

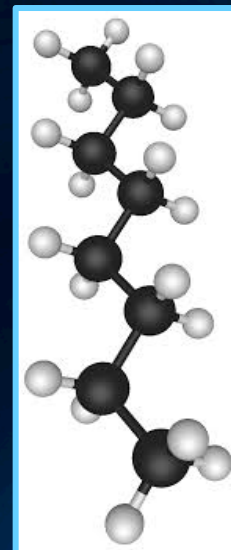
Congrès Intersol 2020 : Gestion des sites pollués et des friches

DETERMINATION OF TOTAL HYDROCARBONS IN
CONTAMINATED SOIL WITH "THIN LAYER SORPTIVE
EXTRACTION COUPLED WITH ATTENUATED TOTAL
REFLECTANCE - FOURIER TRANSFORM INFRARED
SPECTROSCOPY"

LOUATI HOUSSEIN

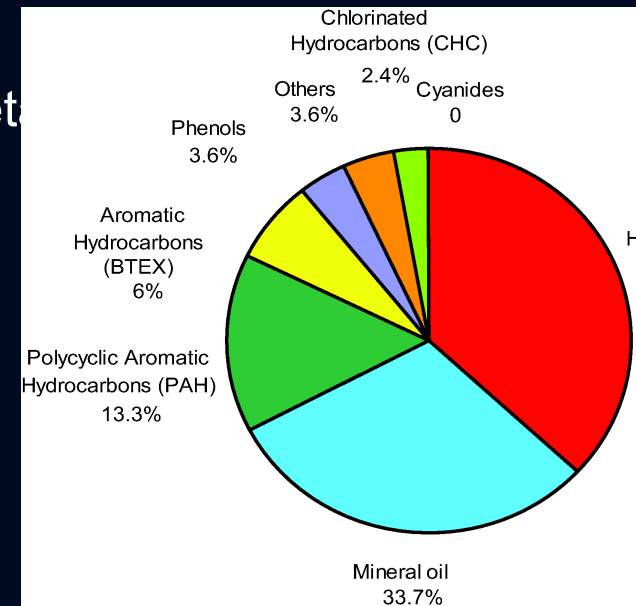
Company : Environnement investigations
Thesis supervisor : LCE- Équipe Trame
Thesis co-supervisor : ICR- équipe Crops

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P. Doumenq
S. Maria



The most frequent contaminants in Europe are mineral oils and heavy metals

According to the European Environment Agency, total hydrocarbons (THC) is one of the main pollutants in European contaminated sites forming **33.7 % of total soil contaminants.**



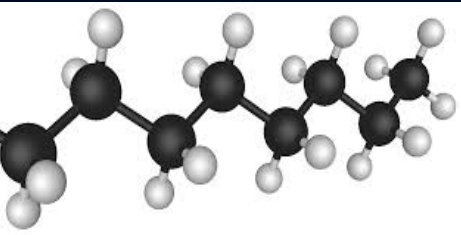
<https://www.eea.europa.eu>

Matrice project → Improving the management of polluted sites and soils and optimizing the diagnostic process,

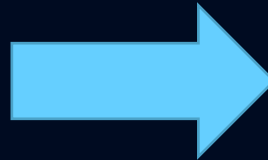


Offering a complete diagnostic chain of measurements and analysis of the most frequently encountered contaminants in the field of polluted sites.

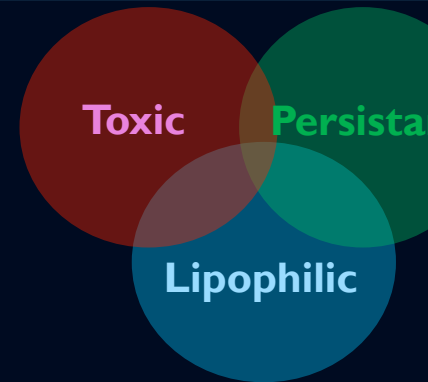
General composition of THC



4 broad fractions



- ✓ Aliphatic saturate hydrocarbons
- ✓ Aromatic hydrocarbons
- ✓ Resins
- ✓ Asphaltene



Major problem for **the environment** and **human health**



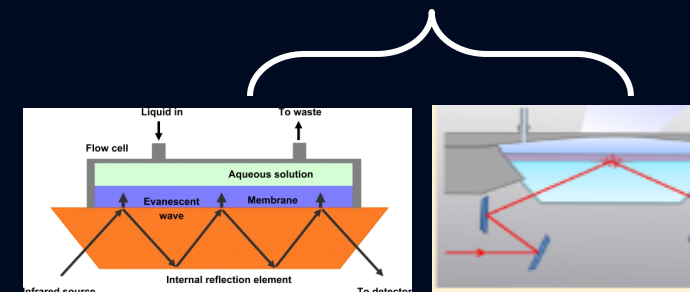
Arrêté du 12 décembre 2014 relating to the conditions for the admission of inert waste to installation

The classic **analytical laboratories** methods are laborious, offsite and long

IR

GC/FID

→ ***In situ alternative method***



Pejcic, B 2012.

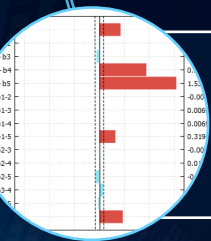
Stach, R 2012.



Subject



Determination of total hydrocarbons (THC): Identification and Quantification

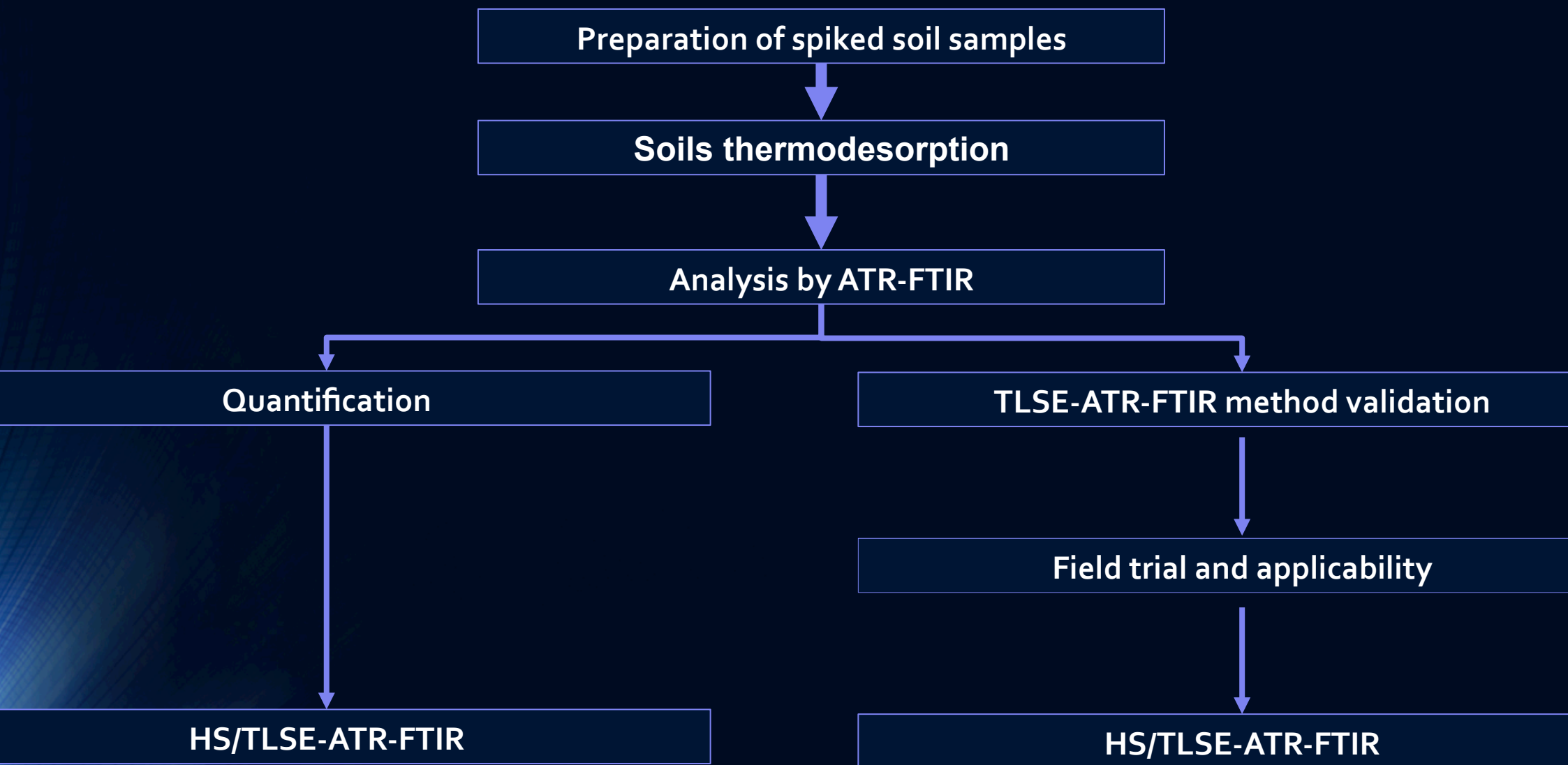


The influence of soil physical and chemicals properties on THC extraction performance and quantification



Validation of the performance of the developed method for the analysis of contaminated soils

MATERIAL AND METHODS



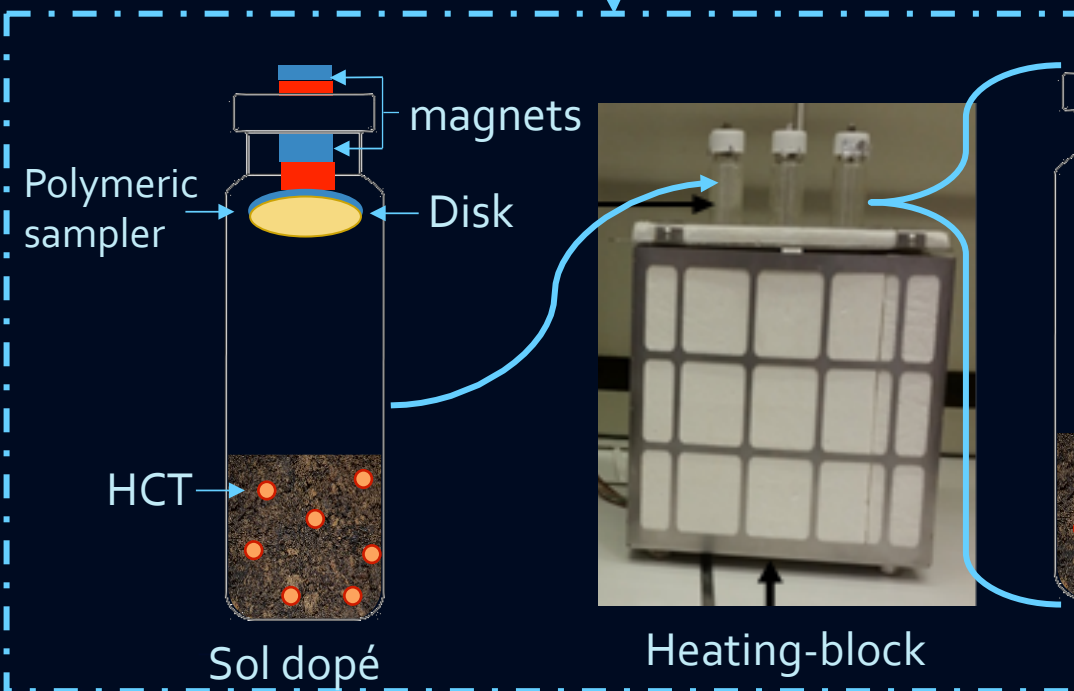
Preparation of spiked soil samples

Soils thermodesorption

Mineral oil and gas oil standards (50/50)

0,820 mg/μl

1 5 g





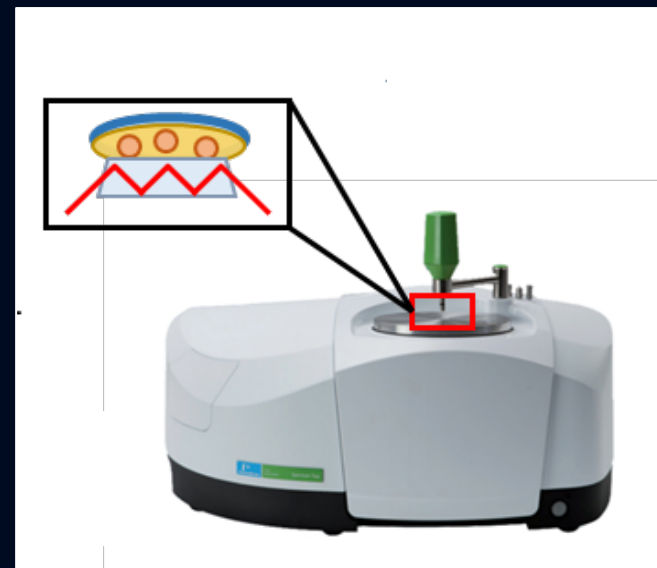
Preparation of spiked soil samples

Soils thermodesorption

Analysis by ATR-FTIR

Quantification

HS/TLSE-ATR-FTIR



Detector : DTGS

Resolution : 4 cm^{-1}

Acquisition range: 4000
 4000 cm^{-1}

interferogram
accumulations : 32 sca

Penetration depth $\approx 1\mu\text{m}$

Preparation of spiked soil samples

Soils thermodesorption

Analysis by ATR-FTIR

TLSE-ATR-FTIR method validation

Field trial and applicability

HS/TLSE-ATR-FTIR



Determination of influencing factors by experimental design

Factor	Code factor	Level -	Level +
TOC (%)	X ₁	<0.5	>2
Humidity (%)	X ₂	1	30
Na ₂ SO ₄	X ₃	Low	High
Concentration (ppm)	X ₅	400	3000
Type of soil	X ₄	Sand	Clay

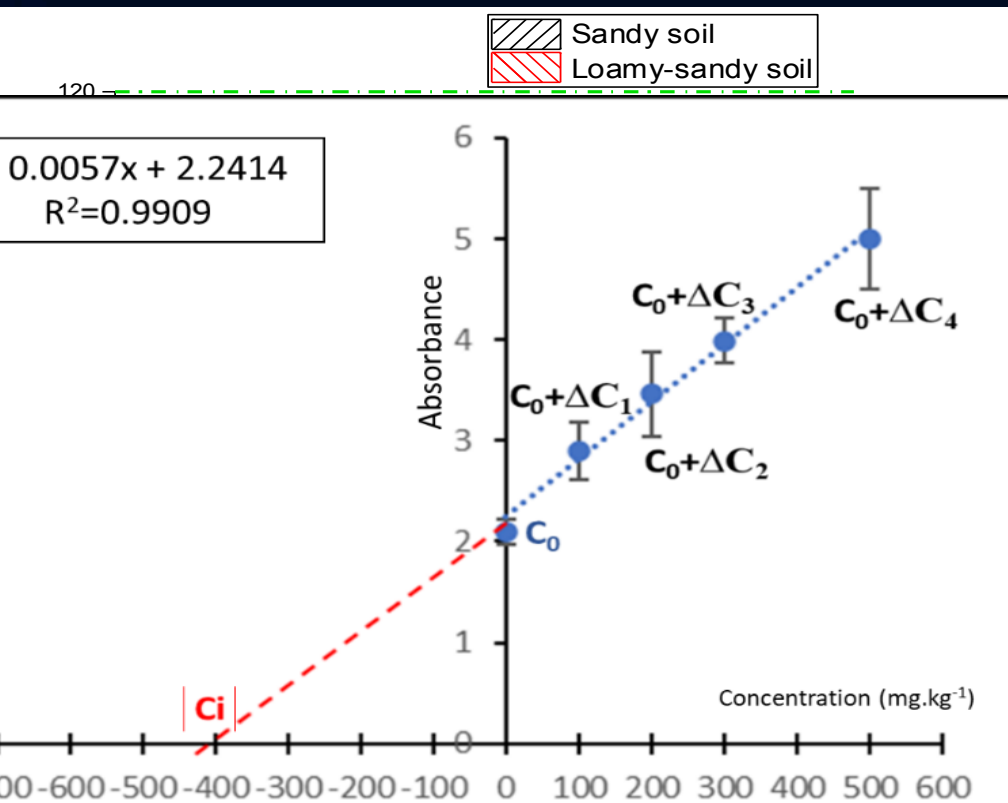
Additional
matrix

EXPERIMENTATION PLAN

Experience	COT	Humidity	Na ₂ SO ₄	Concentration	Soils
1	<0.5	1	Low	400	Sand
2	>2	1	Low	400	Clay
3	<0.5	30	Low	400	Sand
4	>2	30	Low	400	Clay
5	<0.5	1	High	400	Sand
6	>2	1	High	400	Clay
7	<0.5	30	High	400	Sand
8	>2	30	High	400	Clay
9	<0.5	1	Low	3000	Sand
10	>2	1	Low	3000	Clay
11	<0.5	30	Low	3000	Sand
12	>2	30	Low	3000	Clay
13	<0.5	1	High	3000	Sand
14	>2	1	High	3000	Clay
15	<0.5	30	High	3000	Sand
16	>2	30	High	3000	Clay

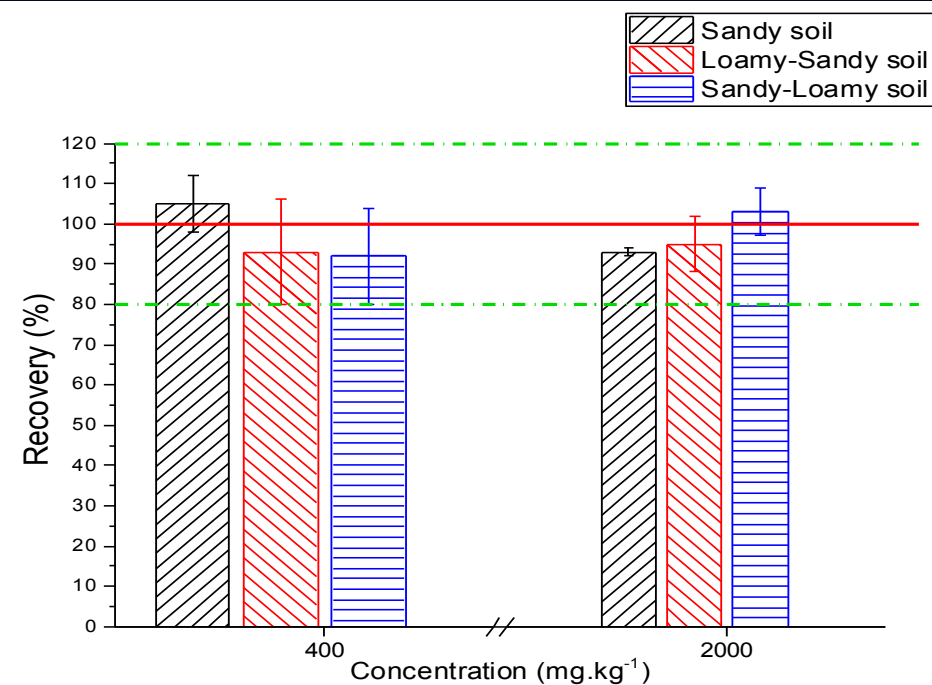
RESULTS AND DISCUSSION

External calibration



! Matrix effects + Recovery values < 70 %

Standard addition



! Avoid the matrix effects + Recovery values 90-110 %

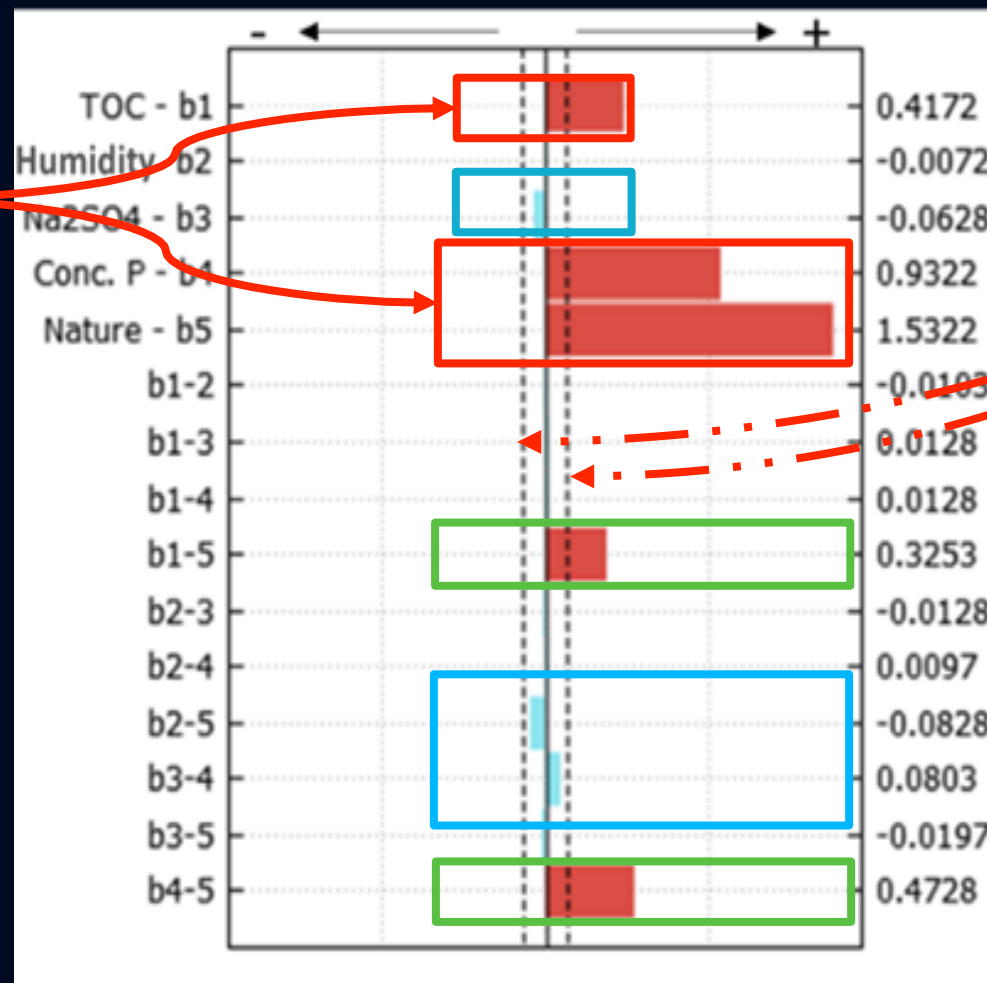
Influence of soil parameters on extraction efficiency

Factors influencing the experimental response

Level - → Level +

Response ↗

Interaction effects → Significant influence



Significative limits

Interaction effects → No Significant influence

→ Low significative limits, good repeatability (CV < 10%)

Graphical study of the effects of factors influencing the extraction of THC in soils

SE-ATR-FTIR Method validation



Linearity : Correlation coefficient values R^2 and R^2_{adj} higher than 0.99



Accuracy : the results were in good agreement with the expected concentration ($< 10\%$)



Precision : % RSD values are lower than 15 % both for repeatability and intermediate precision .



Limit of quantification : $LOQ = 300 \text{ mg.kg}^{-1}$

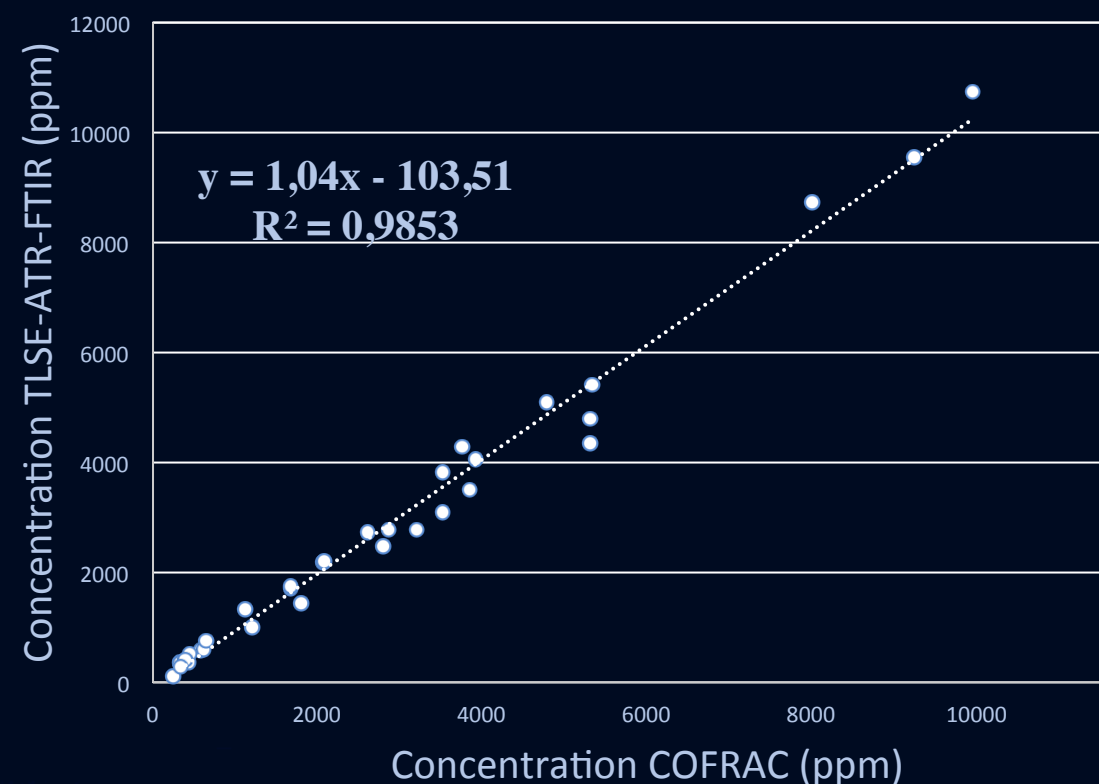


This LOQ meets regulatory requirements of 500 mg.kg^{-1}

TLSE-ATR-FTIR IMPLEMENTATION TO FIELD CONTAMINATED SOILS

- After the validation of the TLSE-ATR-FTIR, 35 different soils sampled from different regions in France were analysed
- These real soil samples had relatively distinct composition and physicochemical properties

Sample Name	Ajouts en μ l	3	4	5
	Conc added ppm	+501	+668	+835
1 ^{er} gare centre	Initial measured			
1 ^{er} replicat	5,05	5,5	6,020	6,29
2 ^{em} replicat	5,19	5,9	5,85	5,97
3 ^{em} replicat	5,20	5,7	6,1	6,13
Mean	5,12	5,70	5,94	6,13
Standard deviation	0,10	0,28	0,12	0,23
RSD %	1,93	4,96	2,03	3,69
Ci estimated		4422	4196	4232
Mean Ci	4284			
Standard deviation	121			
concentration ppm	4800			
Accuracy	14,24			



TLSE-ATR-FTIR implementation to field contaminated soils

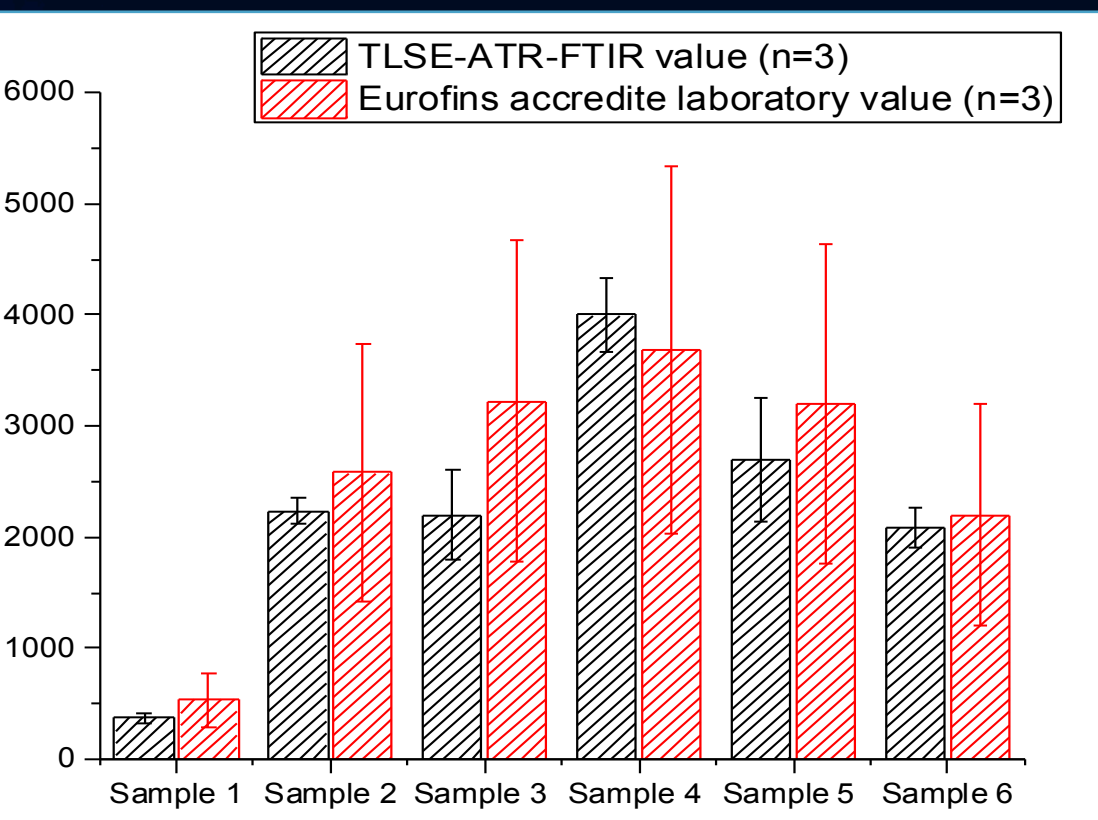
	COFRAC Value	TLSE ATR-FTIR Value	Accuracy (%)	Humidity (%)	Texture	TOC (%)
on 1	584	582±53	0,34	10	Sandy	3,27
	1670±660	1715±84	2,66	11	Sandy-clay	1,41
2	609±248	604±40	0,82	5	Sandy	1,08
	3850±1544	3509±230	9,27	16	Sandy	1,85
1	1800±720	600±134	70	9	Clay	0,99
	380±152	372±33	2,13	2	Sandy-loamy	0,16
,8m	9240±3696	3552±1754	80.23	11	Clay	6,2
5m	4780±1912	5097±168	6,42	6	Sandy	3,9
6m	5330±2132	5409±604	1,47	3	Sandy-loamy	3,7
n	5310±2114	4349±154	10,34	3	Sandy-loamy	3,5
II	5310±2114	4788±289	19,90	3	Loamy-clay	3,5
3m	2610±1044	2733±289	4,60	12	Loamy-clay	6
5m	9950±3980	10750±1059	7,73	21	Sandy-loamy	3,8
ra	24000±9600	24755±1741	3,10	11	Sandy	1,38
4m	1120±407	1328±57	16,99	3	Sandy-loamy	3,6

✓ The organic carbon content vary from 0.6 à 7%.

✓ Humidity in soil vary from 2% à 21%.

This method presents good recoveries for sandy and loamy soils but not for clay soils

SITU APPLICATION OF TLSE-ATR-FTIR



Quantification of THC: 35 samples from 3 main on-site remediation works

→ The results are in very good match with those supplied by the accredited laboratory

Analysis of hydrocarbons directly on site in real-world conditions

QuEChERS method (quick, easy, cheap, effective, rugged, and safe)

→ Used for long term to monitor the remediation process of soil by engineering and design departments.

Problems: Good recoveries for different types of soil except clay soils



Solid-Liquide extraction for clay soil

THANK YOU FOR
YOUR ATTENTION