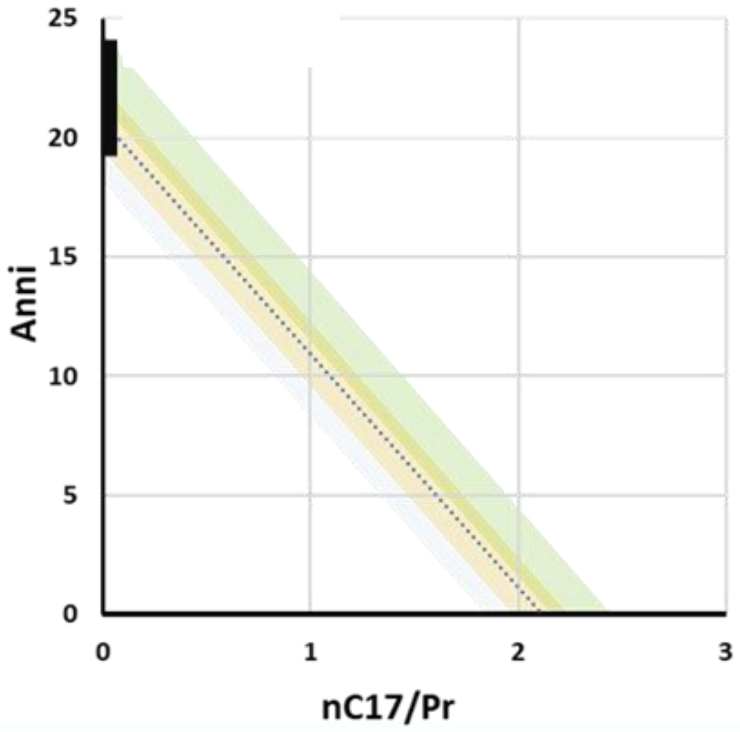
Small traces of fresh gasoline over degraded oil



Do we have other recent contribution rather than the fresh gasoline?

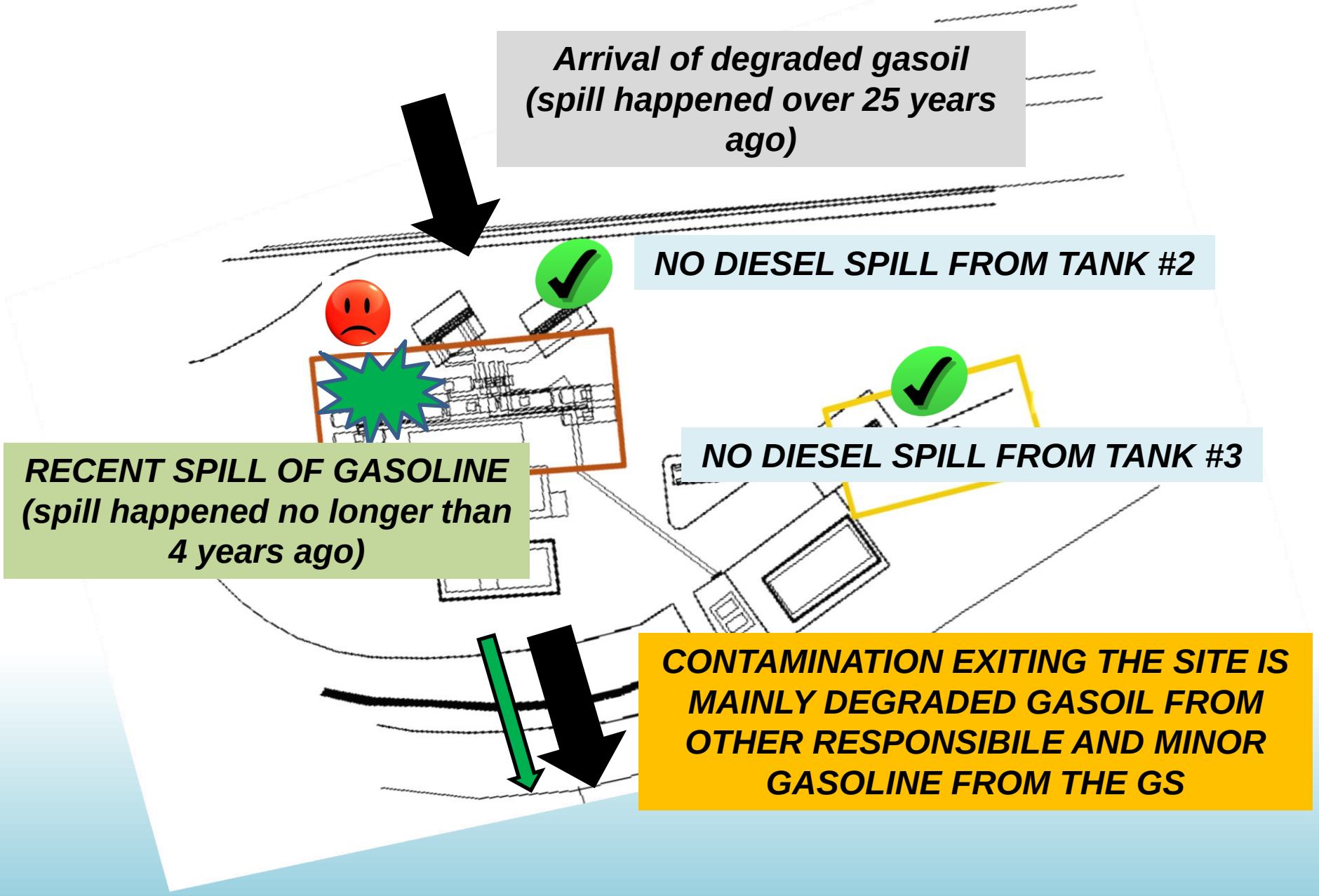
Is the gasoline derived from different sources?

time of the potential releases



Fase di Kaplan	Degradazione		
	Aggressiva	Moderata	Debole
1. *n*-alcani completi	0–2	0–4	0–8
2. *n*-alcani leggeri, benzene e toluene rimossi	2–4	4–8	8–16
3. *n*-alcani medi, etilbenzene e xileni rimossi	4–6	8–12	16–24
4. *n*-alcani rimossi oltre il 50%	6–8	12–16	24–32
5. *n*-alcani rimossi oltre il 90%, alchilbenzeni e alchilcicloesani iniziano a degradarsi	8–10	16–20	32–40
6. *n*-alcani e alchilbenzeni rimossi completamente	10–12	20–24	40–48
7. isoprenoidi rimossi significativamente	>12	>24	>48

CONCEPTUAL MODEL



VALUABLE ADDED VALUE for understanding the conceptual model through compositional and isotopic fingerprinting analysis

Why not running once at the site in order to better (i) plan remedial strategies, (ii) to understand more about te spills occurring within the property and to (iii) find potential external responsabilities

THANKS FOR YOURS ATTENTION

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