Parma 29/03/2019

Activity A.T1.5

Trainings for capacity building & improving technical skills

PoliMI, Dr. Massimo Marchesi

Interreg CENTRAL EUROPE AMIIGA

European Union European Regional Development Fund

12 partners from central Europe within 7 countries:

ITALY : (Parma and Milano, RL & PoliMi

GERMANY

POLAND

CROATIA

SLOVENIA

CECK REPUPBLI

https://www.interreg-central.eu/Content.Node/AMIIGA.html

AMIIGA is a project pulling together 12 partners from central Europe all with an interest in improving the quality of groundwater, especially of former industrial brownfield sites, by treating urban cores and their surroundings as one unit.

AMIIGA - MILANO

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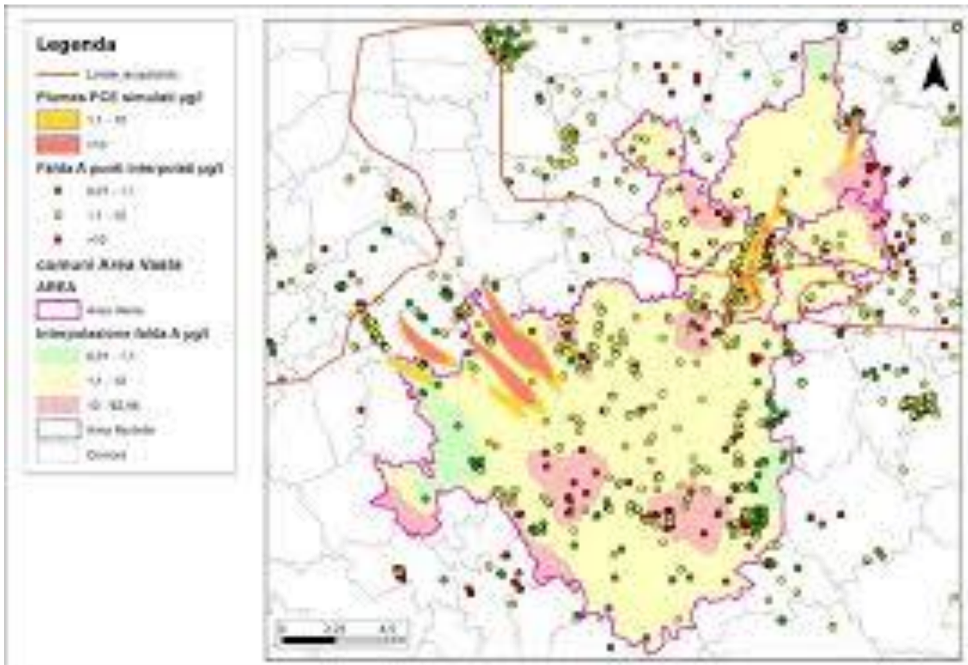
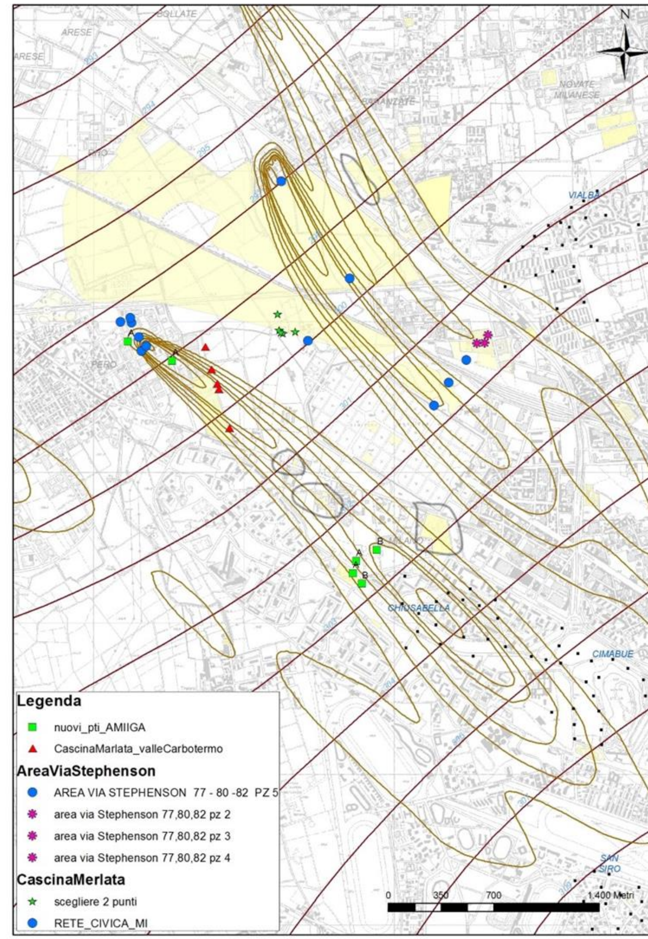
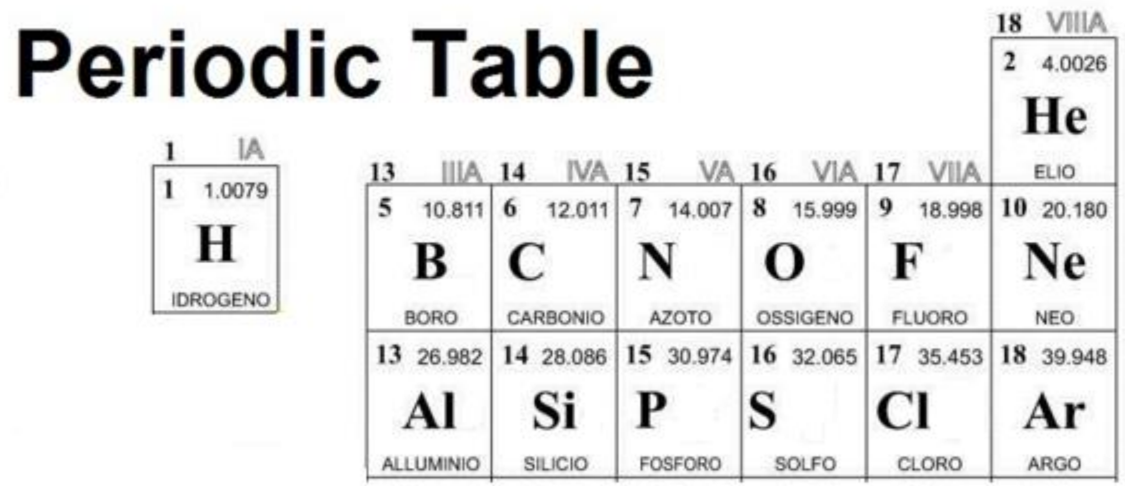
AMIIGA
European Union European Regional Development Fund

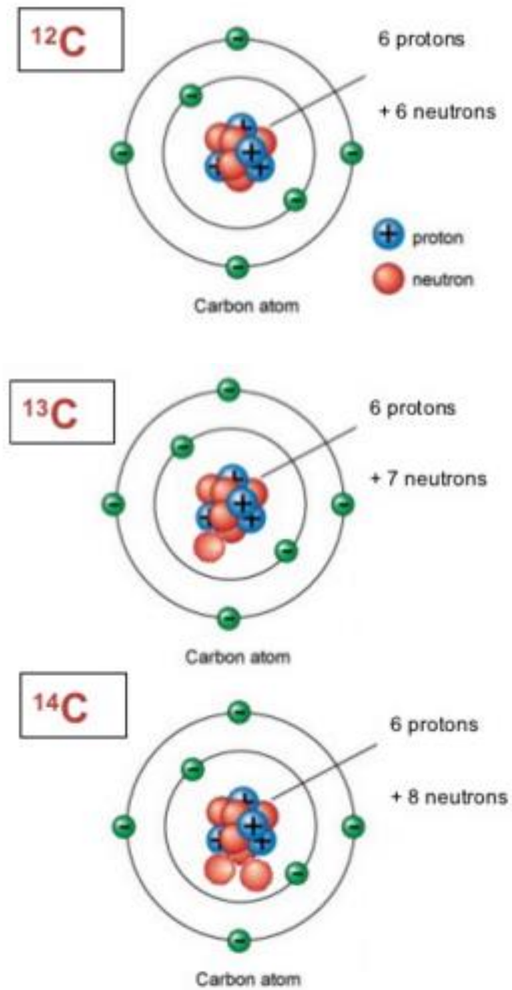




Miglior caratterizzazione e distizione inquinamento diffuso vs. plumes e attribuzione di relative responsabilità: come lo strumento CSIA può aiutare

COSA SONO GLI ISOTOPI?

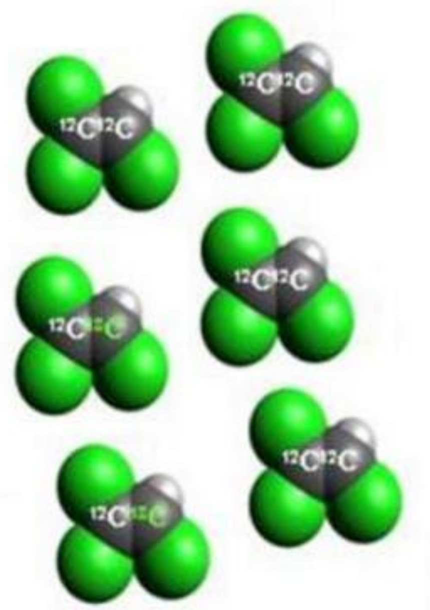


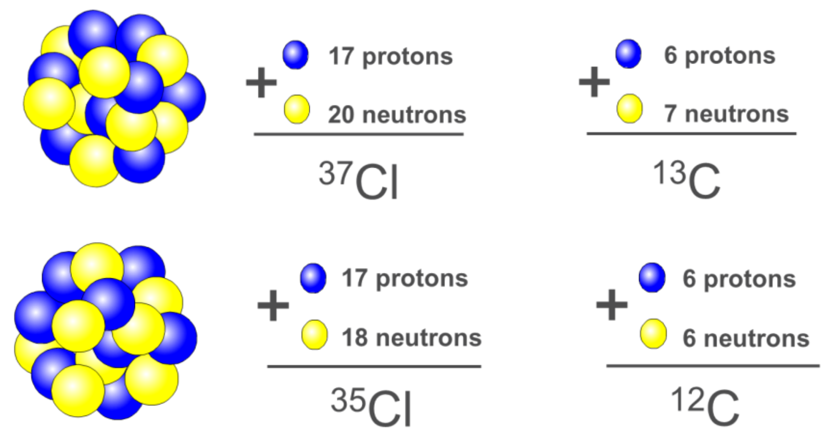


Un isotopo (dal greco ἴσος (isos) τόπος (topos) che significa **"stesso posto"**) è un atomo di uno stesso elemento chimico, e quindi con lo **stesso numero atomico** Z, ma con differente numero di massa A, e quindi **differente massa atomica** M. La differenza dei numeri di massa è dovuta ad un diverso numero di neutroni presenti nel nucleo dell'atomo a parità di numero atomico.

ISOTOPI STABILI E RADIOATTIVI

								Al 26.9814			Al 23 0.47s	Al 24 2.07s	Al 25 7.23s	Al 26 7.3E5y	Al 27 100%	Al 28 2.24m	Al 29 6.5m	Al 30 3.6s	Al 31 0.64s
								Mg 24.305	Mg 20 0.6s	Mg 21 122ms	Mg 22 3.86s	Mg 23 11.3s	Mg 24 78.99%	Mg 25 10.00%	Mg 26 11.01%	Mg 27 9.45m	Mg 28 21.0h	Mg 29 1.4s	Mg 30 ~1.2s
							Na 22.98977		Na 19 30ms?	Na 20 446ms	Na 21 22.5s	Na 22 2.601y	Na 23 100 %	Na 24 15.02h	Na 25 60s	Na 26 1.07s	Na 27 0.29s	Na 28 30.5ms	Na 29 43ms
							Ne 20.179	Ne 17 109ms	Ne 18 1.67s	Ne 19 17.2s	Ne 20 90.51%	Ne 21 0.27%	Ne 22 9.22%	Ne 23 37.5s	Ne 24 3.38m	Ne 25 0.61s			
					F 18.998403			F 16 ~1E-20s proton	F 17 64.5s	F 18 109.8m	F 19 100%	F 20 11.0s	F 21 4.33s	F 22 4.23s	F 23 2.2s				
					O 15.9994	O 13 8.9ms	O 14 70.5s	O 15 122ms	O 16 99.758%	O 17 0.038%	O 18 0.204%	O 19 26.8s	O 20 13.5s						
			N 14.0067			N 12 11.0ms	N 13 9.97m	N 14 99.63%	N 15 0.37%	N 16 7.10s	N 17 4.17s	N 18 0.63s	N 19 0.42s						
			C 12.011	C 9 127ms	C 10 19.3s	C 11 20.3m	C 12 98.89%	C 13 1.11%	C 14 5730y	C 15 2.45s	C 16 0.75s								
	B 10.81			B 8 770ms	B 9 ~8E-19s proton	B 10 20%	B 11 80%	B 12 20.4ms	B 13 17.3ms	B 14 16ms									
	Be 9.01218		Be 6 ~5E-21s proton	Be 7 53.28d	Be 8 ~1E-16s alpha	Be 9 100%	Be 10 1.6E6y	Be 11 13.8s	Be 12 ~11.4ms										
Li 6.941			Li 5 ~1E-21s proton	Li 6 7.5%	Li 7 92.5%	Li 8 844ms	Li 9 177ms												
He 4.00260		He 3 0.00014%	He 4 99.99986%	He 5 ~8E-22s neutron	He 6 805ms		He 8 122ms												
H 1.0079	H 1 99.985%	H 2 0.015%	H 3 12.33y																
		n 1 10.4m																	

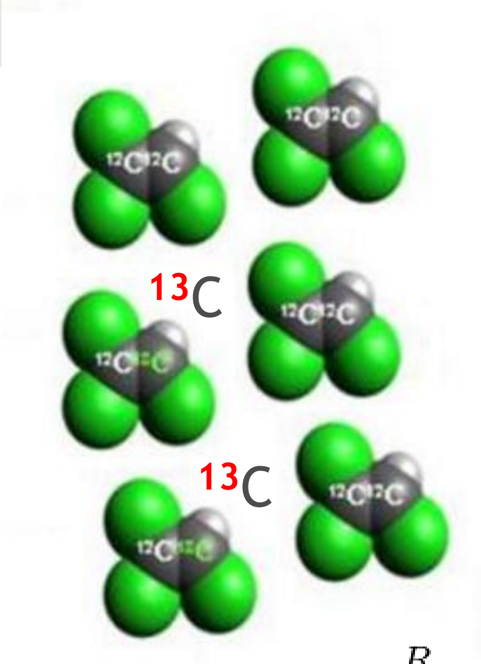


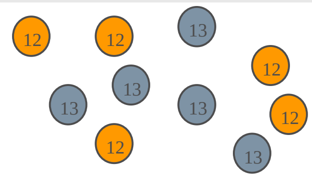


circa un atomo ogni 4 (25%)

circa un atomo ogni 100 (1%)

RAPPORTO ISOTOPICO, δ (‰)





TCE

Molecules with light isotope

Molecules with heavy isotope

rapporto isotopico (assoluto)

$^{13}C/^{12}C$

$^{2}H/^{1}H$

$^{37}Cl/^{35}Cl$

^{12}C 98.89 ^{13}C 1.11%

(0,01122)

^{1}H 98.985 ^{2}H 0.015%

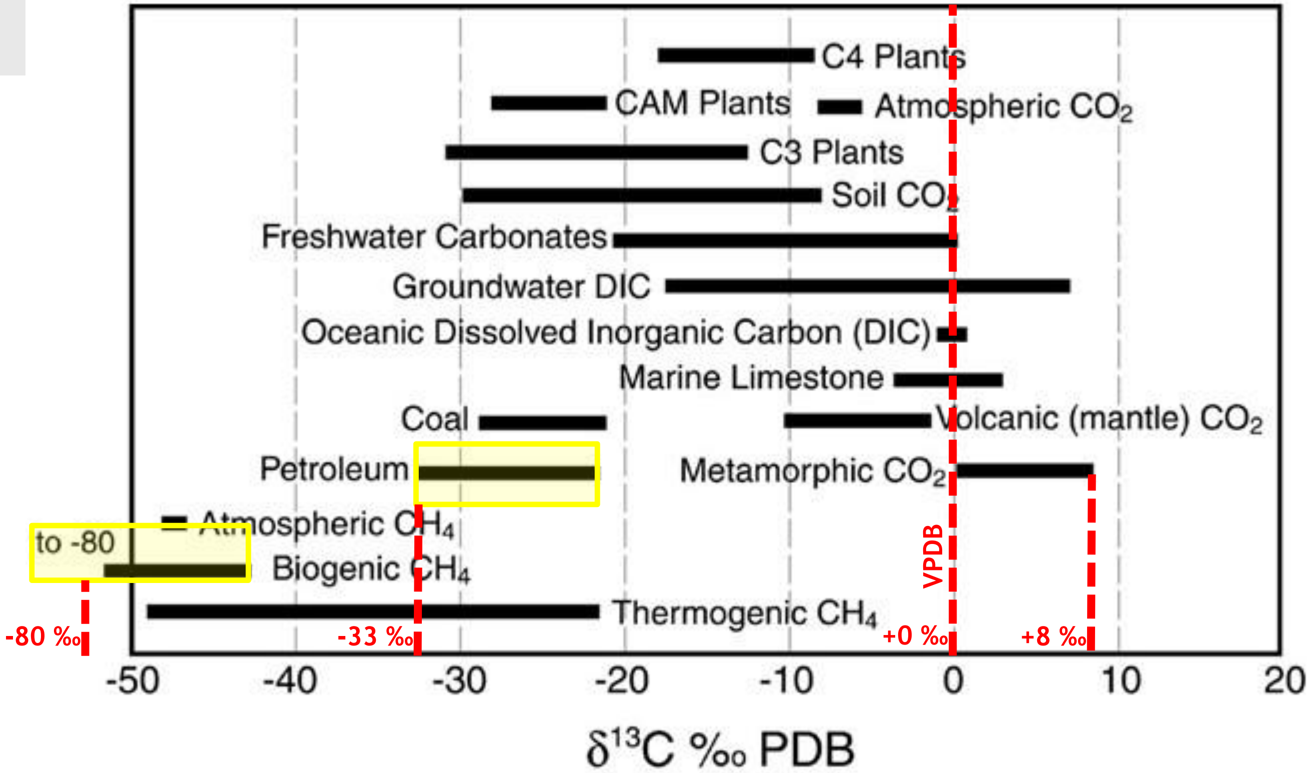
(0,0001515)

rapporto isotopico (relativo ad uno standard)

$$\delta = \frac{R_{campione} - R_{standard}}{R_{standard}} \times 1000$$

$$\delta^{13}C(‰) = \left[\frac{(^{13}C/^{12}C)_{sample} - (^{13}C/^{12}C)_{standard}}{(^{13}C/^{12}C)_{standard}}\right] \times 1000$$

Element	Relative ab. (%)	Standard	Abbreviat.	Abund. ratio
Hydrogen	^{1}H 99.985 ^{2}H 0.015	Vienna standard Mean Ocean water	VSMOW	1.5575×10^{-4}
Carbon	^{12}C 98.89 ^{13}C 1.11%	Carbonate from Vienna Pee Dee Belemnite	VPDB	0.011237
Chlorine	^{35}Cl 75.8 ^{37}Cl 24.2	Chloride ion in ocean water Standard Mean Ocean Chloride	SMOC	0.324



rapporto isotopico (relativo)

$$\delta = \frac{R_{\text{campione}} - R_{\text{standard}}}{R_{\text{standard}}} \times 1000$$

Arricchimento ↑ / *impoverimento* ↓

δ = +8 ‰

δ = +0 ‰

δ = -33 ‰

δ = -80 ‰

rapporto isotopico (assoluto)

$^{13}C/^{12}C$

R = 0.011327

R = 0.011237

R = 0.010867

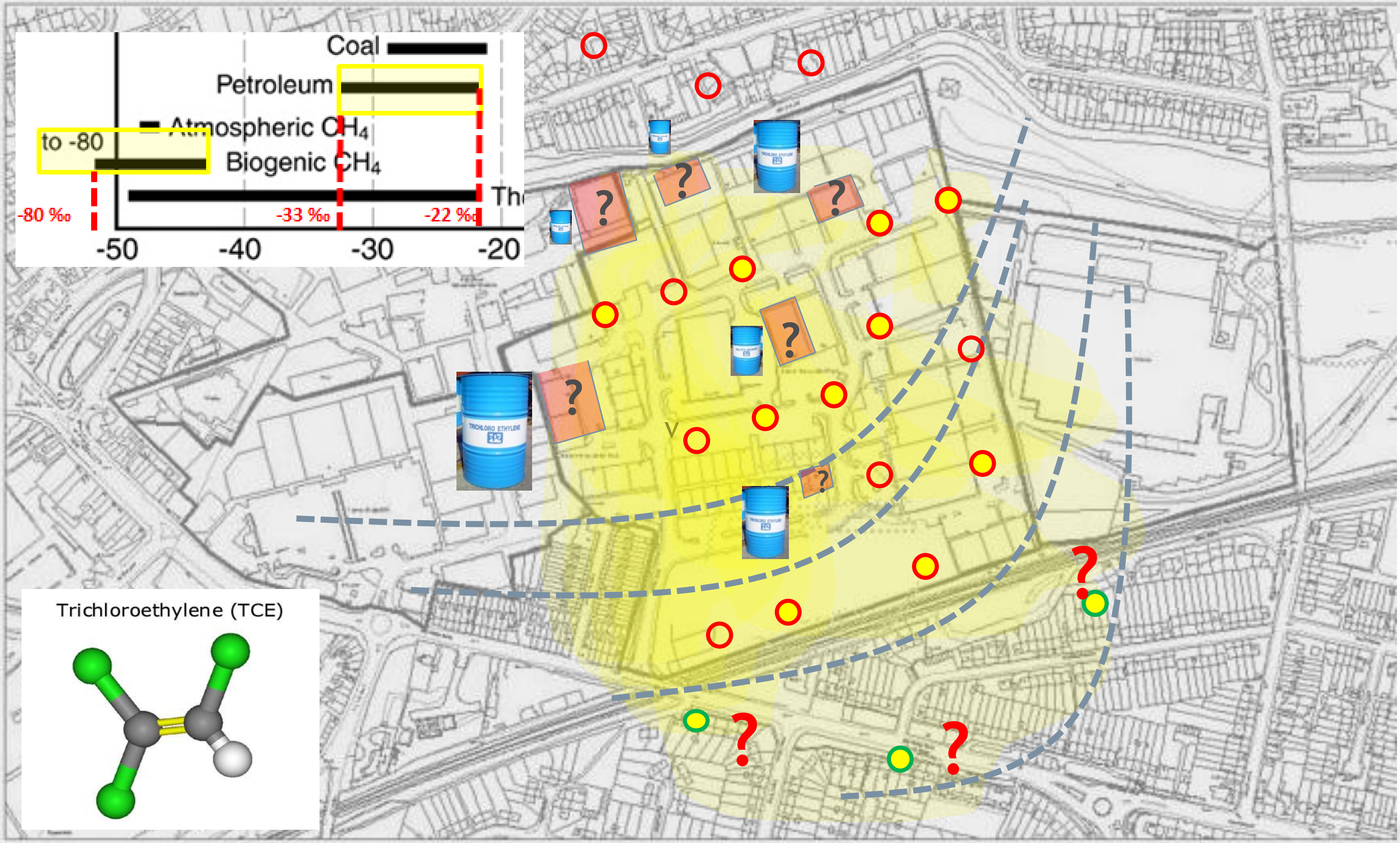
R = 0.010338

Abbondanza isotopico (relativo)

Arricchimento ↑ / *impoverimento* ↓

^{13}C (%)	^{12}C (%)
1,12	98,88
1,11	98,89
1,07	98,93
1,02	98,98

APPLICAZIONI: FINGERPRINTING



Differenze nella δ^{13}C di potenziali fonti?

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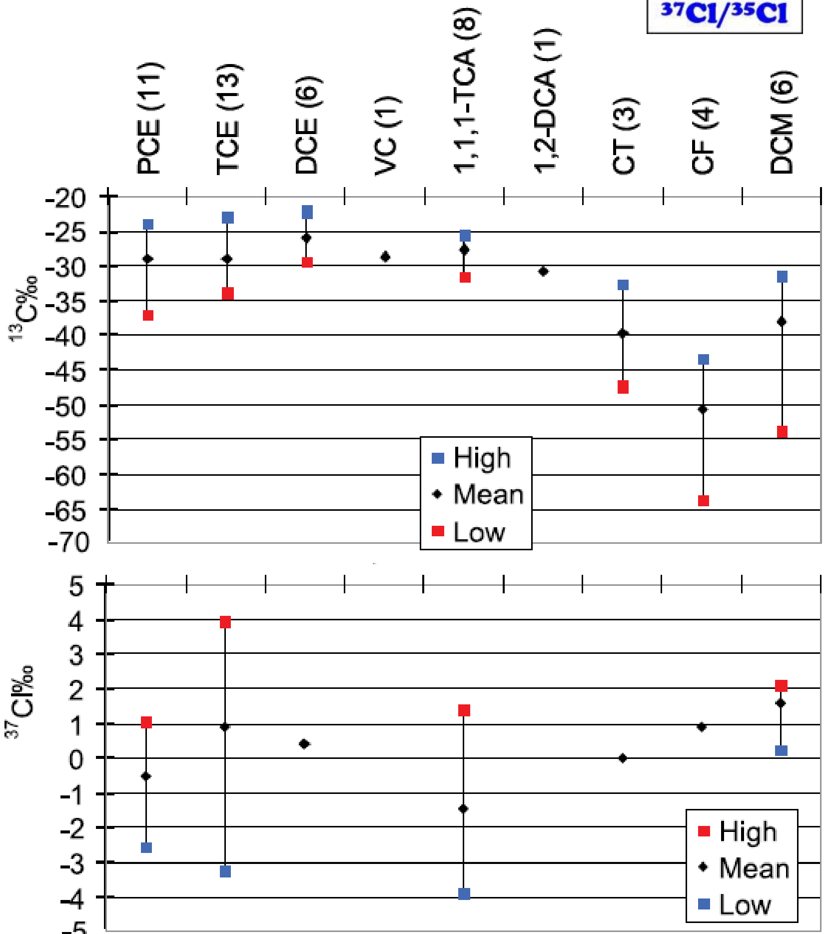
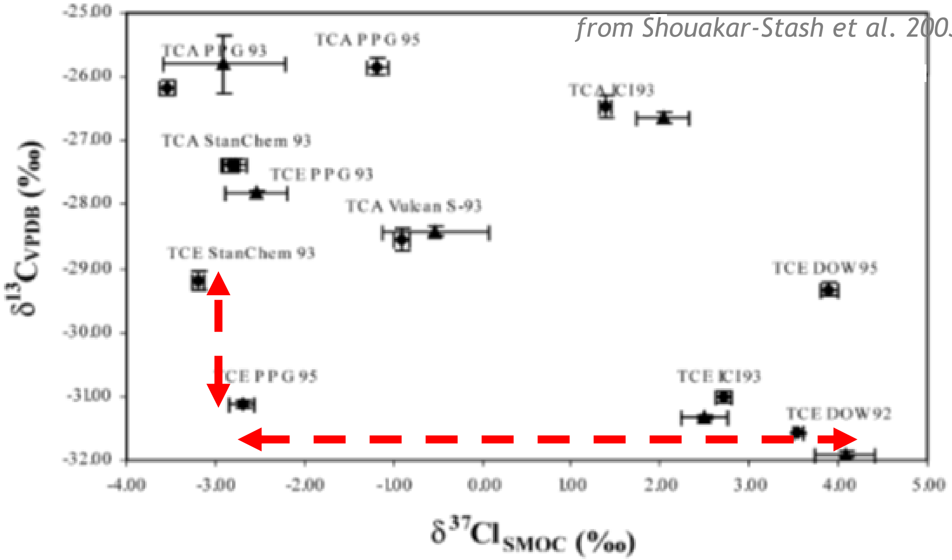
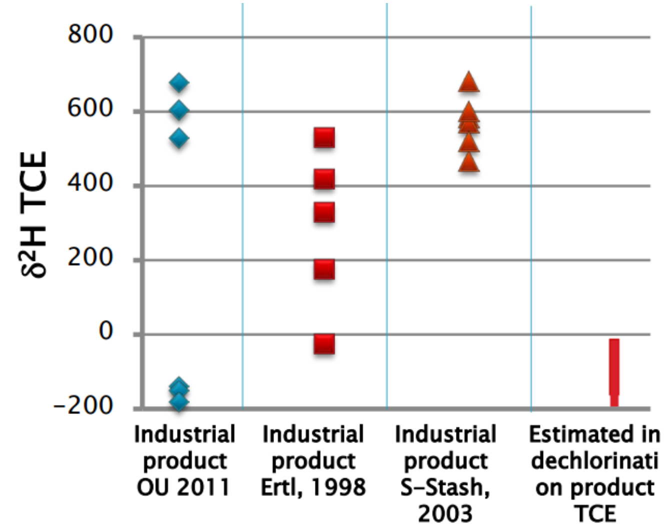
$^{13}C/^{12}C$
$^{2}H/^{1}H$
$^{37}Cl/^{35}Cl$



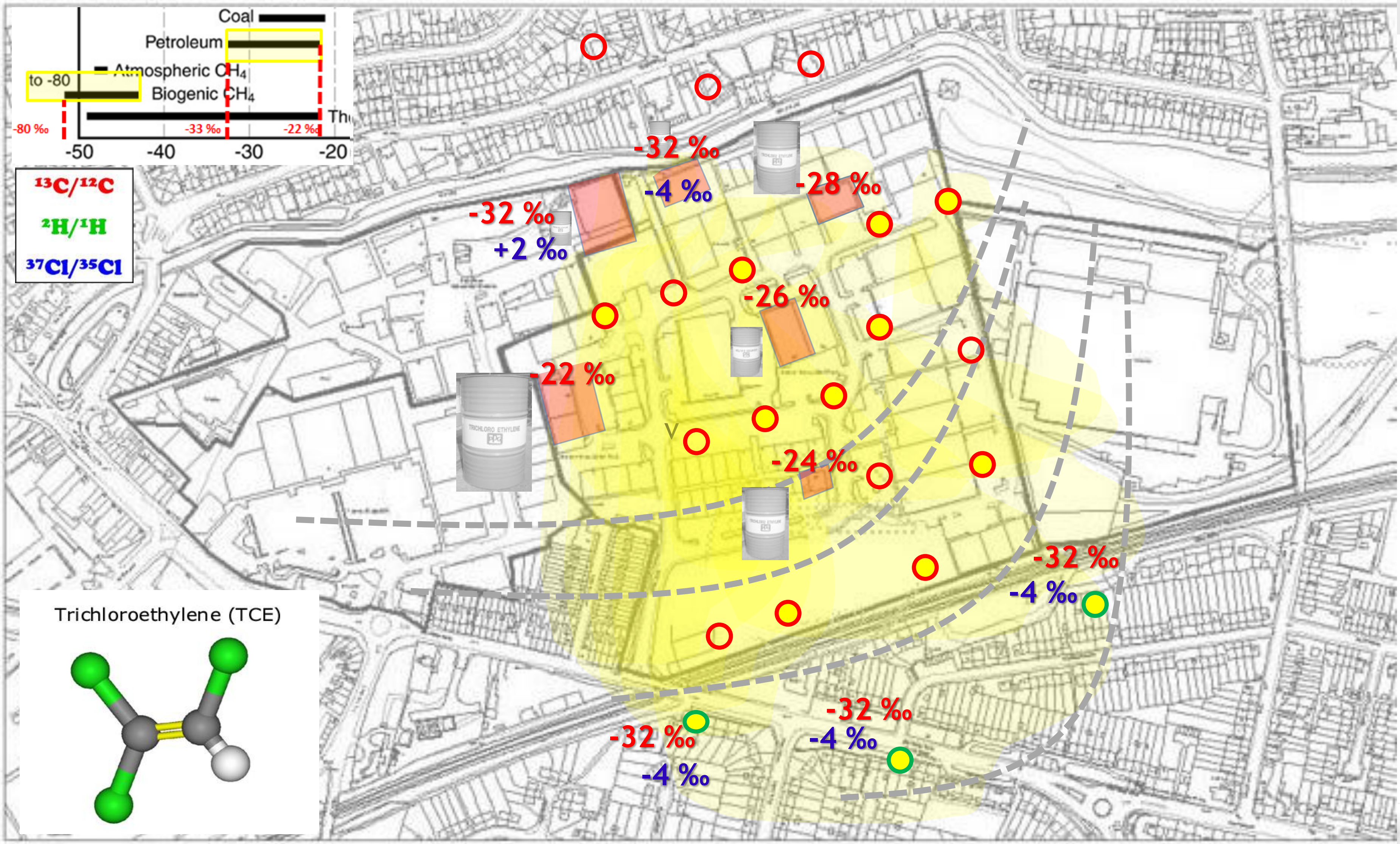
Modified from EPA, 2008



from Shouakar-Stash et al. 2003

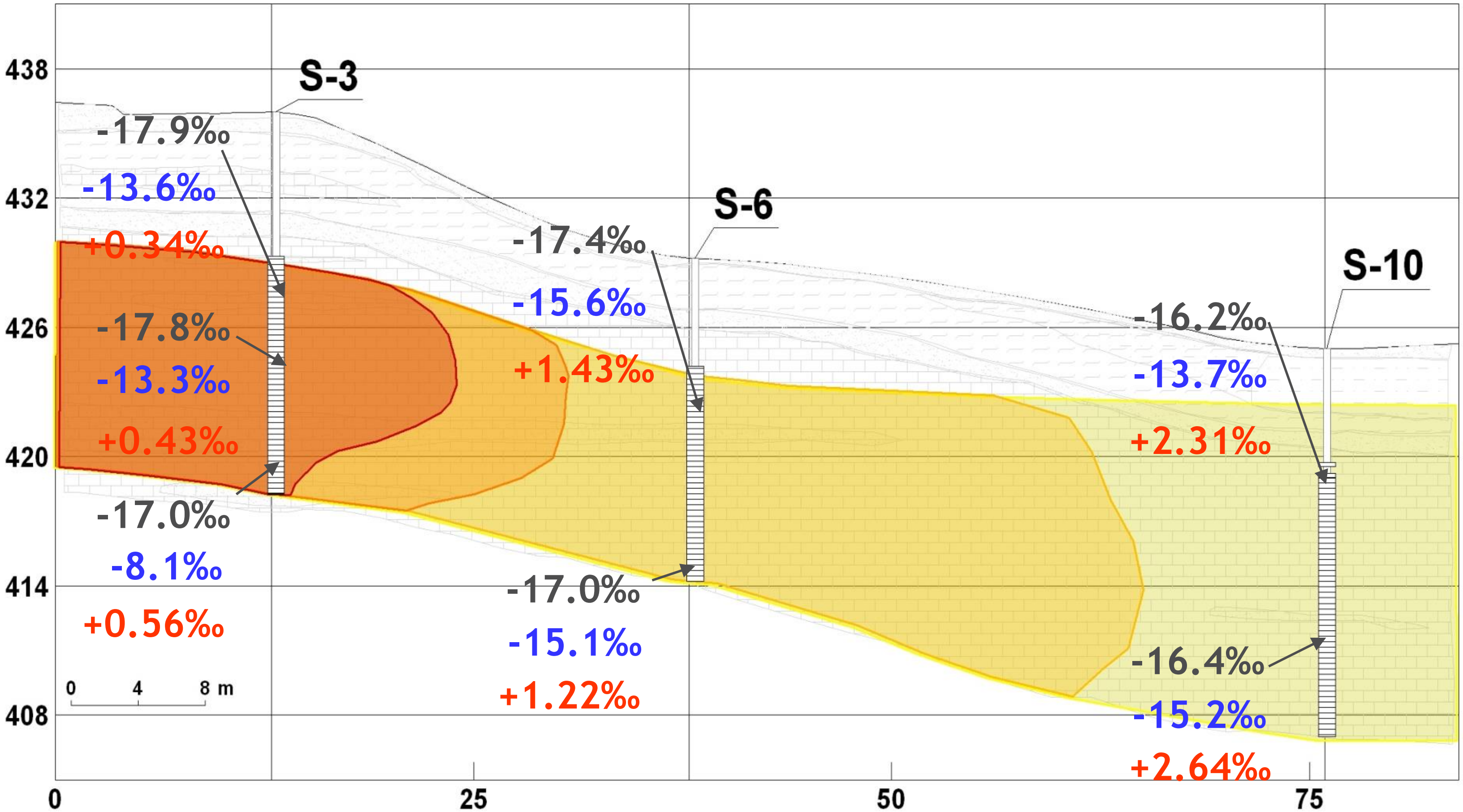


APPLICAZIONI: FINGERPRINTING



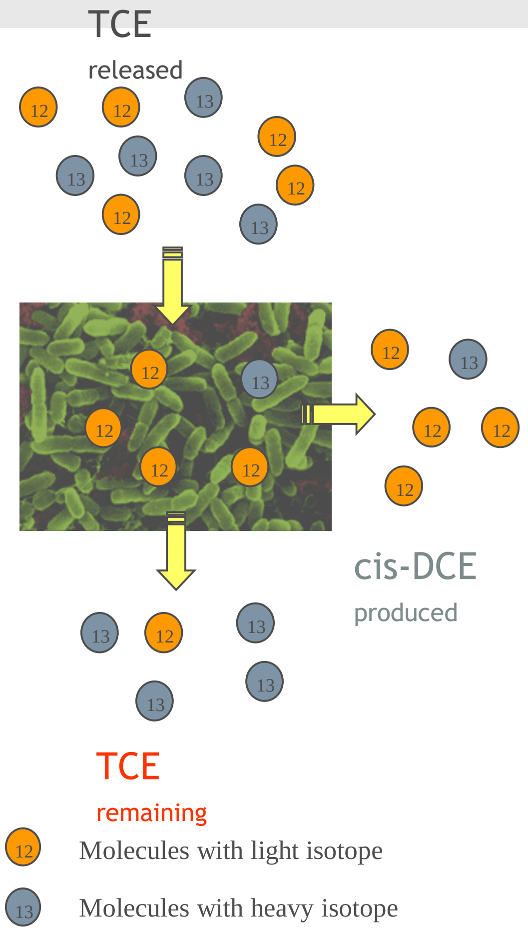
-18.5‰ $\delta^{13}C$ PCE
-16.0‰ $\delta^{13}C$ TCE
+0.53‰ $\delta^{37}Cl$ TCE

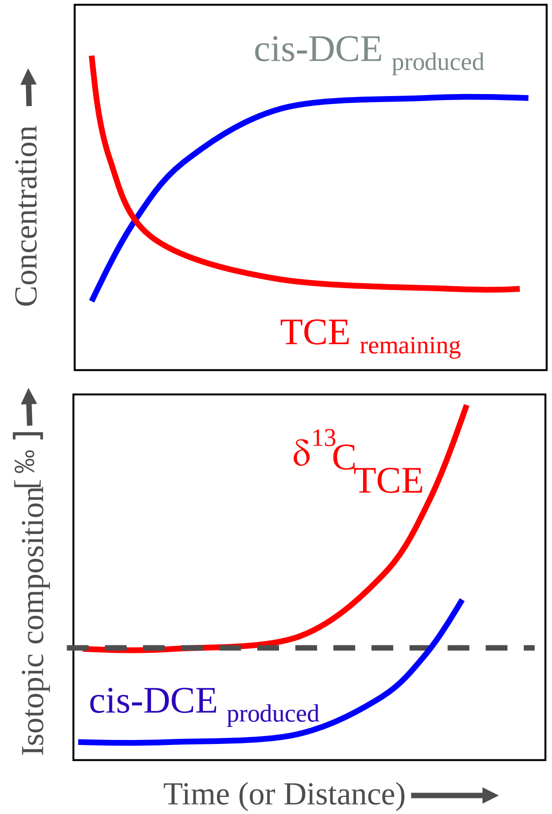
È ^{13}C conservativo?

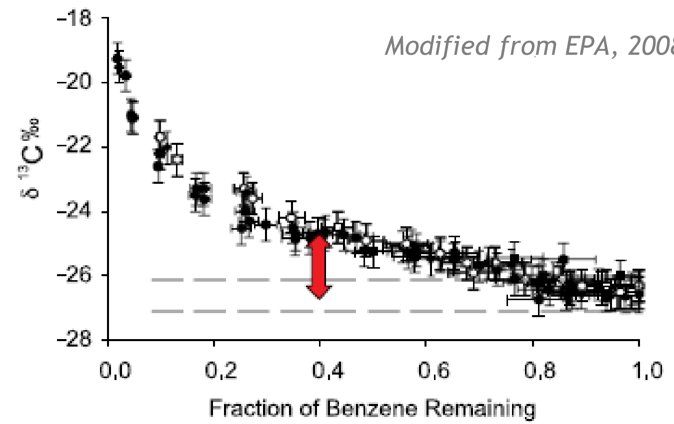


- il ^{13}C (oppure $^{37}Cl/^{35}Cl$, $^{2}H/^{1}H$) puo cambiare durante processi di biodegradazione

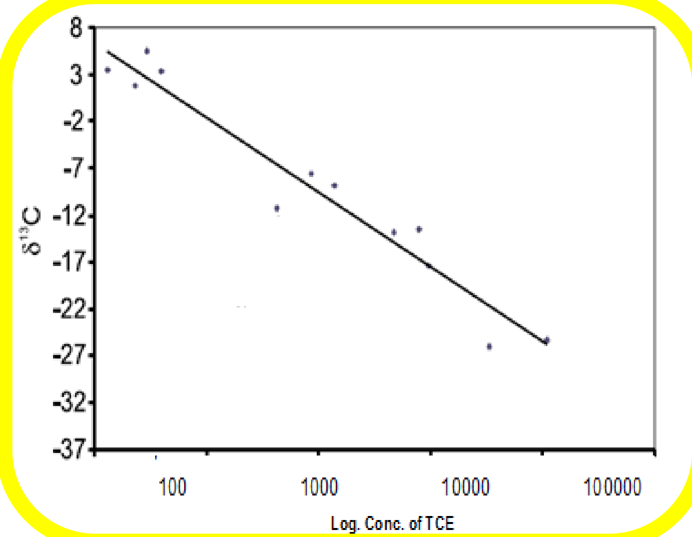
BIODEGRADAZIONE E FRAZIONAMENTO ISOTOPICO





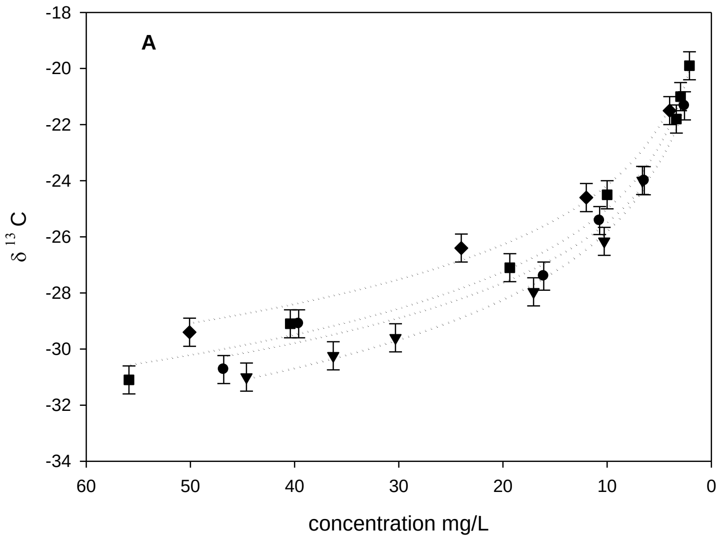


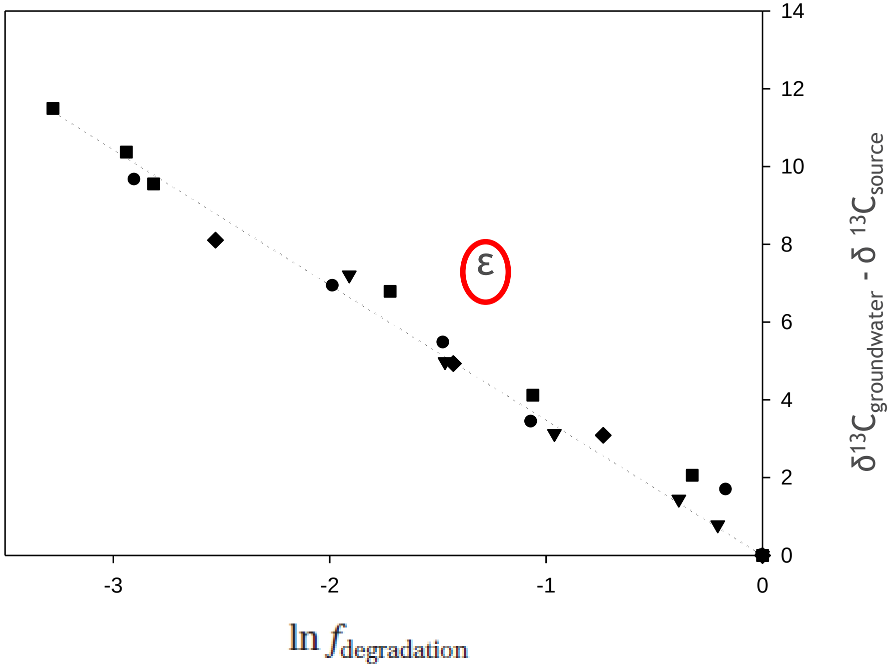
Modified from EPA, 2008



Gli isotopi di uno stesso elemento, avendo massa diversa, hanno proprietà chimiche e fisiche leggermente diverse. Per questo, durante le trasformazioni chimiche e fisiche avviene un *frazionamento isotopico*, cioè i due isotopi si distribuiscono con un'abbondanza differente nei reagenti e nei prodotti.

BIODEGRADAZIONE E FRAZIONAMENTO ISOTOPICO





$$f = e^{(\delta^{13}C_{groundwater} - \delta^{13}C_{source})/(\varepsilon)}$$

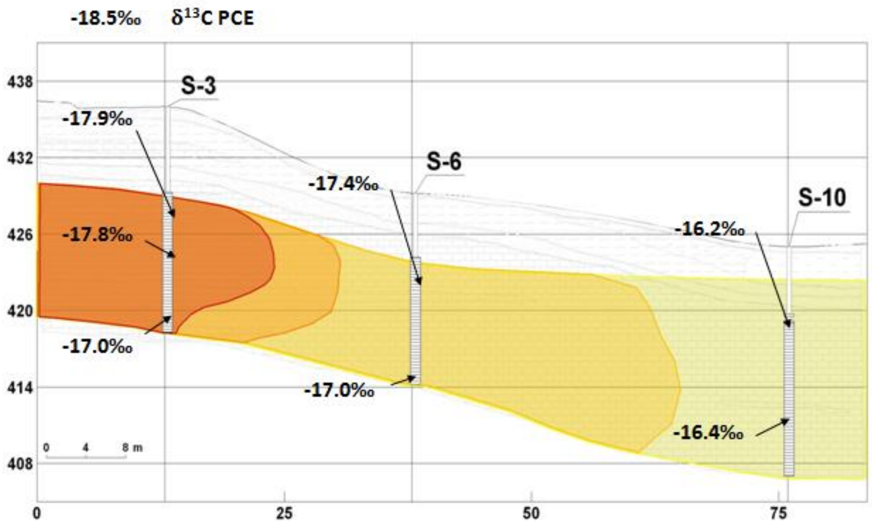
ε: fattore di arricchimento

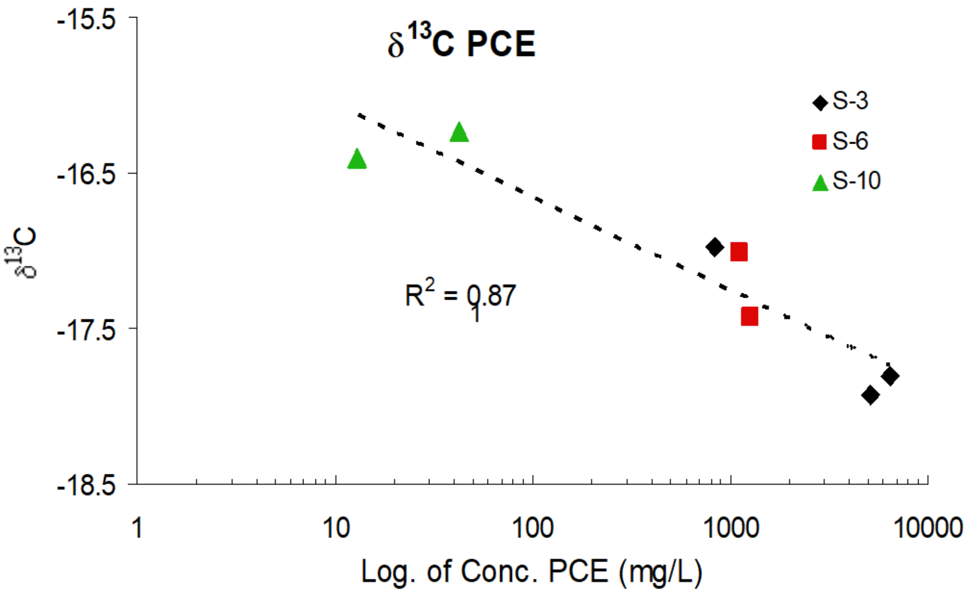
$$f_{degradation} = \frac{C}{C_0}$$

fattore/costante per descrivere il frazionamento di un composto in determinate condizioni

> ε > $\delta^{13}C_{groundwater} - \delta^{13}C_{source}$

BIODEGRADATION: ISOTOPE FRACTIONATION





$\delta^{13}C_{r,0}$= -18.5‰
in the focus

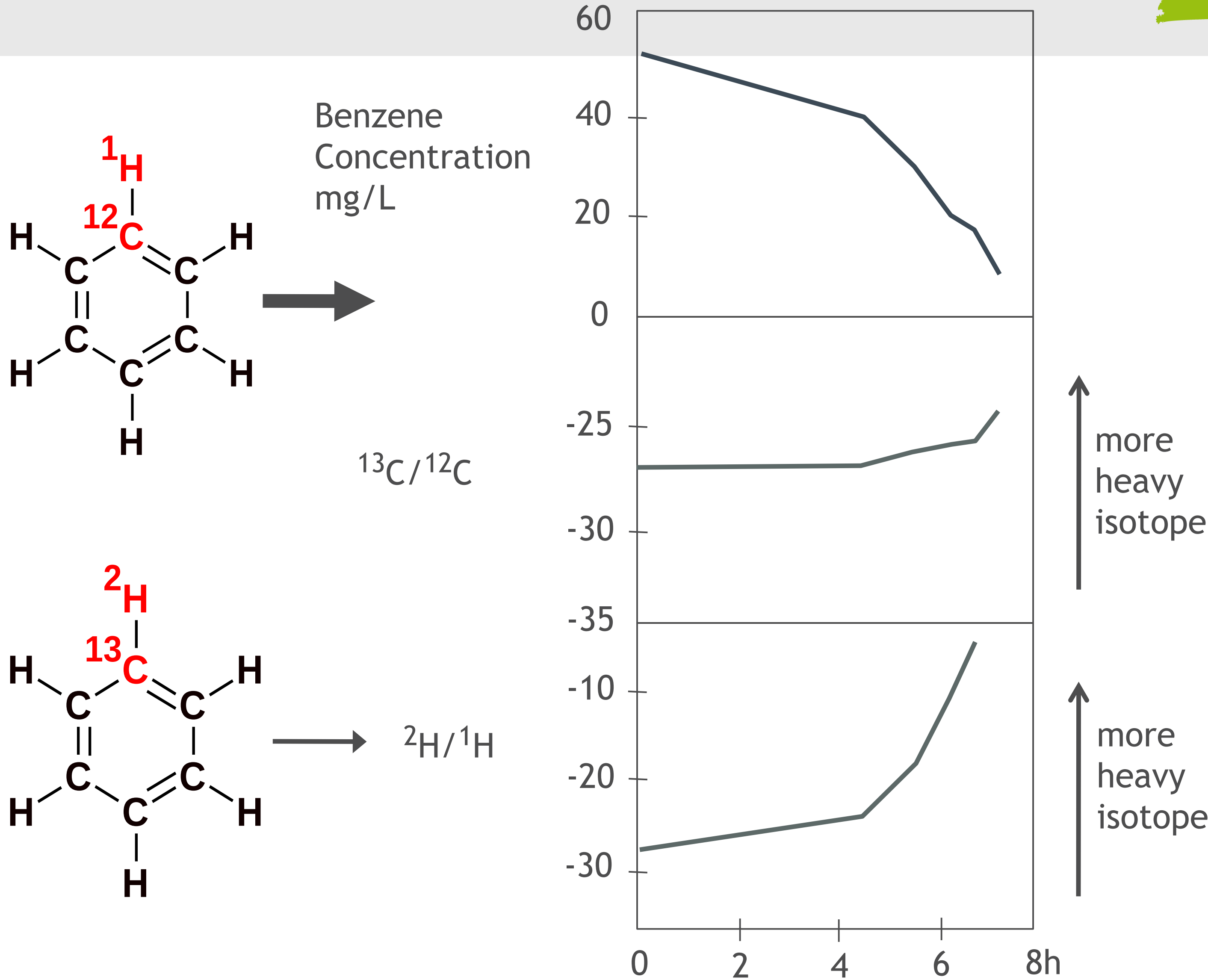
ε (-1.7 to -8.8 ‰)

$$f = e^{(\delta^{13}C_{groundwater} - \delta^{13}C_{source})/\varepsilon)}$$

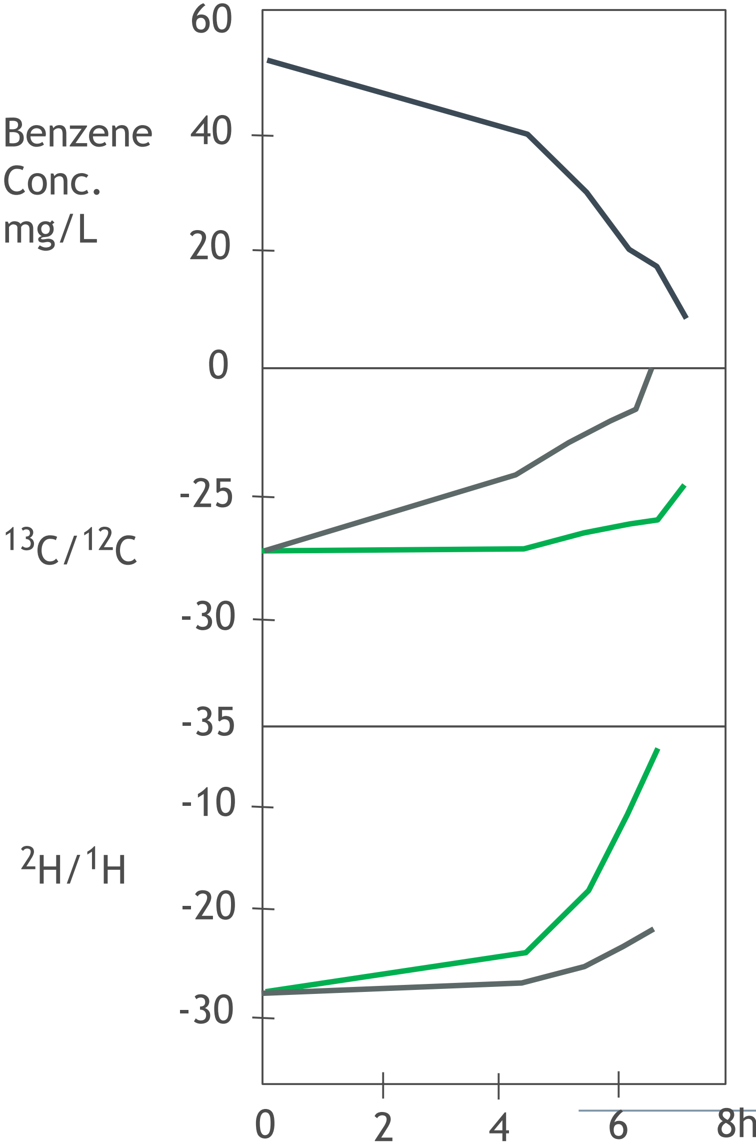
Biodegradation

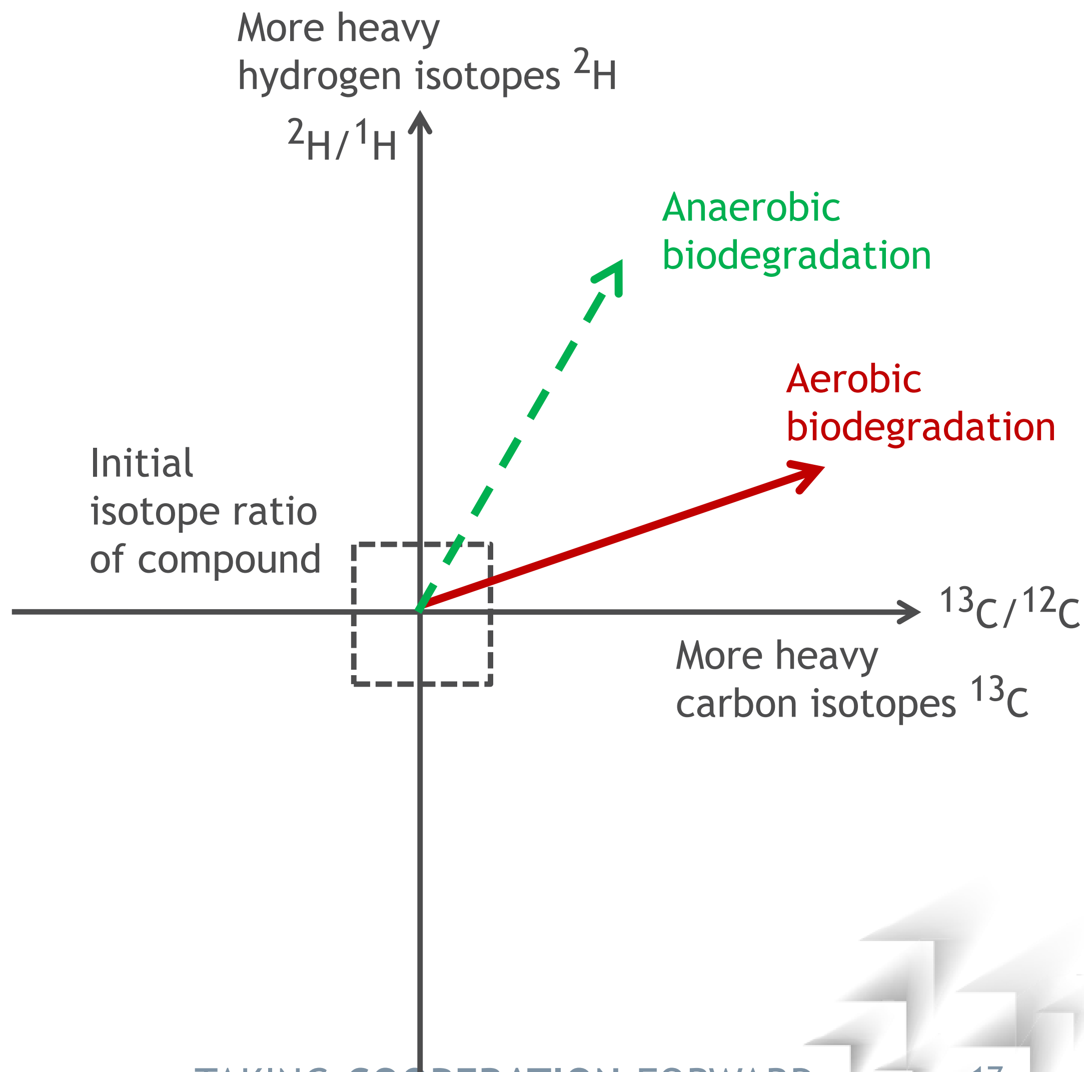
5 - 25%
40 - 75%

PATHWAYS: DUAL ISOTOPE APPROACH

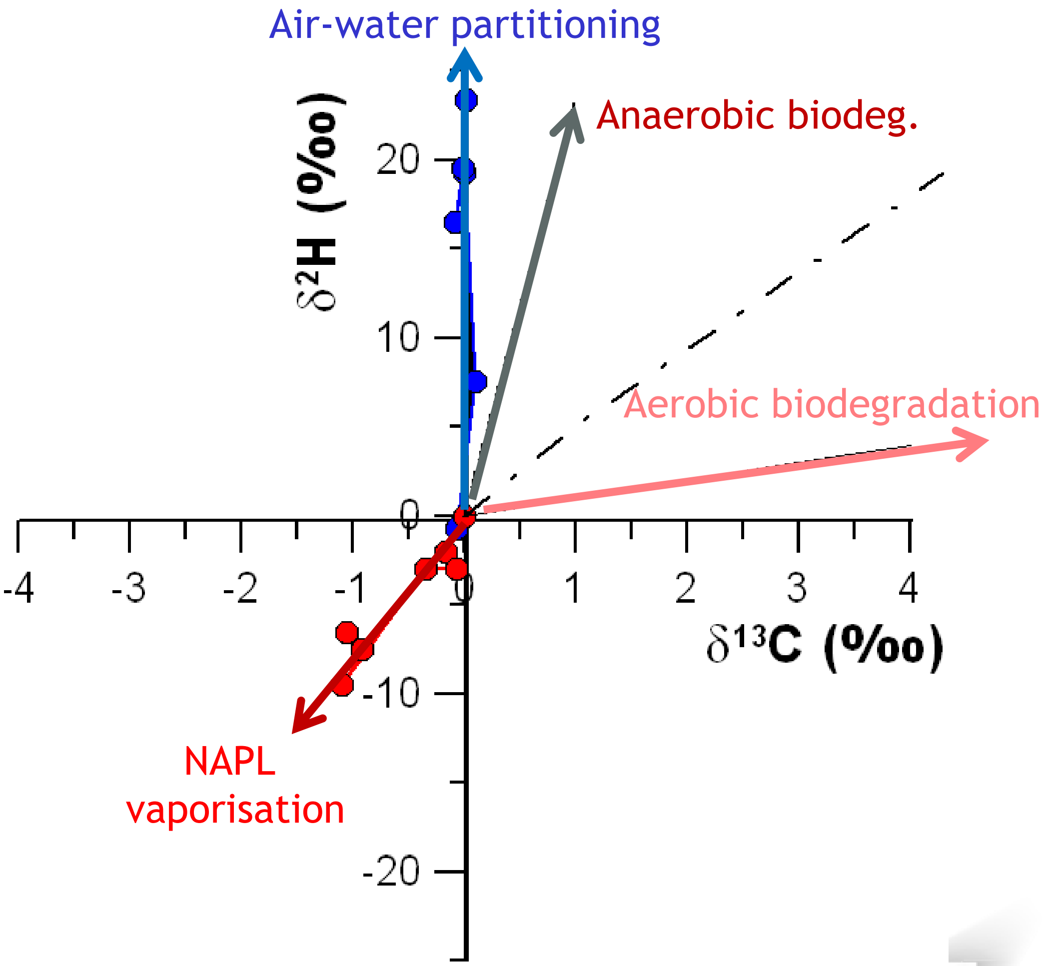


DUAL ISOTOPE PLOT FOR BIODEGRADATION

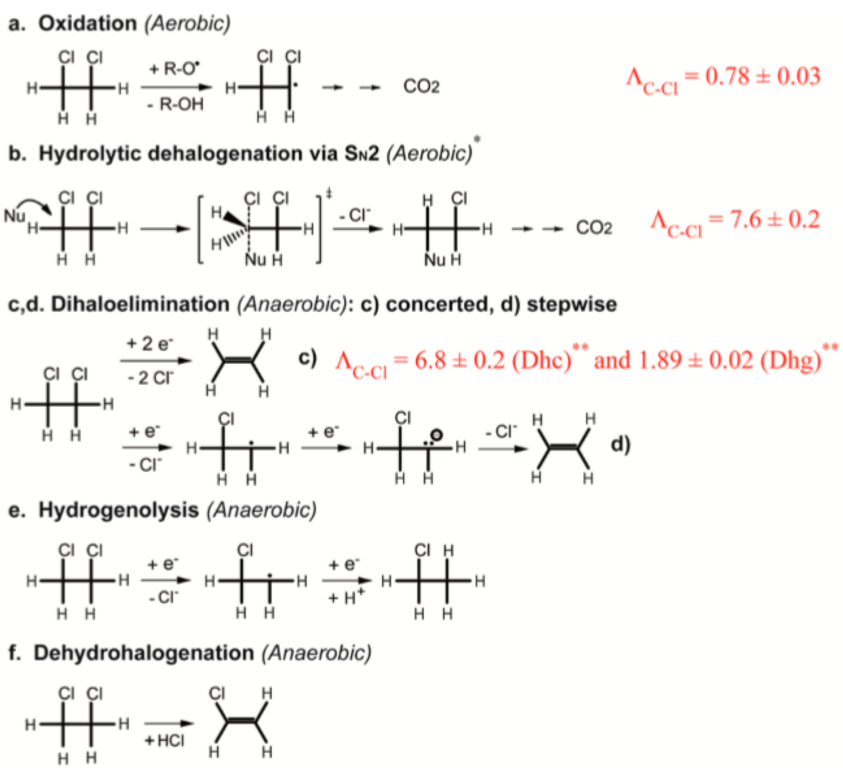




PHISICAL PROCESSES



MECCANISMO DI DEGRADAZIONE



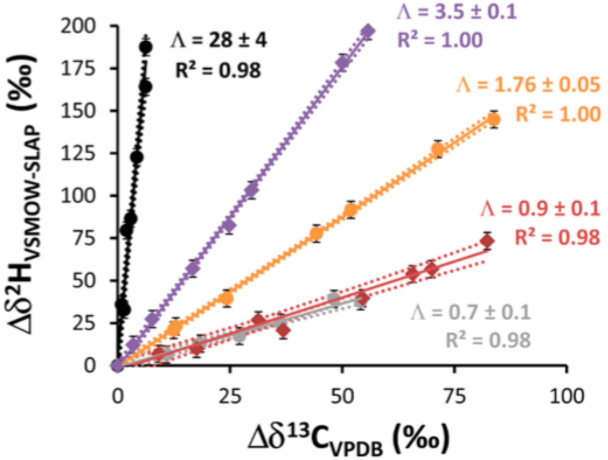
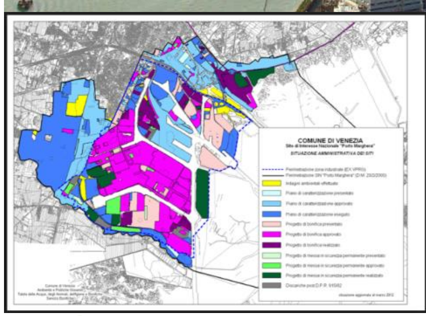


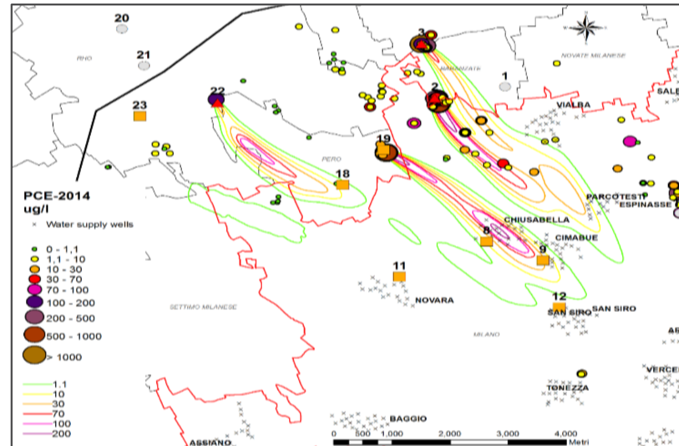
Figure 2. Dual C−H isotope trends during the biodegradation of 1,2-DCA via oxidation by *Pseudomonas* sp. (black circles), hydrolytic dehalogenation by *A. aquaticus* (gray circles) and *X. autotrophicus* (red diamonds), and dihaloelimination by *Dehalococcoides*- (orange circles) and *Dehalogenimonas*-containing cultures (violet diamonds). Dotted lines indicate the 95% confidence intervals of the linear regression. Error bars of $\Delta\delta^{13}C$ values are smaller than the symbols. Λ values (±95% confidence interval) are given by the slope of the linear regressions.

Palau et al, 2017

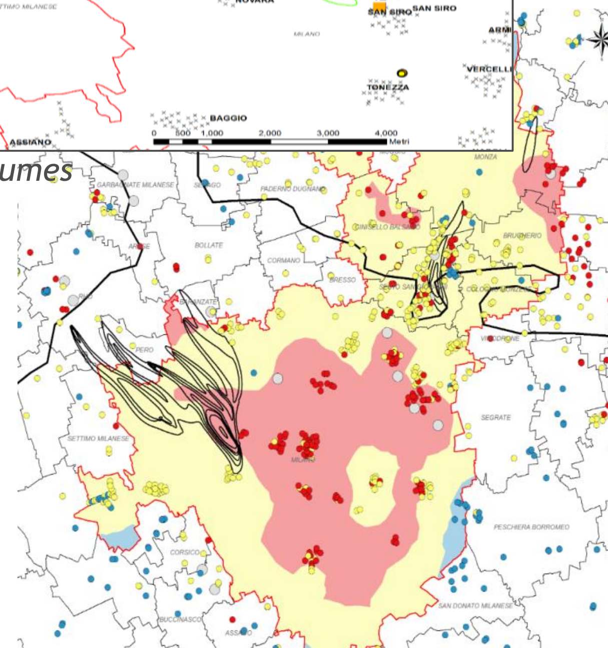
POTENZIALITÀ

- Fingerprinting – tracking responsabilities (Pulluter pays principle)





Progetto Plumes

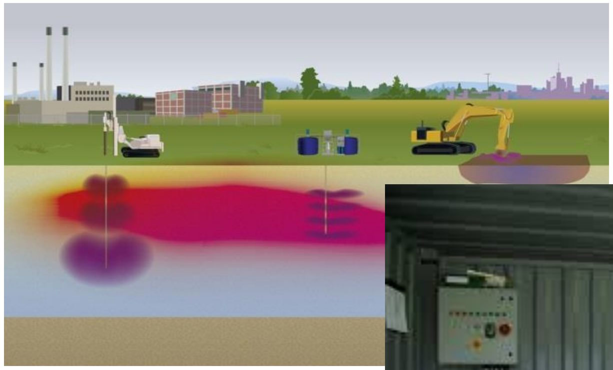


- Valutare i processi di attenuazione naturale

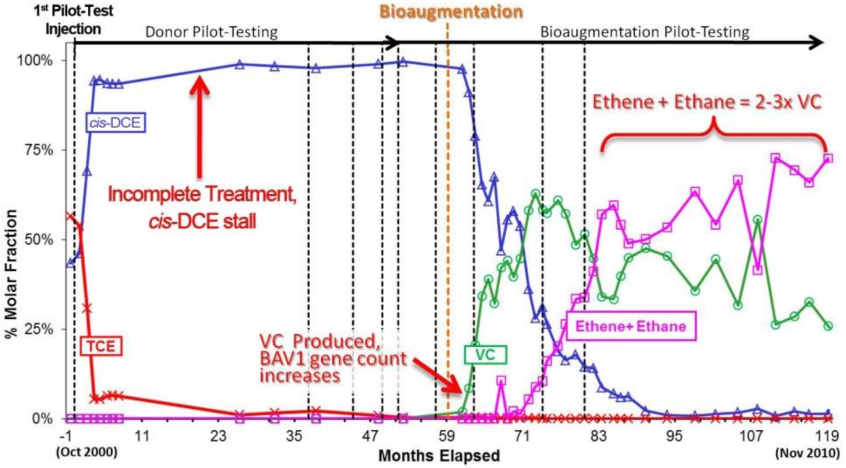
APPLICAZIONI

- **Remediation assesment**

ISCO

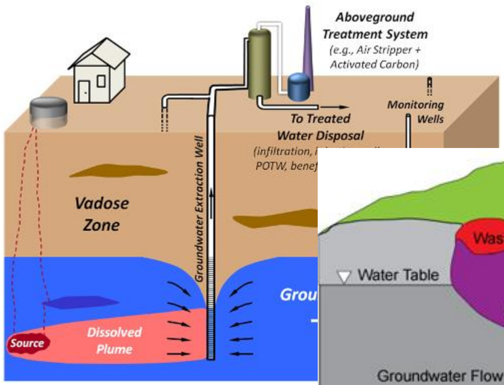


Enhanced bioremediation

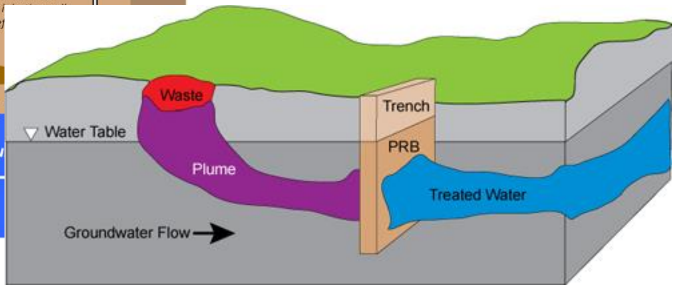


https://clu-in.org/products/newsltrs/tnandt/view_new.cfm?issue=1212.cfm

P&T



PRB



PHISICAL BARRIERS