

Environmental Forensics: Case Studies on the Use of CSIA for Site Characterization and Source Determinations

ORFAN SHOUAKAR-STASH

Isotope Tracer Technologies Inc. – University of Waterloo – University of Guelph

MASSIMO MARCHESI

Isotope Tracer Technologies Europe SRL. - Sapienza Università di Roma

LUCA ALBERTI

Politecnico di Milano

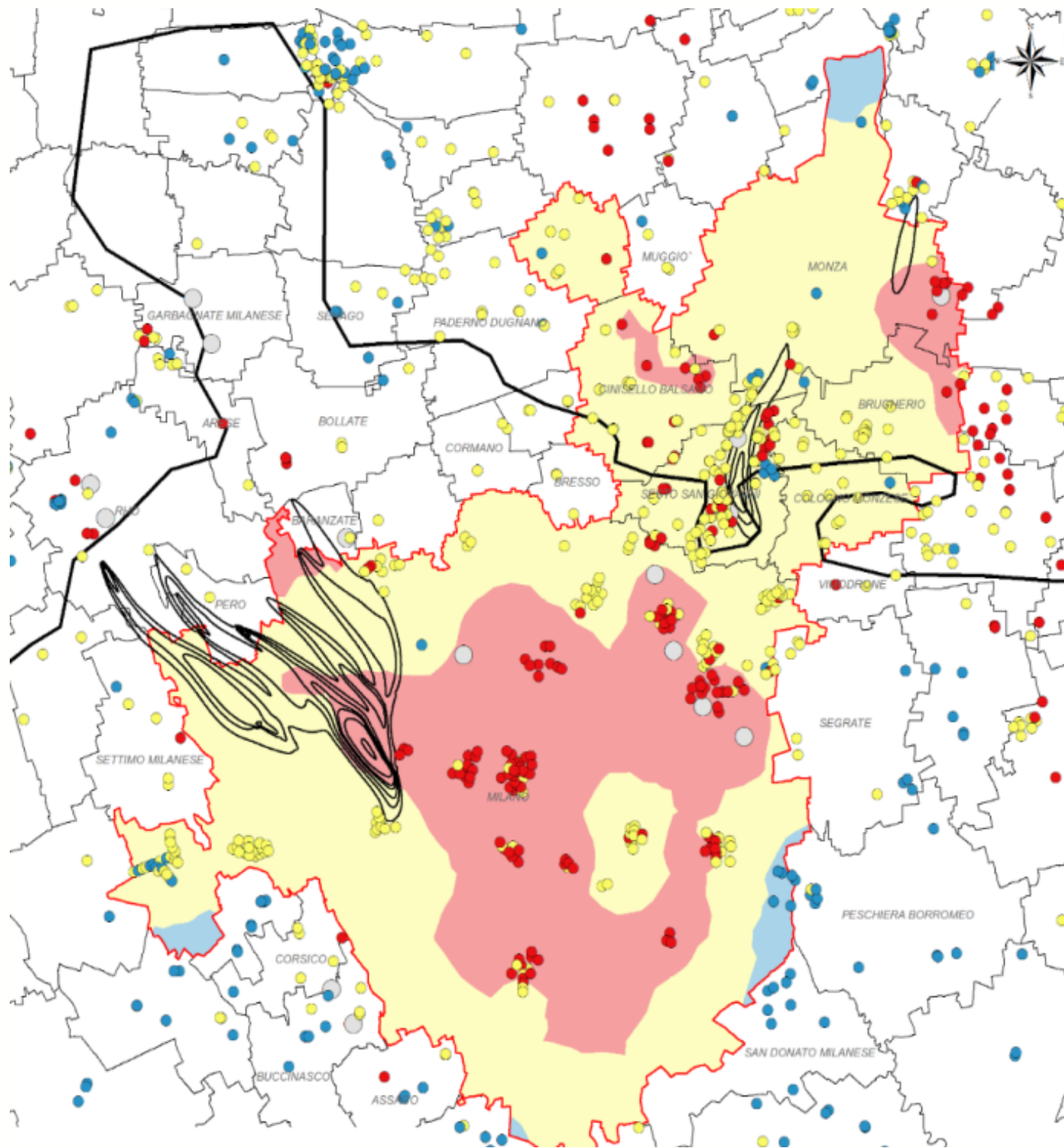
Jun. 6, 2024

2024 Chlorinated Conference

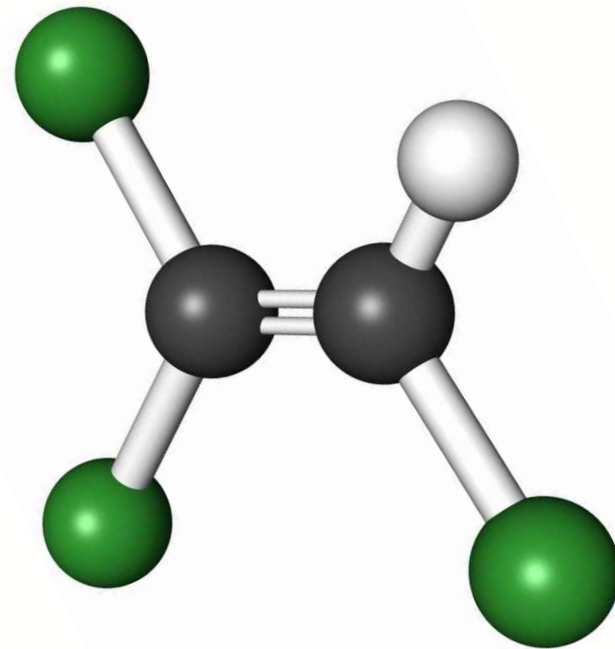


CSIA and CONTAMINANTS

- Fingerprinting – tracking responsibilities (Identifying Principle Polluter)
- Understanding Processes – The fate of contaminants
- Evaluating remediation actions
- Investigating Mechanisms

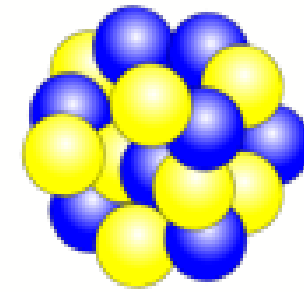


CONCEPT

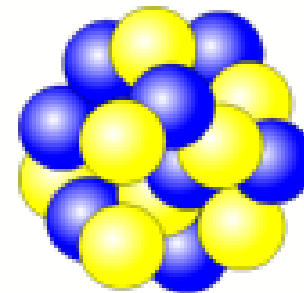


Abbondanza isotopico
(relativo)

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



$$\begin{array}{r}
 + \quad \begin{array}{l} \text{17 protons} \\ \text{20 neutrons} \end{array} \\
 \hline
 {}^{37}\text{Cl}
 \end{array}$$



$$\begin{array}{r}
 + \quad \begin{array}{l} \text{17 protons} \\ \text{18 neutrons} \end{array} \\
 \hline
 {}^{35}\text{Cl}
 \end{array}$$

Rapporto isotopico
(assoluto)

$$\frac{{}^{13}\text{C}}{{}^{12}\text{C}}$$

$$R = 0.011327$$

$$R = 0.011237$$

$$R = 0.010867$$

$$R = 0.010338$$

$$\begin{array}{r}
 + \quad \begin{array}{l} \text{6 protons} \\ \text{7 neutrons} \end{array} \\
 \hline
 {}^{13}\text{C}
 \end{array}$$

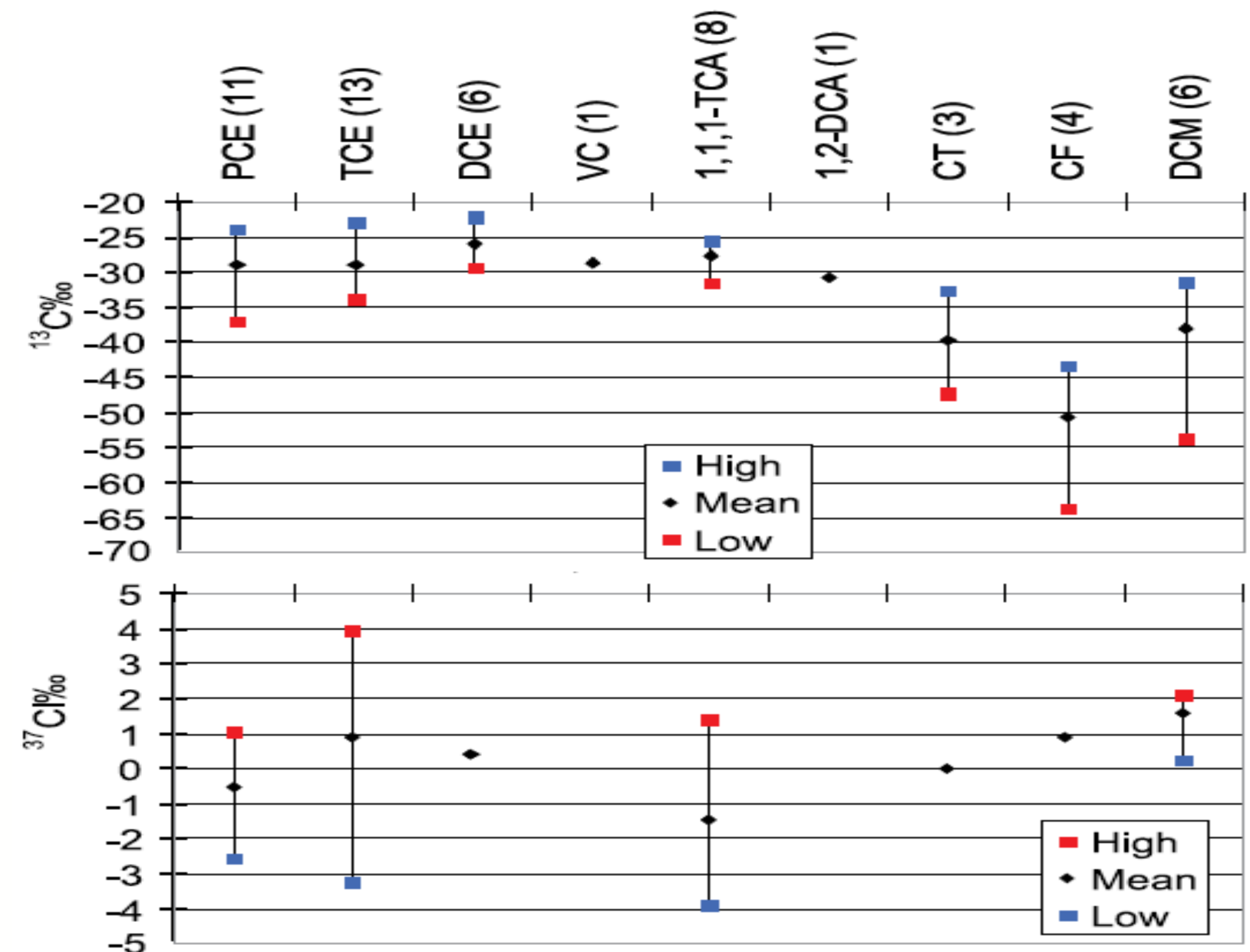
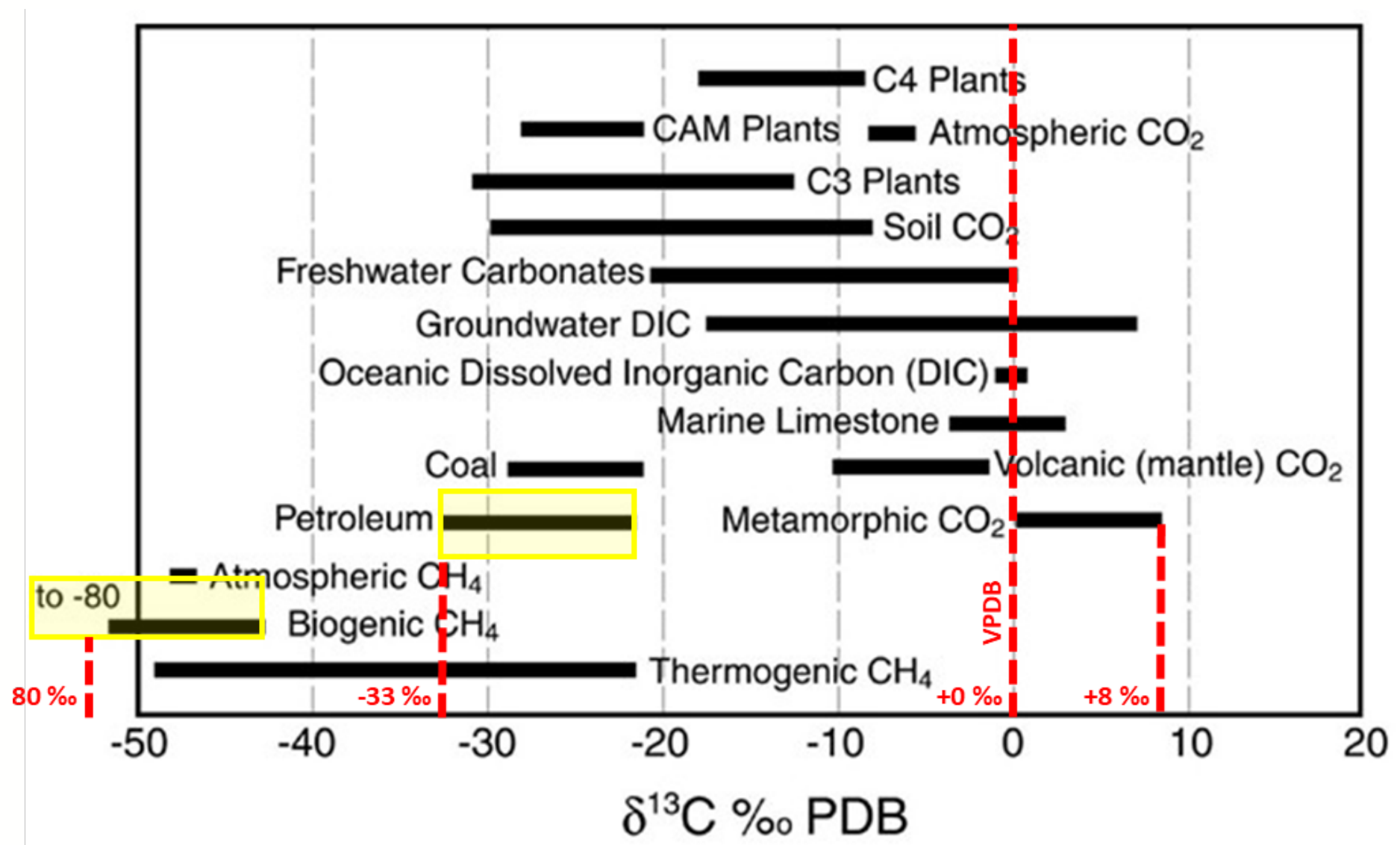
$$\begin{array}{r}
 + \quad \begin{array}{l} \text{6 protons} \\ \text{6 neutrons} \end{array} \\
 \hline
 {}^{12}\text{C}
 \end{array}$$

Rapporto isotopico (relativo)

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

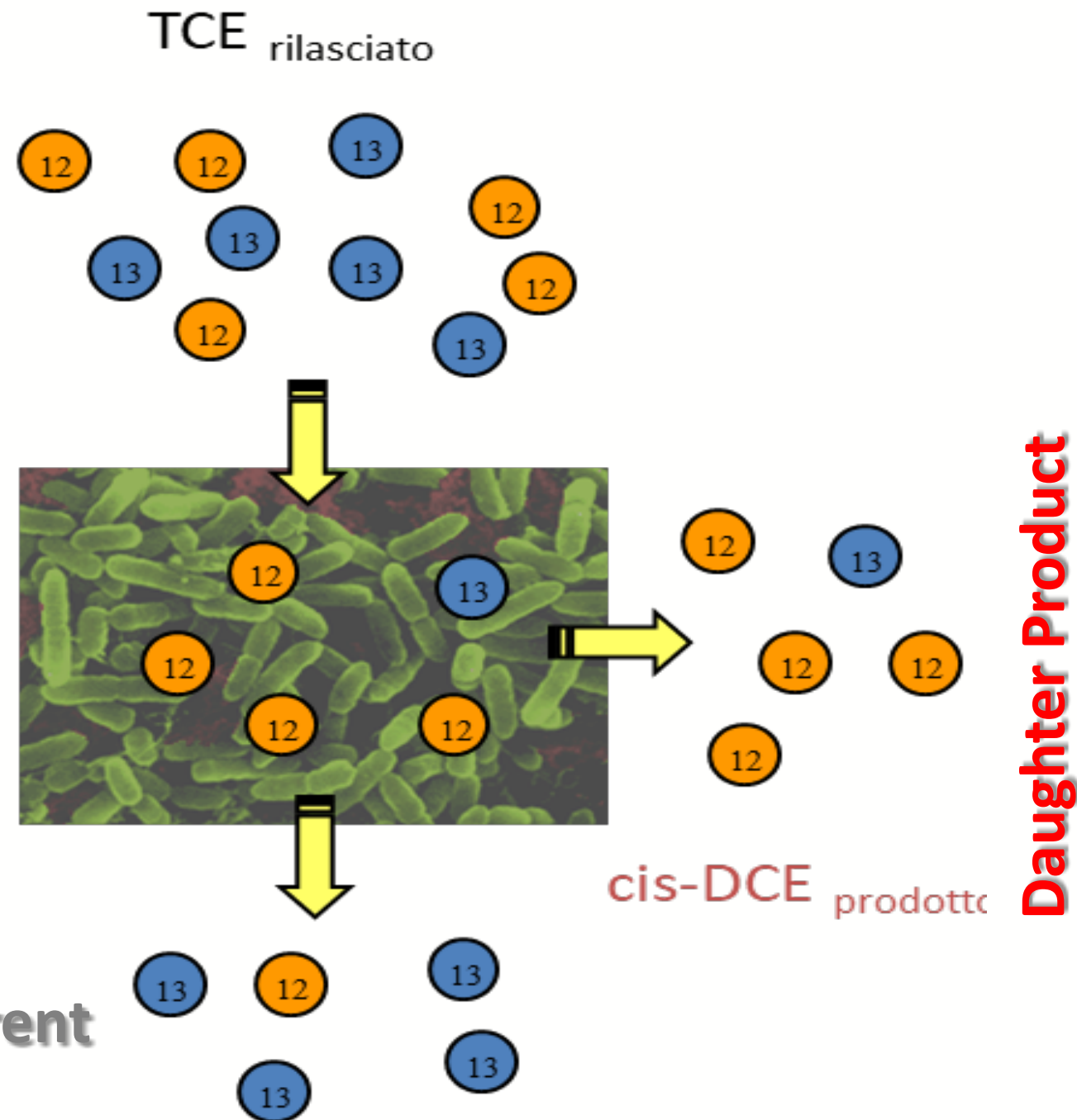
	$\delta = +8 \text{ ‰}$	
	$\delta = +0 \text{ ‰}$	
	$\delta = -33 \text{ ‰}$	
	$\delta = -80 \text{ ‰}$	
↑ Arricchimento		↓ impoverimento

Typical Isotopic Ranges



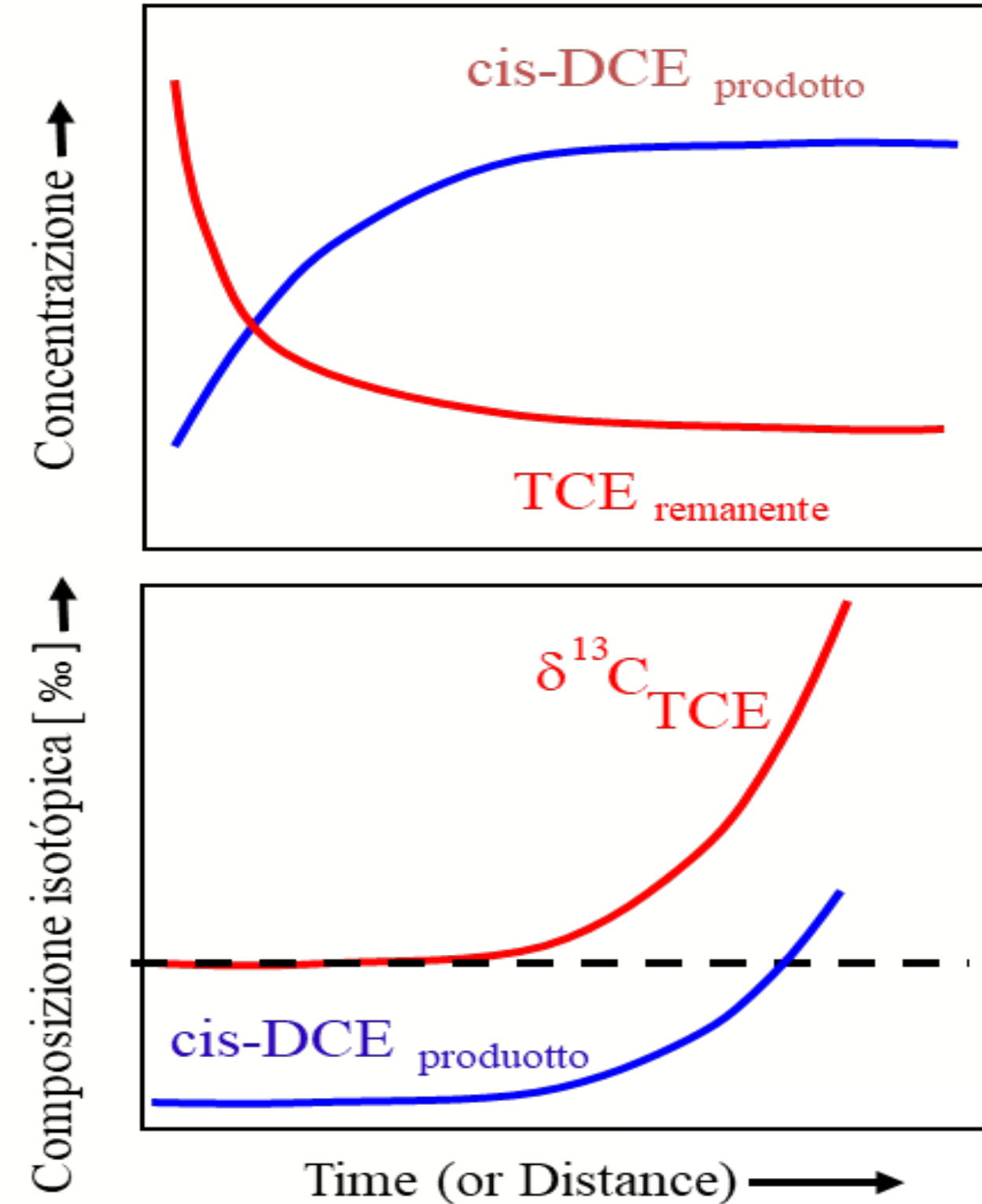
Transformation and Isotopic Ratios

Product / Parent

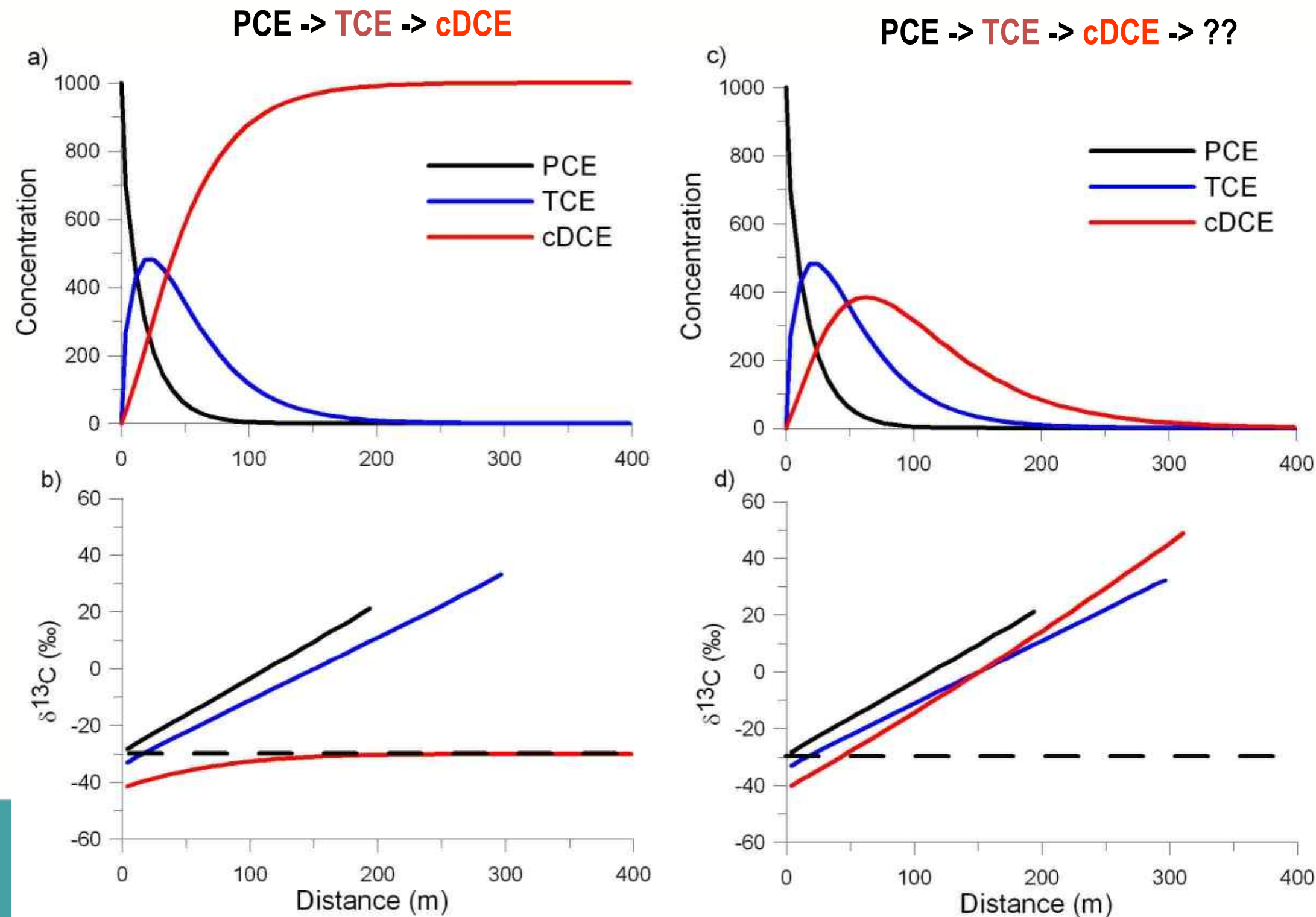


TCE
rimanente

- Molecole con isotopi leggeri
- Molecole con isotopi pesanti



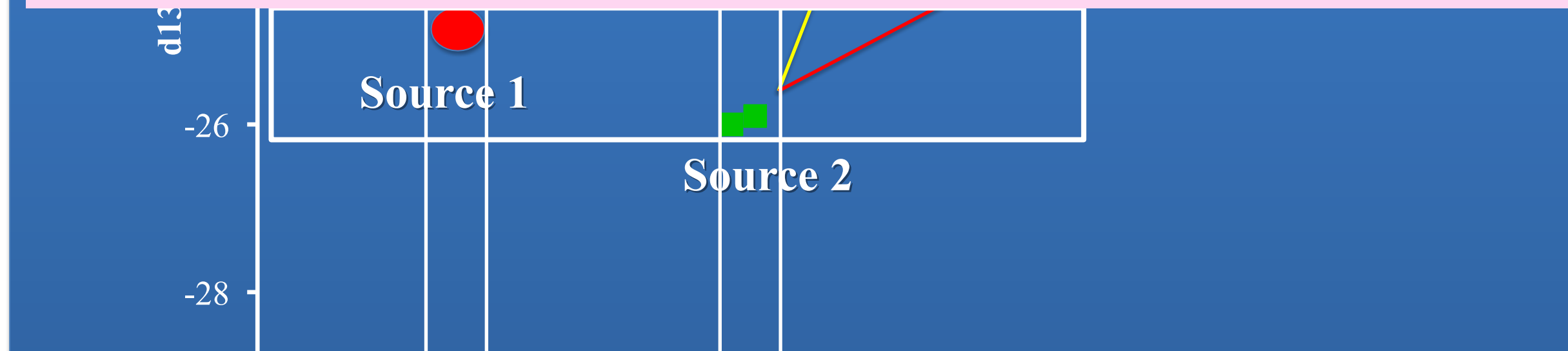
Transformation and Isotopic Ratios



Heavier isotopes form stronger chemical bonds and are therefore less reactive than lighter ones, resulting in an enrichment of heavier isotopes in parent compounds and lighter isotopes in their products (kinetic isotope effects (KIEs)).

Multi Dimensional Isotope Approach

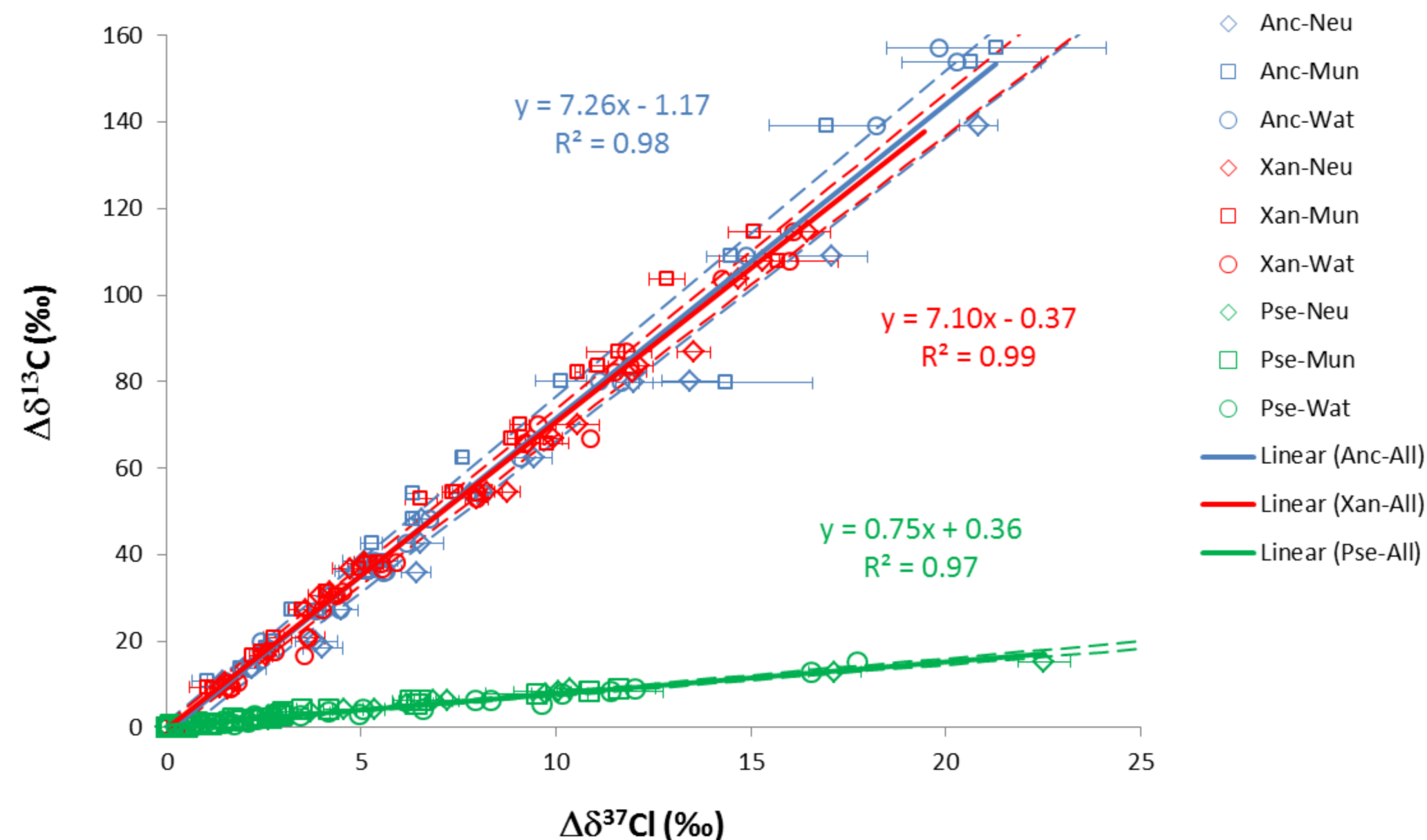
- Increasing the resolution when identifying contaminant sources.
- Better investigating physical processes.
- Assessing the effectiveness of remediation actions.
- Understanding chemical and biological processes
- Exploring reaction mechanisms.



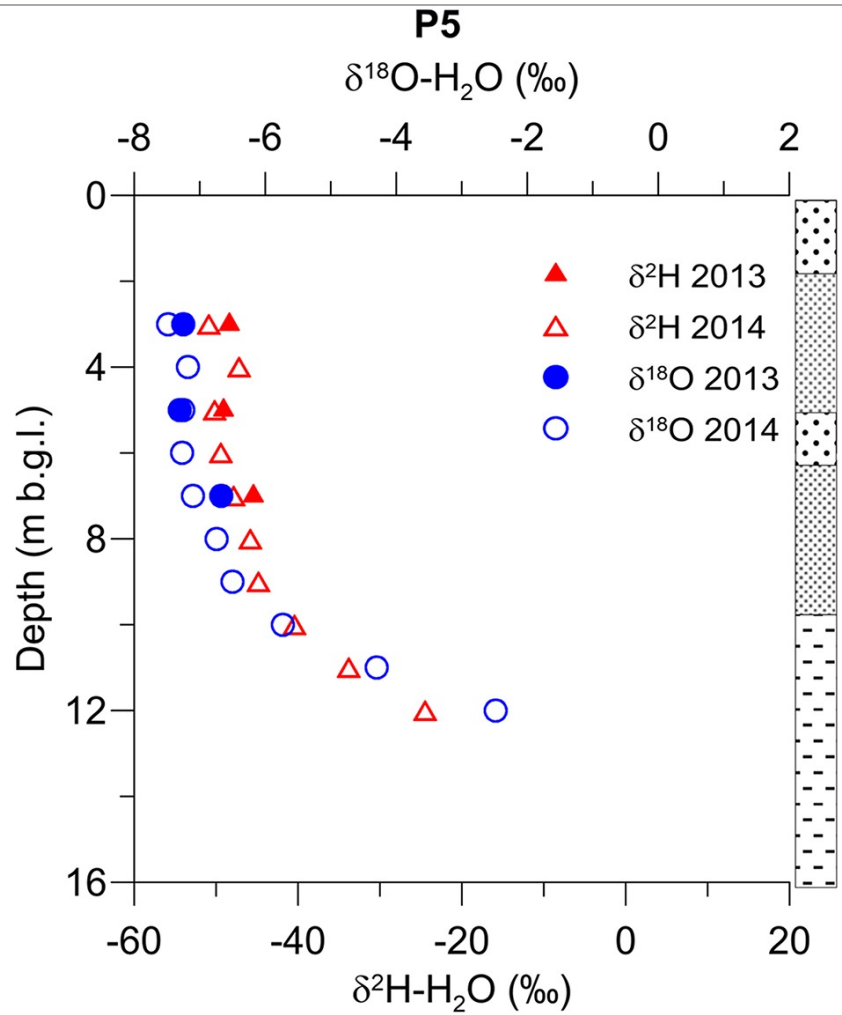
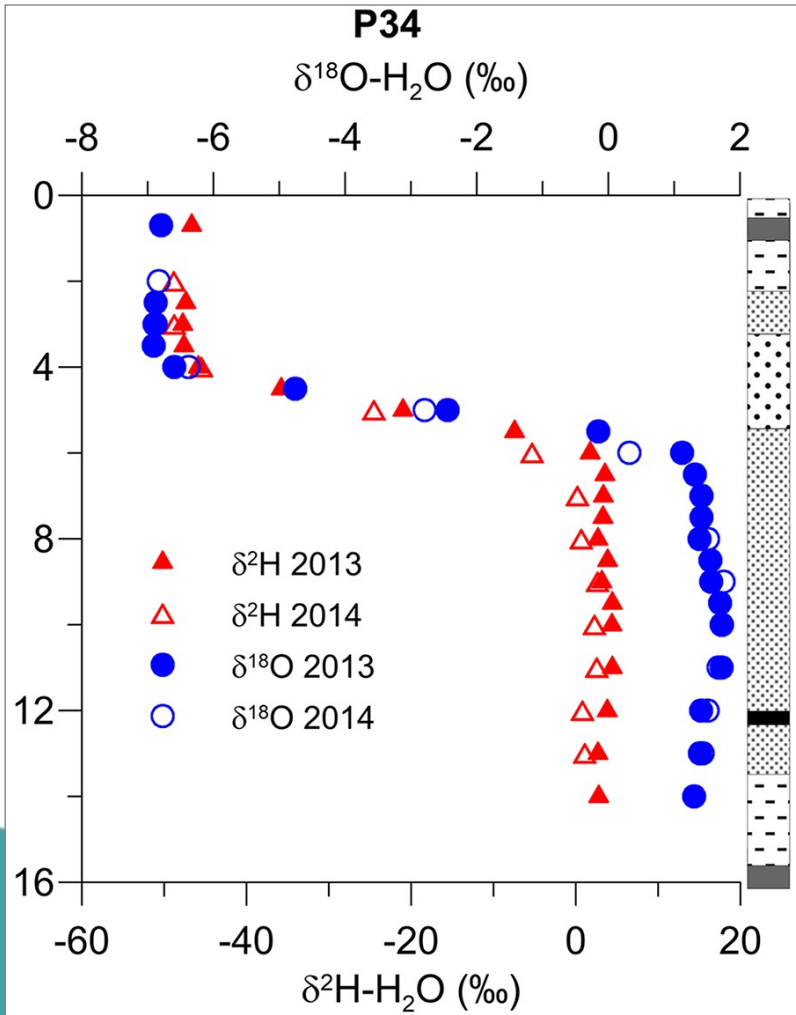
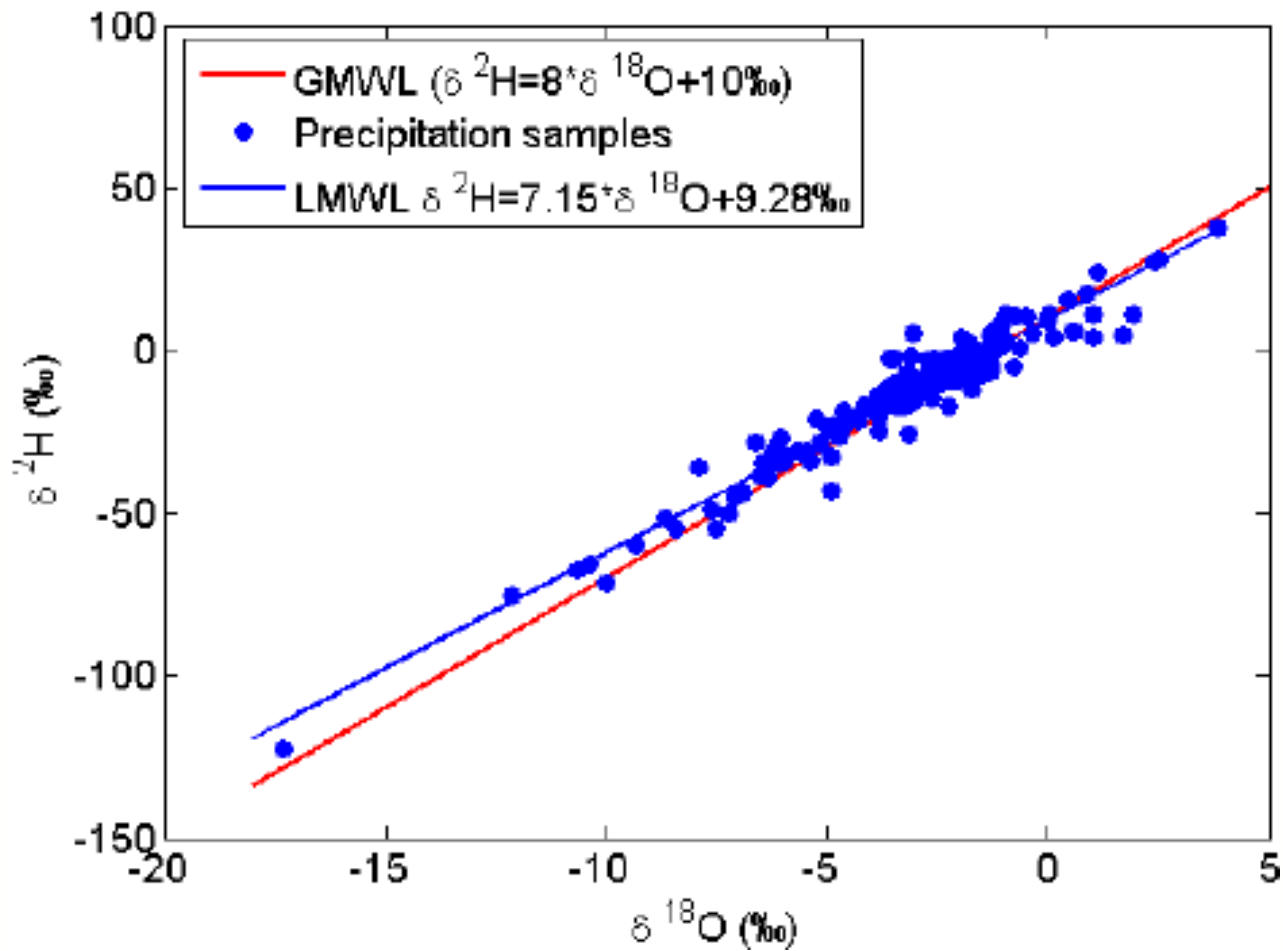
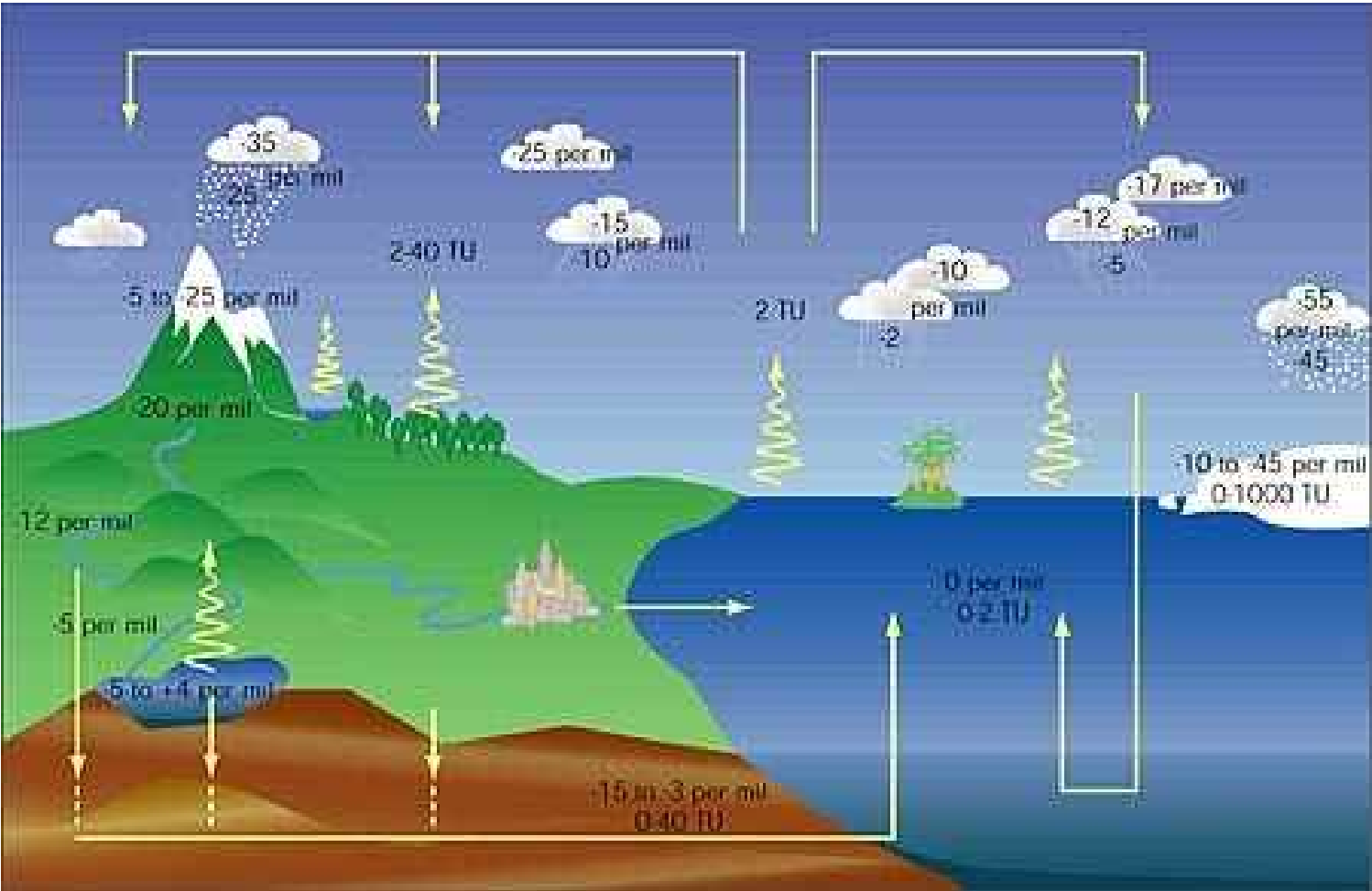
C and Cl Isotope Fractionation of 1,2-Dichloroethane Displays Unique $\delta^{13}\text{C}/\delta^{37}\text{Cl}$ Patterns for Pathway Identification and Reveals Surprising C–Cl Bond Involvement in Microbial Oxidation

Jordi Palau,^{*,†} Stefan Cretnik,[‡] Orfan Shouakar-Stash,[§] Martina Höche,[‡] Martin Elsner,[‡] and Daniel Hunkeler[†]

		$\Delta \pm \text{c.i. 95\%}$
<i>X. autrophicus</i>	$\text{S}_{\text{N}}2$	7.1 ± 0.2
<i>A. Aquaticus</i>	$\text{S}_{\text{N}}2$	7.3 ± 0.3
<i>Pseudomonas</i>	C-H bond oxidation	0.75 ± 0.03



ENVIRONMENTAL ISOTOPES

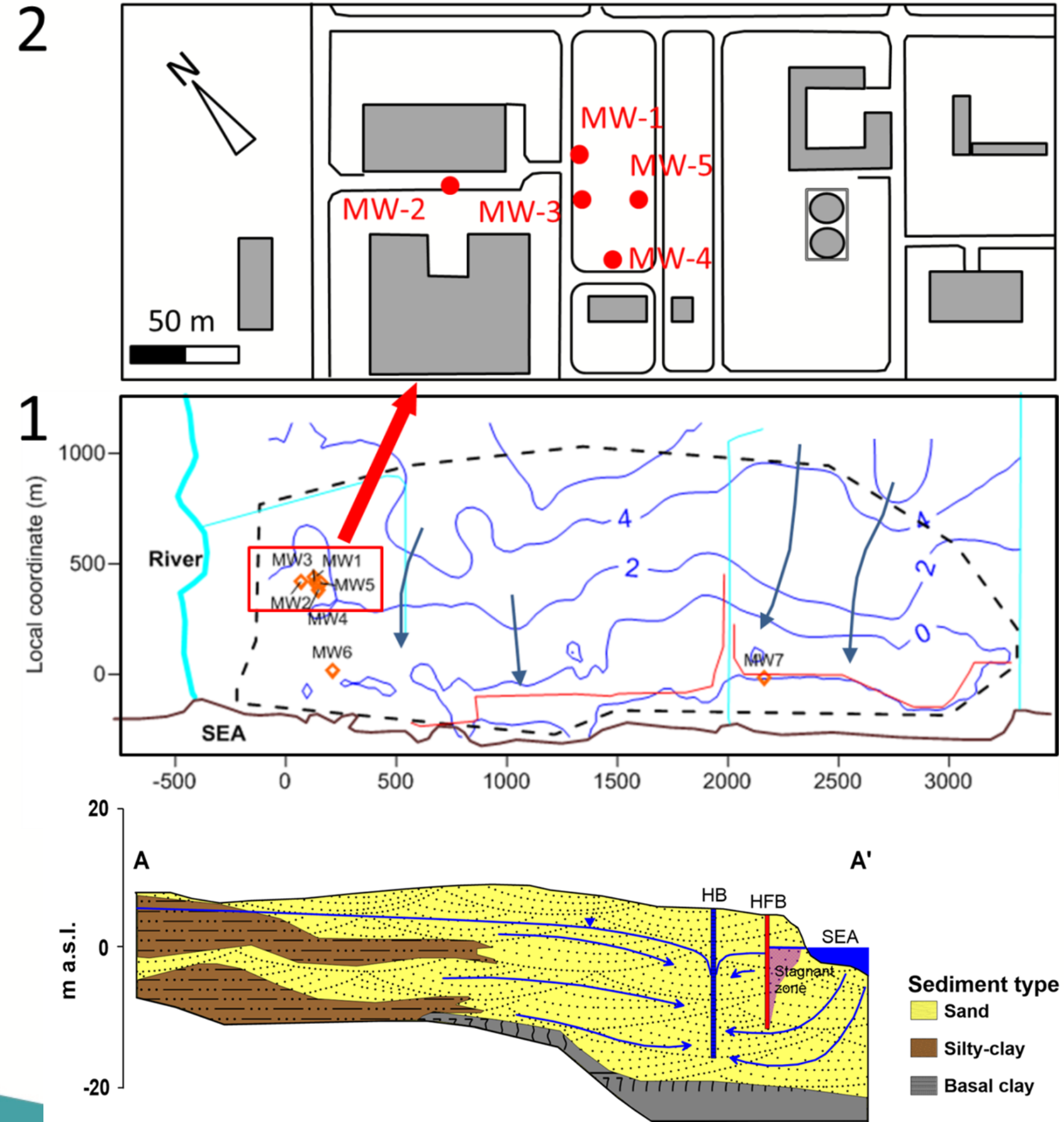




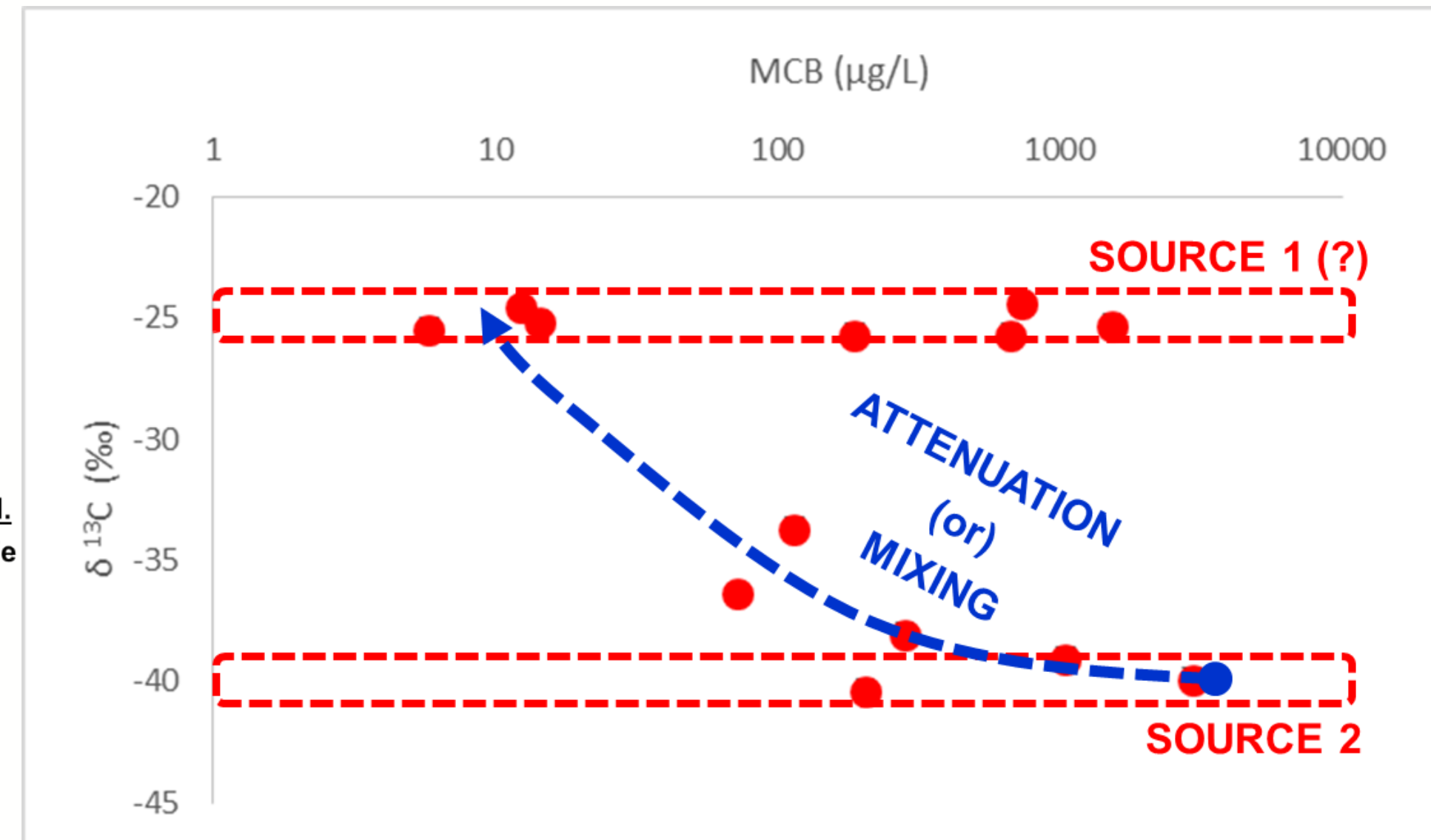
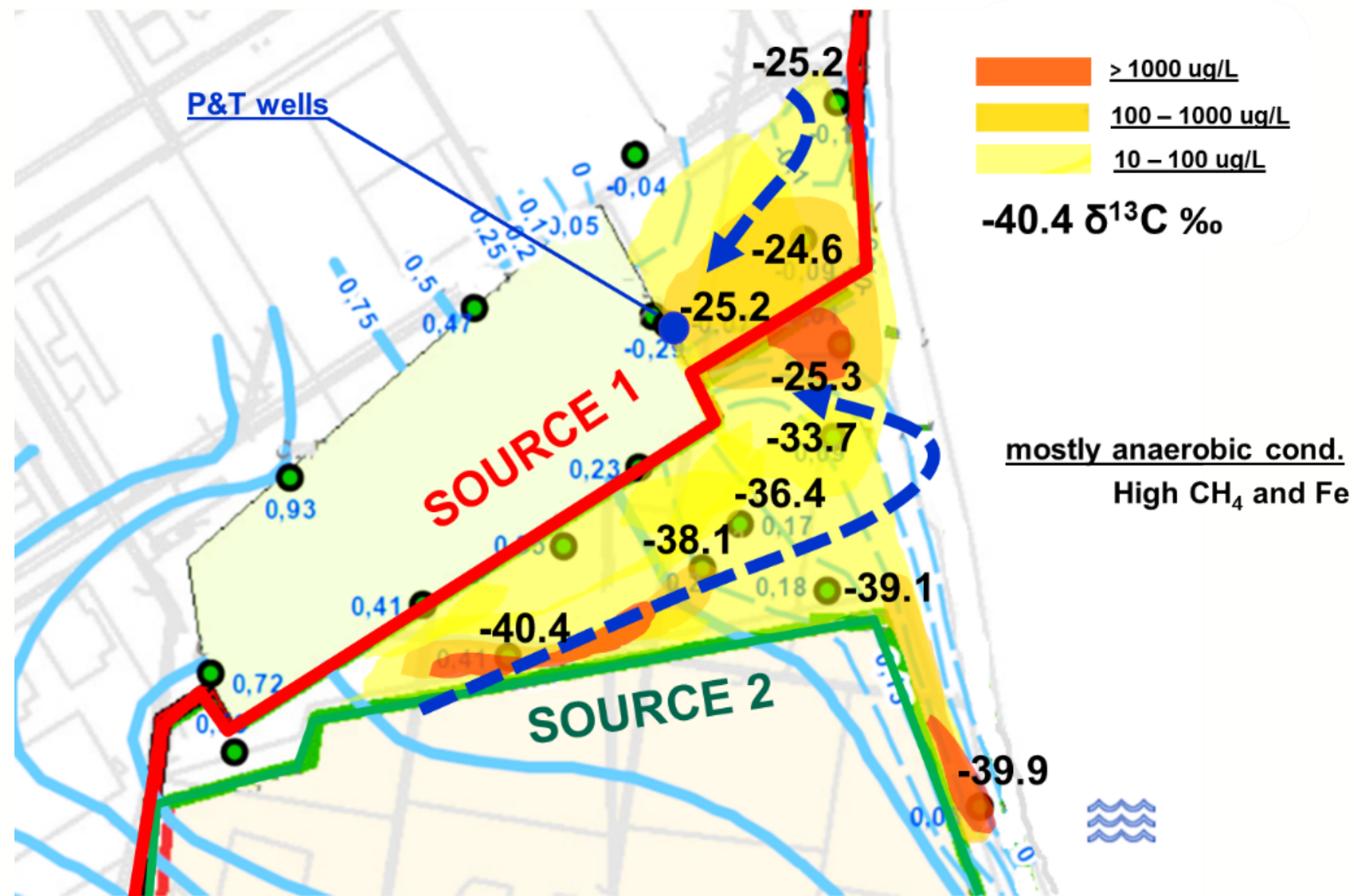
IDEAL SITE SCALE APPLICATION

Site A: Petrochemical plant in Italy

- Site impacted from the early 60s by petroleum hydrocarbons, chlorinated solvents, heavy metals etc.
- Groundwater under reducing conditions
- 1,2-DCA concentrations range between **2410 and 0.03 mg/L**
- 1,2-DCA conc. < **1 mg/L**:
 +28.4 to +35.6‰ for $\delta^{37}\text{Cl}$
 +33.5 to +51.5‰ for $\delta^{13}\text{C}$
- 1,2-DCA conc. > **1 mg/L**:
 +1.1 to +7.1‰ for $\delta^{37}\text{Cl}$
 -21.7 to -12.2‰ for $\delta^{13}\text{C}$



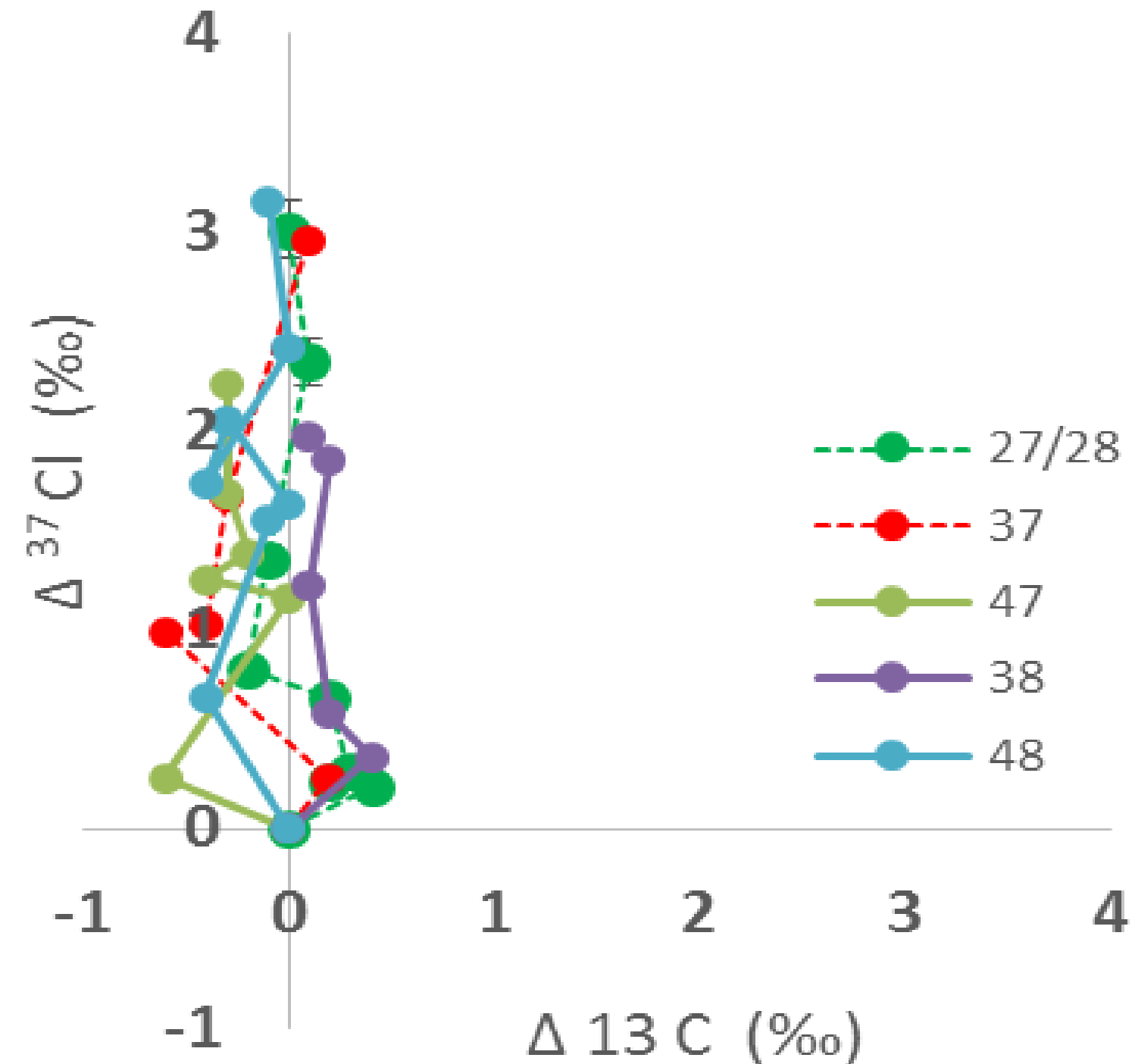
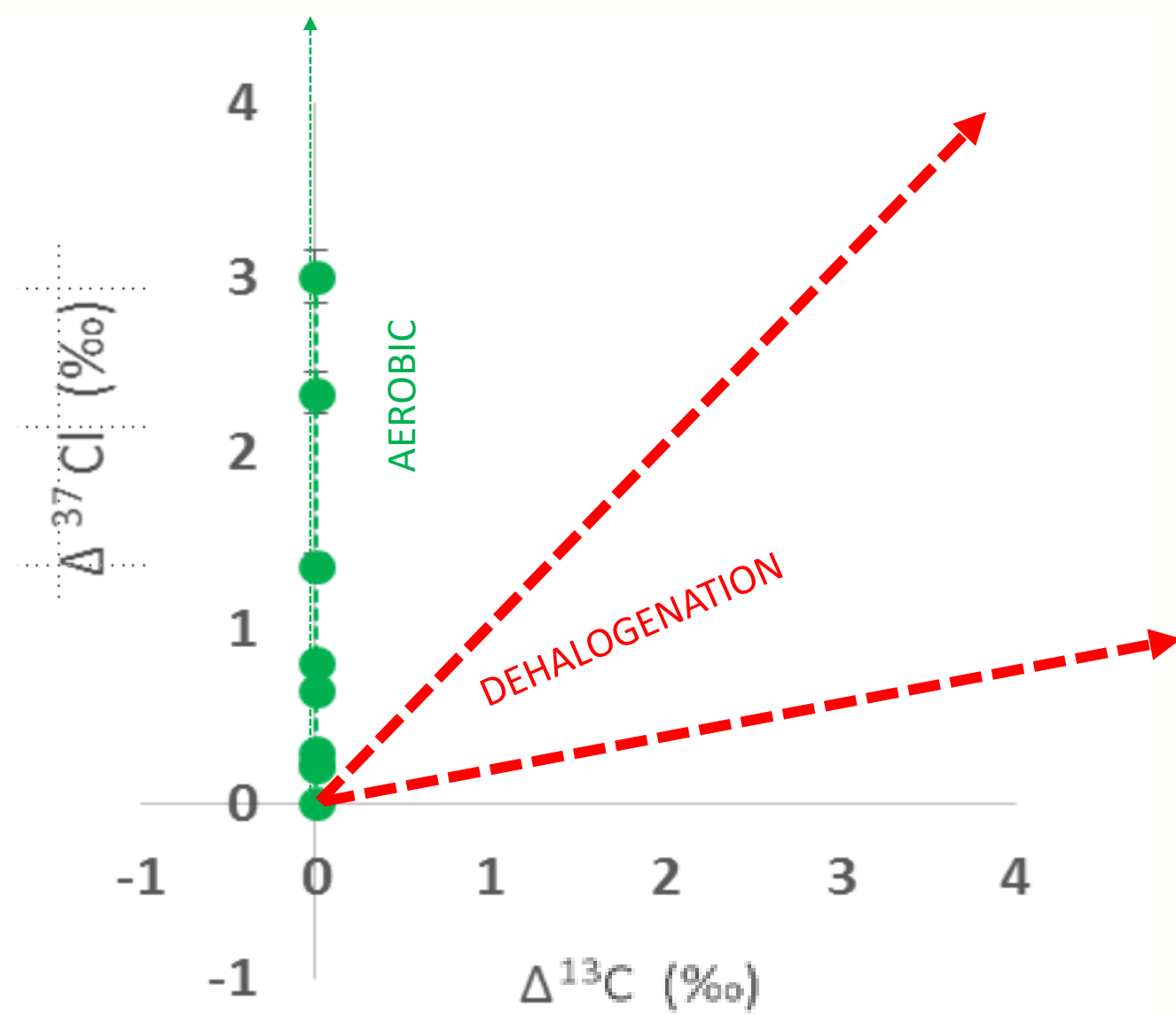
Site B: Industrial Area in Milan, Italy

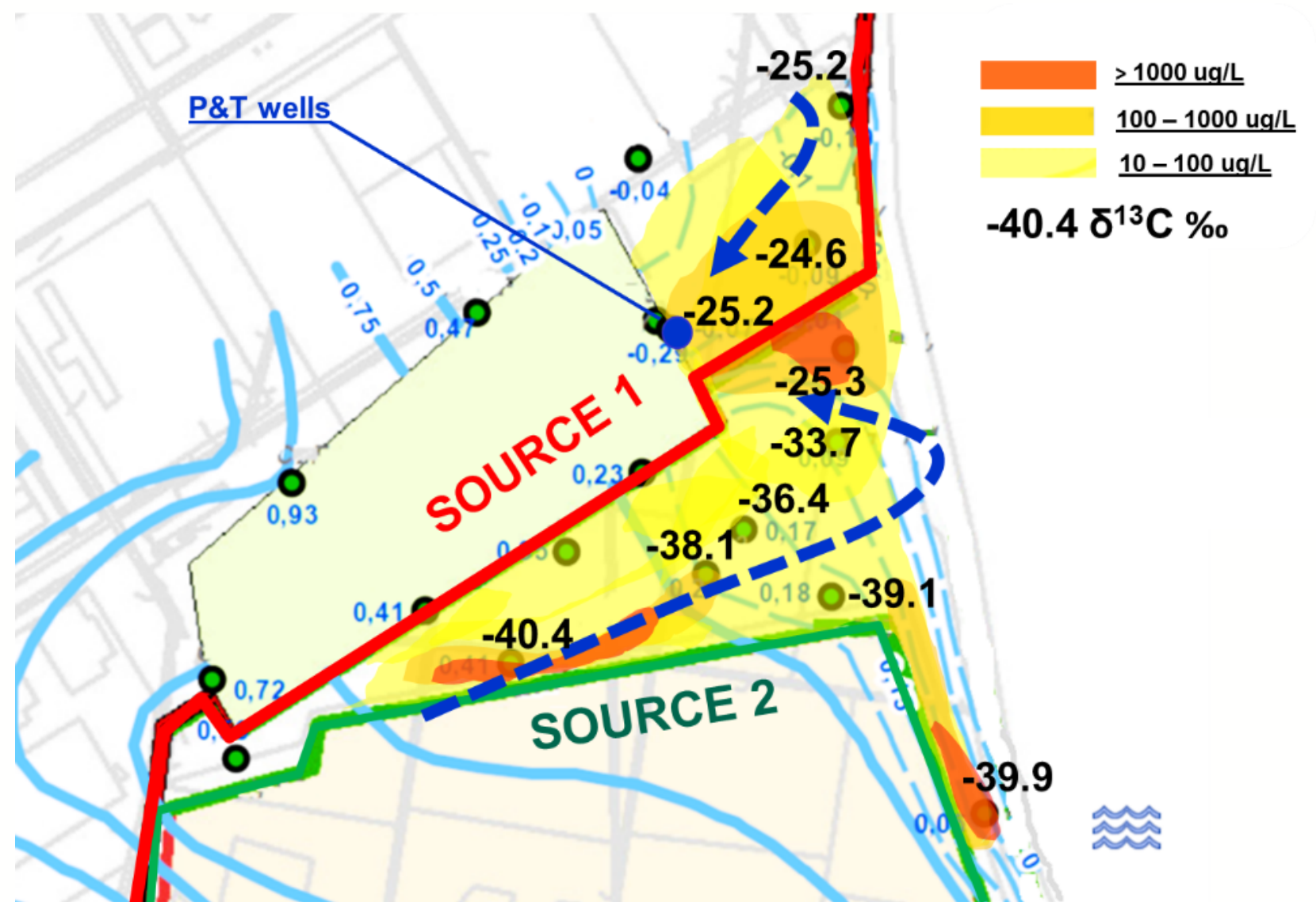


$\delta^{13}\text{C}$ - CSIA

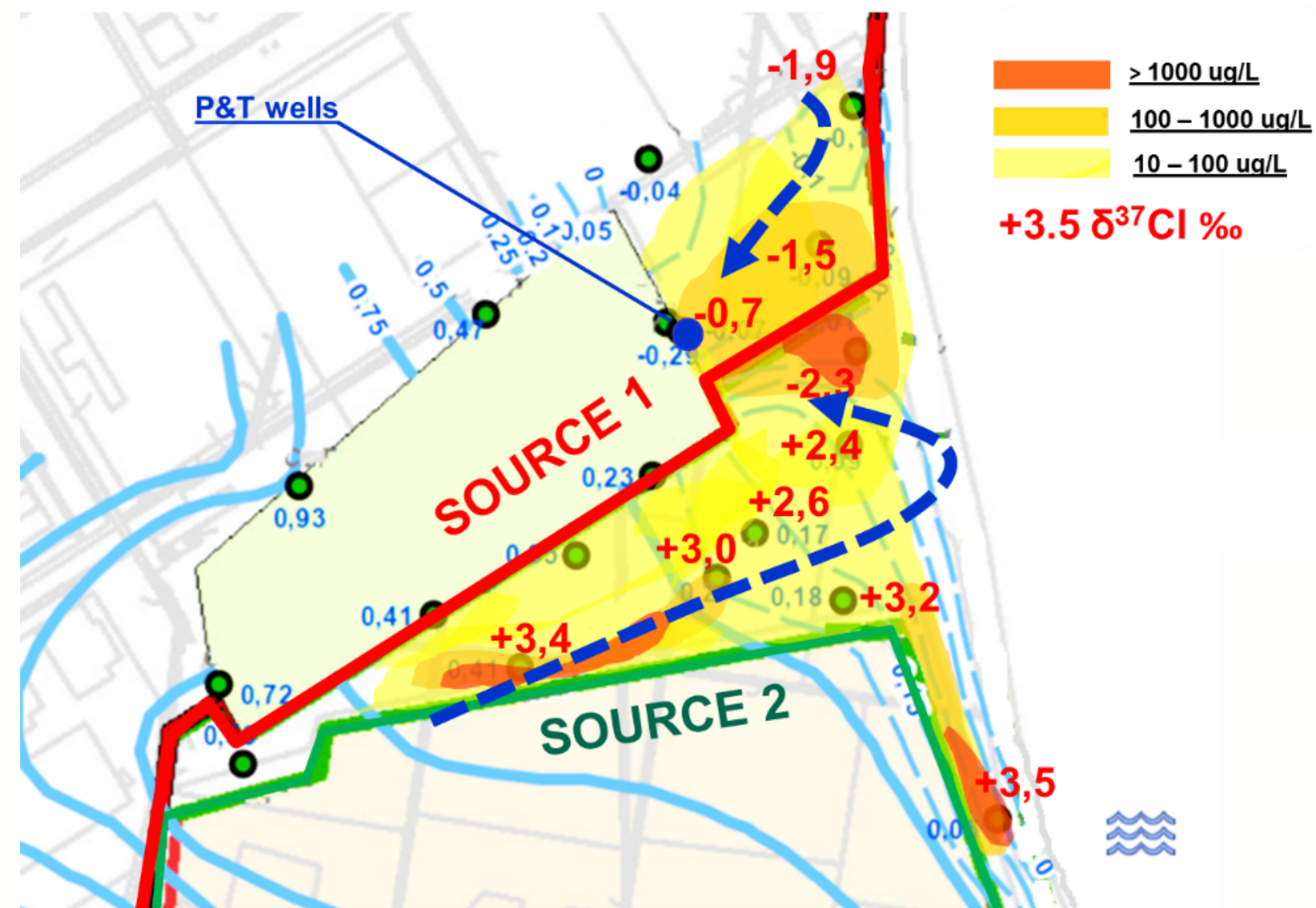
By using only $\delta^{13}\text{C}$ it is not possible to differentiate between mixing and biodegradation

Laboratory Experiment

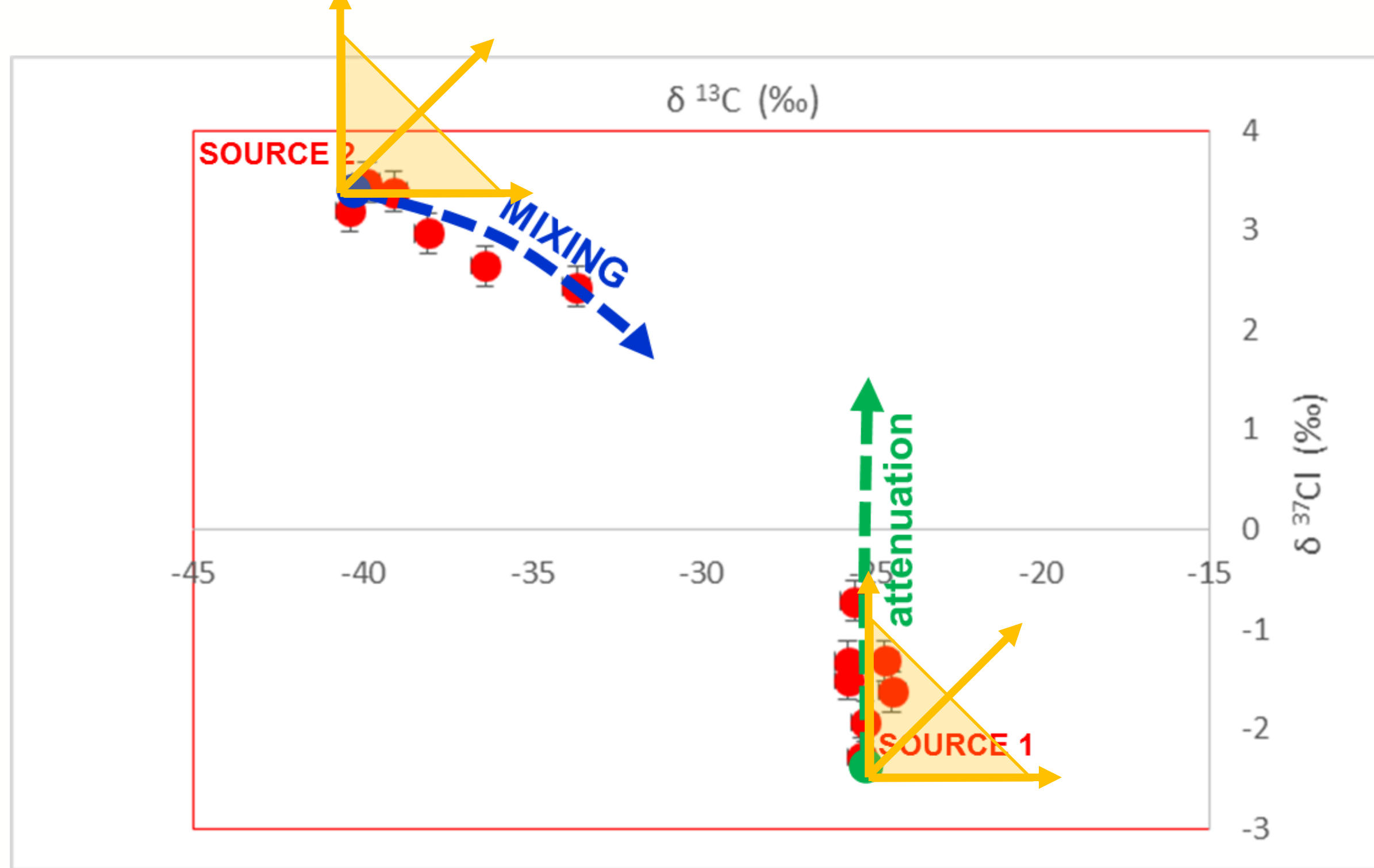




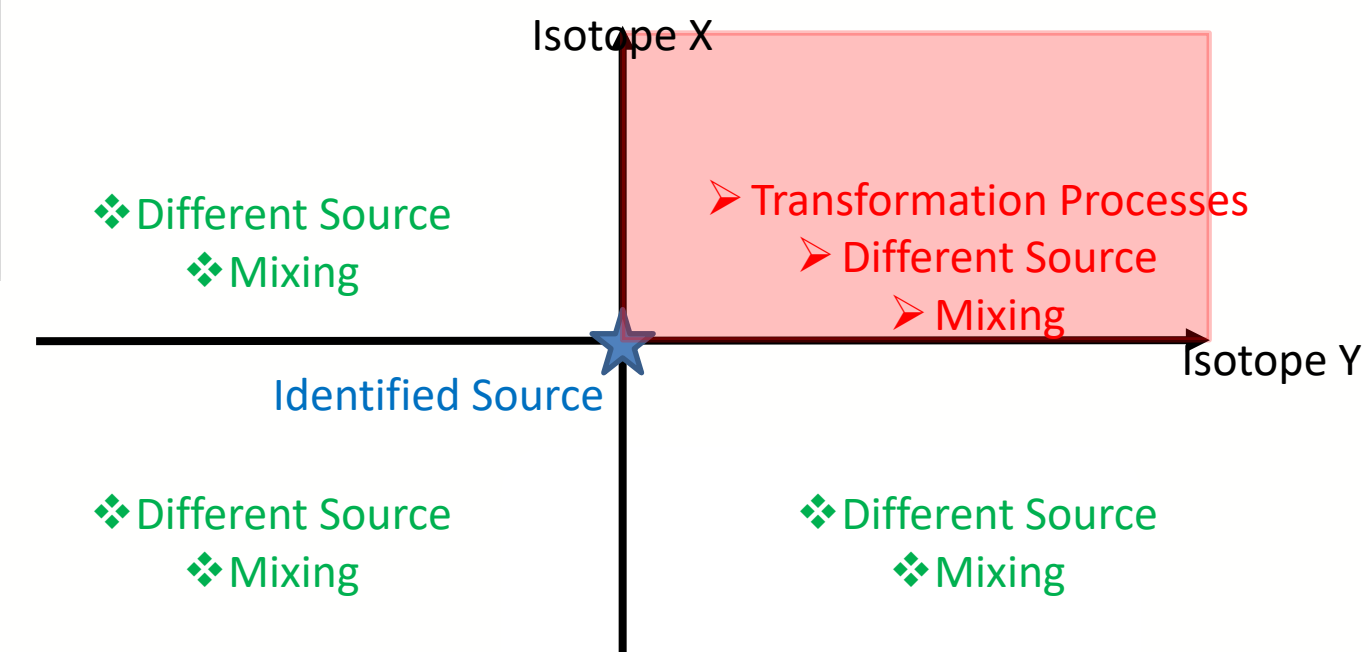
$\delta^{13}\text{C}$ - CSIA



$\delta^{37}\text{Cl}$ - CSIA



The two dimensional CSIA allows the differentiation between mixing and biodegradation

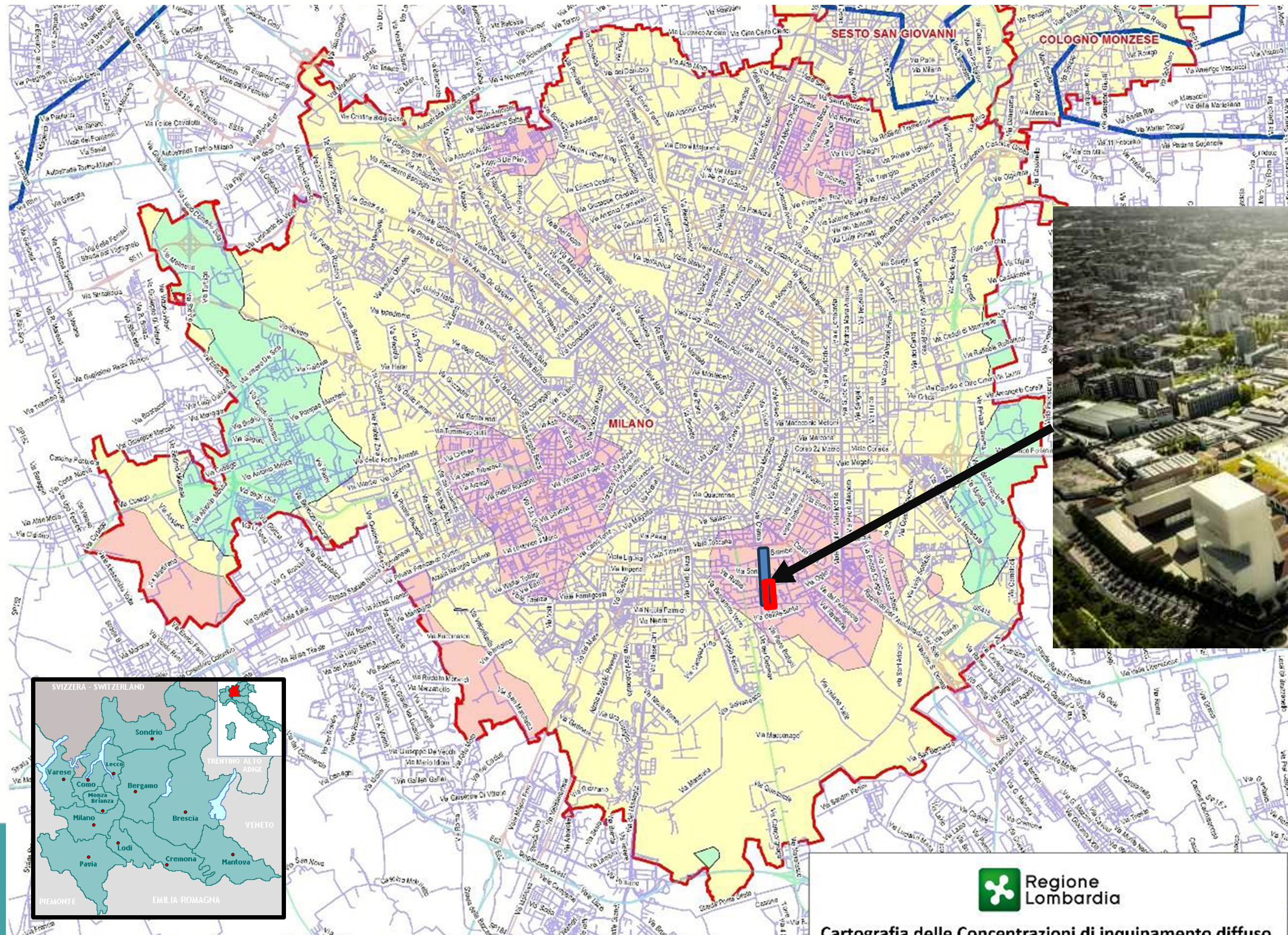


Well	ug/L	$\delta^{13}\text{C}$ ‰	$\delta^{37}\text{Cl}$ ‰	$\delta^2\text{H}$ ‰	Source 1 %	Source 2 %	Biodegradation %
P-10	1050	-39,1	3,4	63	100		-
P-6	2950	-39,9	3,5	59	100		-
P-5	205	-40,4	3,2	60	100		-
P-3	282	-38,1	3,0		90	10	-
P-2	72	-36,4	2,6	55	80\95	5\20	-
P-1	115	-33,7	2,4	25	60\80	20\40	40 - 85 %
P-8	735	-24,4	-1,6	-91		100	65 %
P-9	1530	-25,3	-2,3	-91		100	-
P-86	188	-25,7	-1,3			100	75 %
B-28	670	-25,7	-1,5	-96		100	70 %
B-53	14	-25,2	-1,9			100	45 %
B-27	12	-24,6	-1,3			100	75 %
P-84	5	-25,5	-0,7			100	95 %

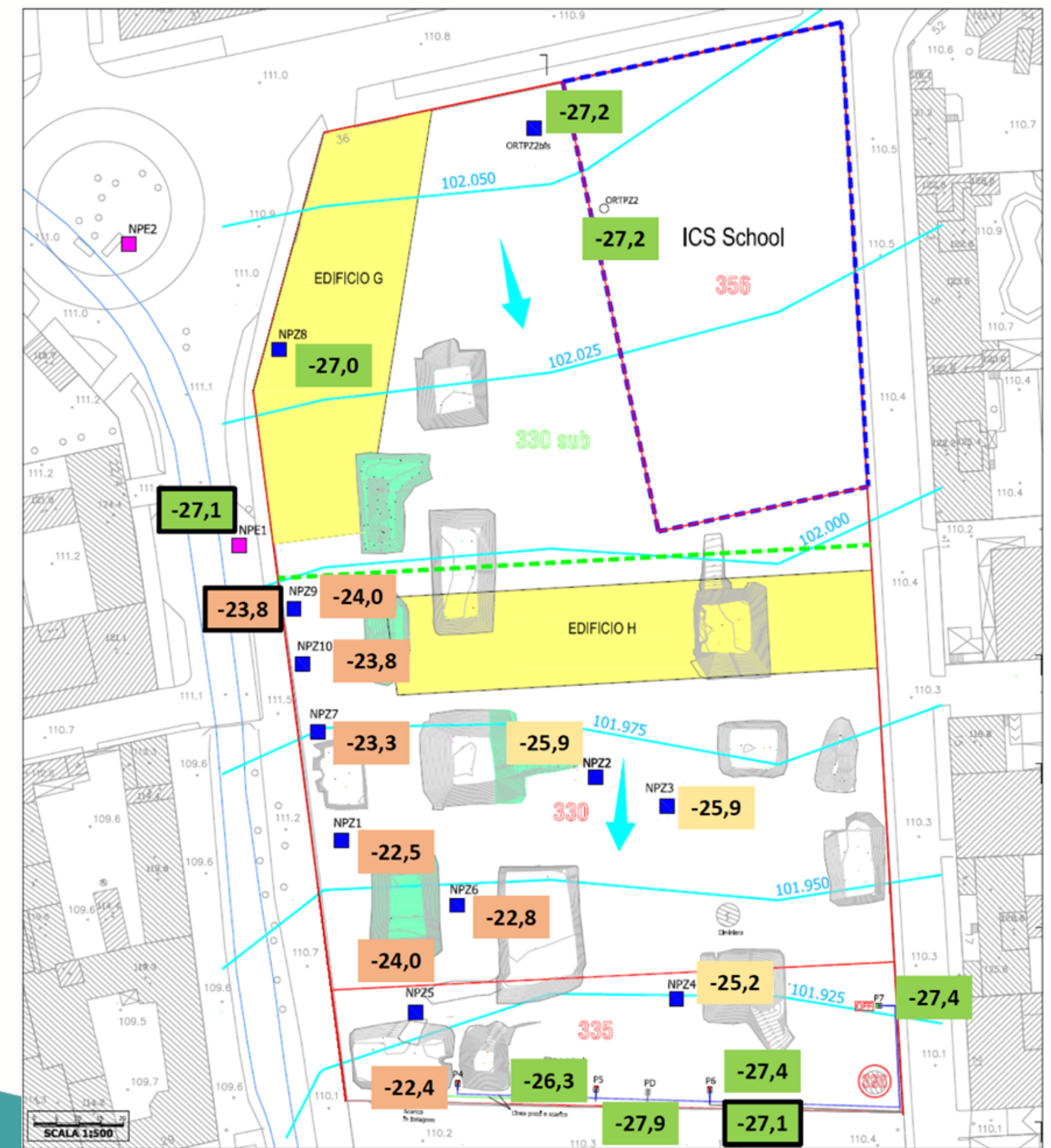
An aerial photograph of a rural landscape featuring a patchwork of agricultural fields in various shades of brown, green, and yellow. Small clusters of houses and buildings are scattered throughout the fields. A large, semi-transparent white letter 'A' is overlaid on the left side of the image. The title 'SITE SCALE APPLICATION' is centered in the middle of the image in a white, serif font.

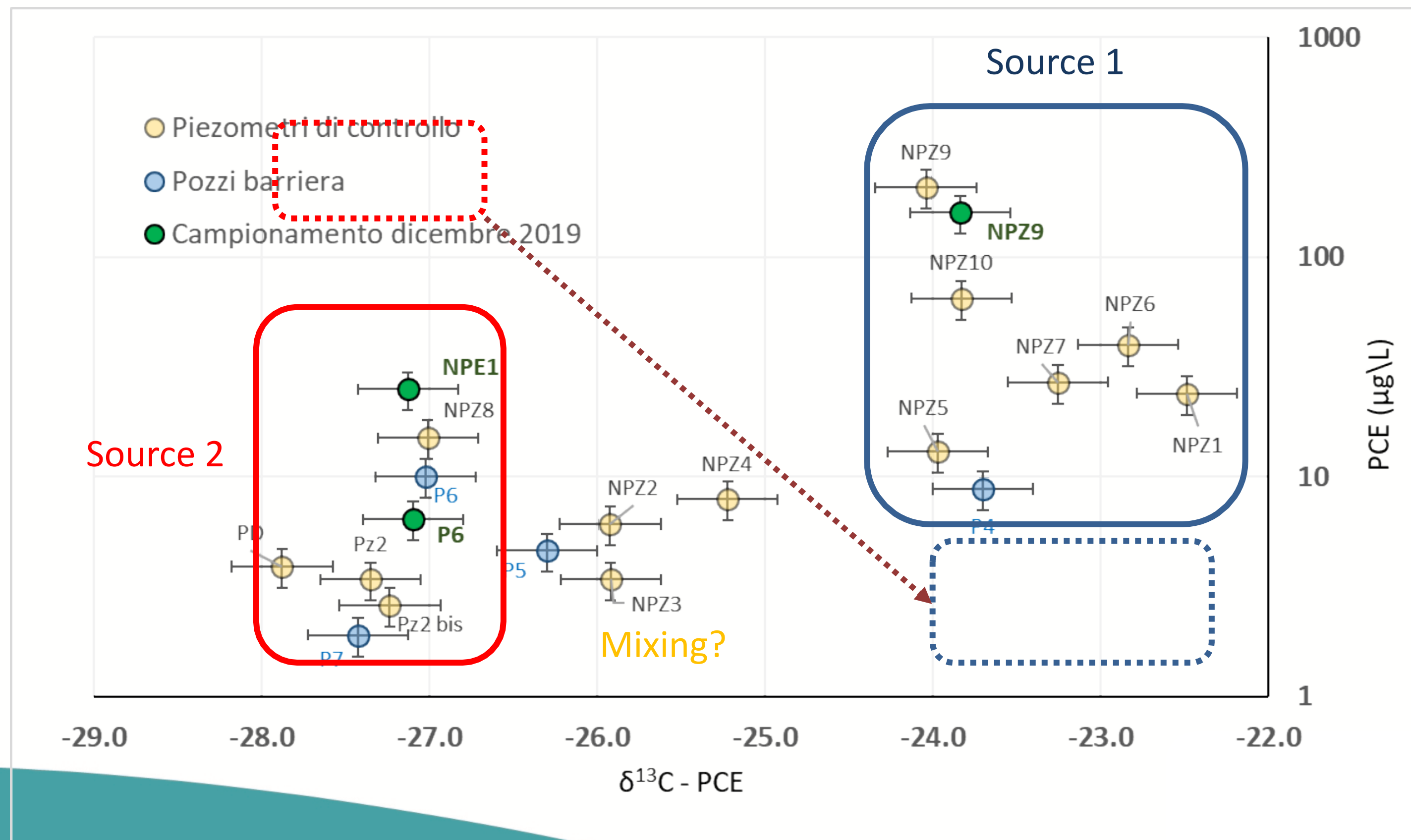
SITE SCALE APPLICATION

ITE SCALE



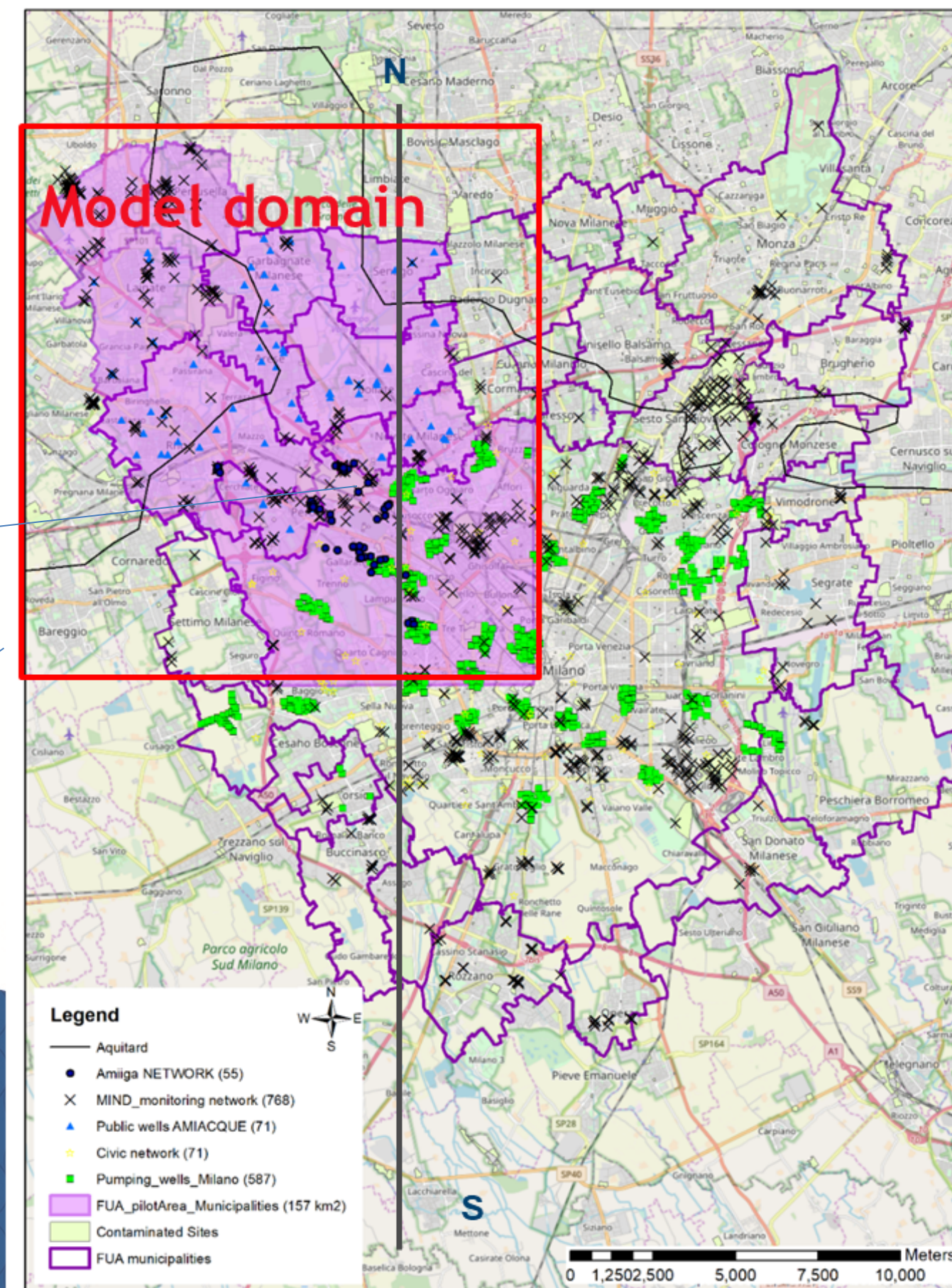
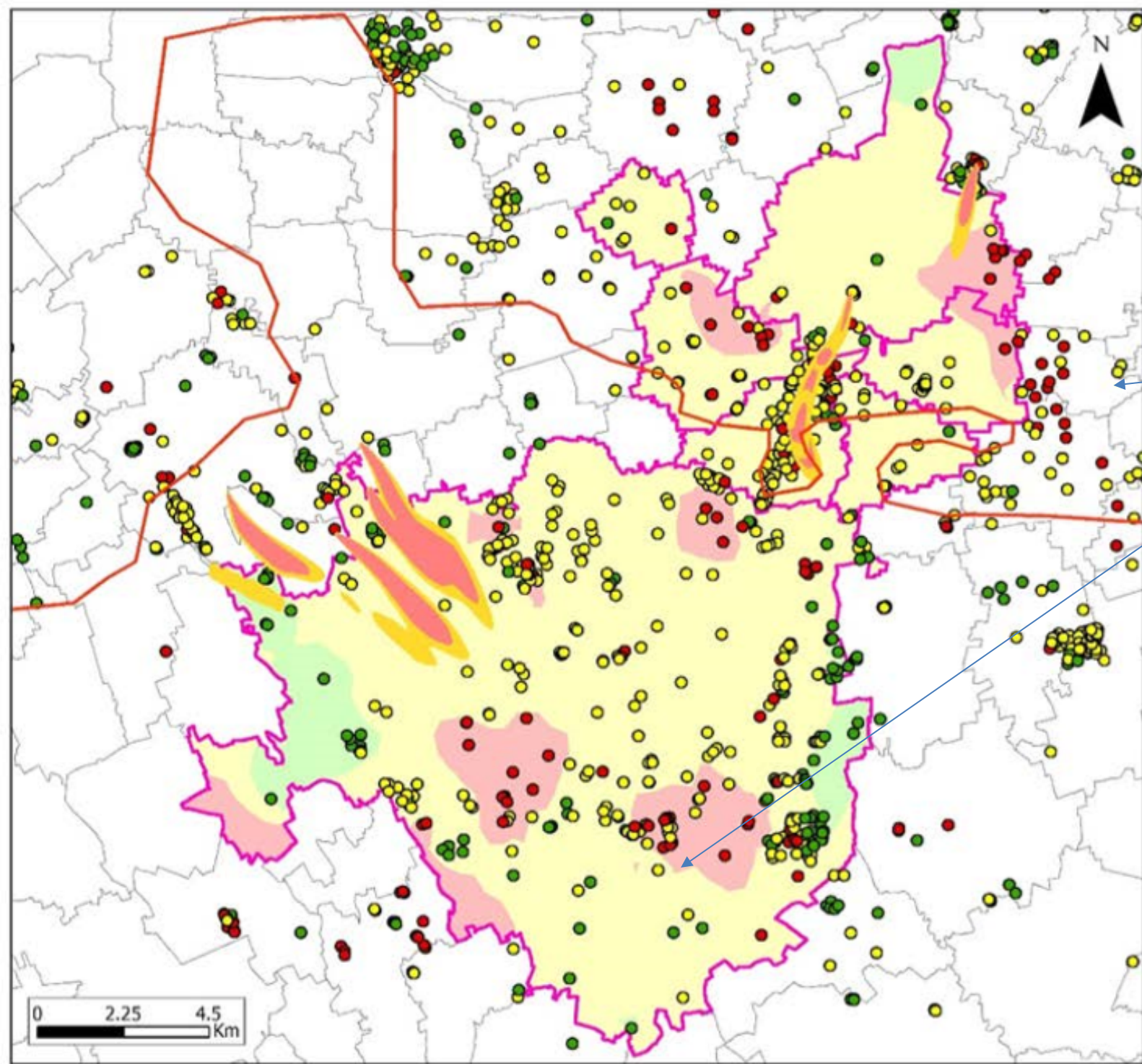
Milano
Italy

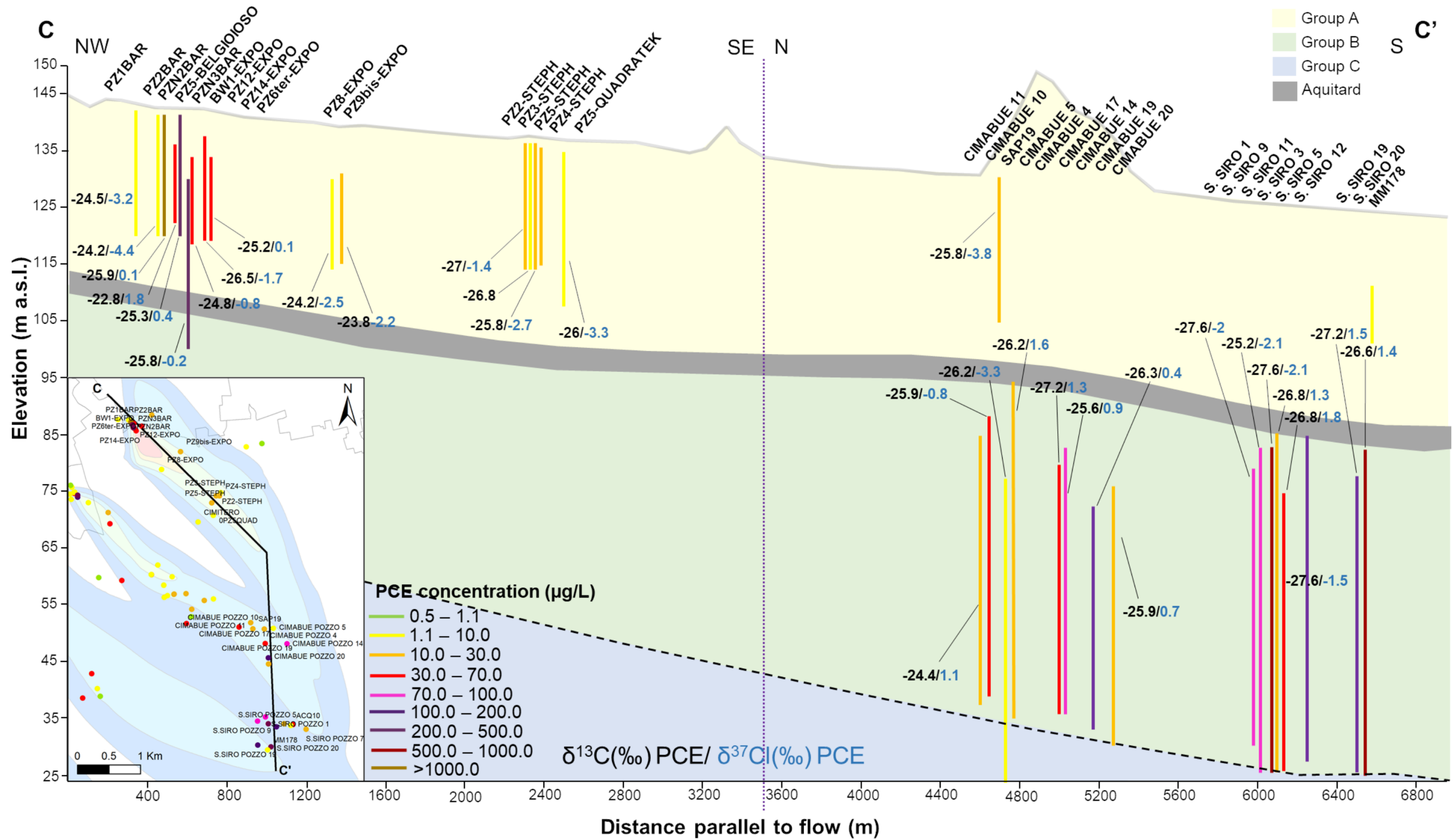
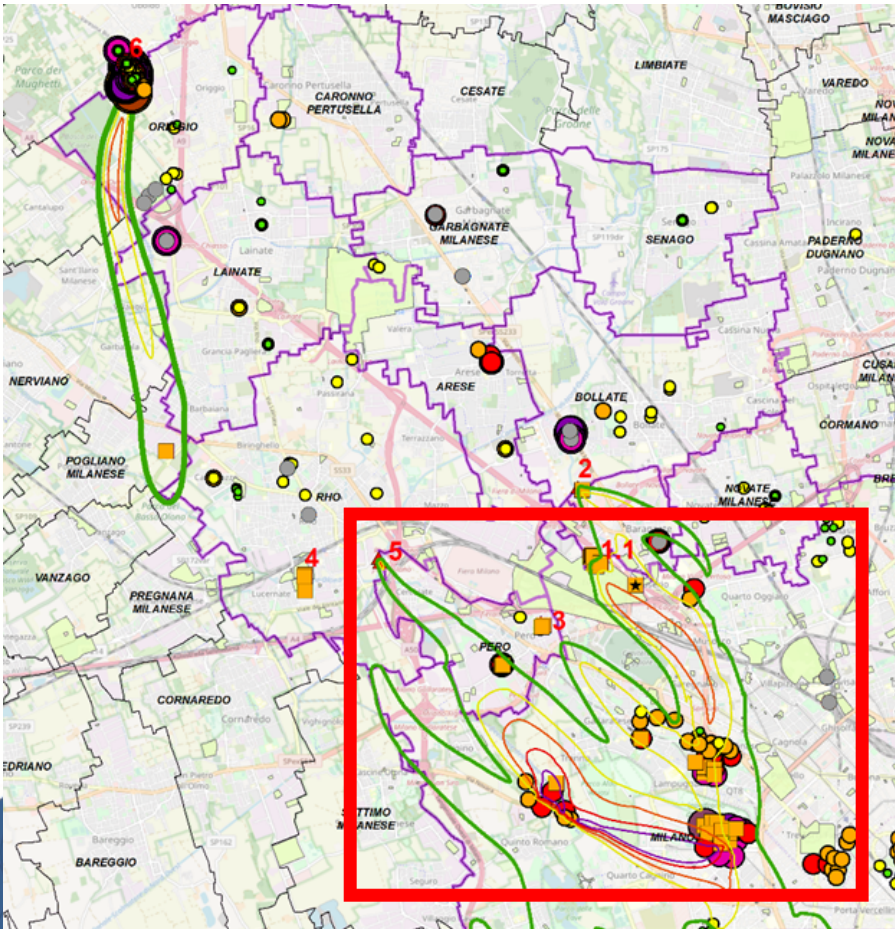


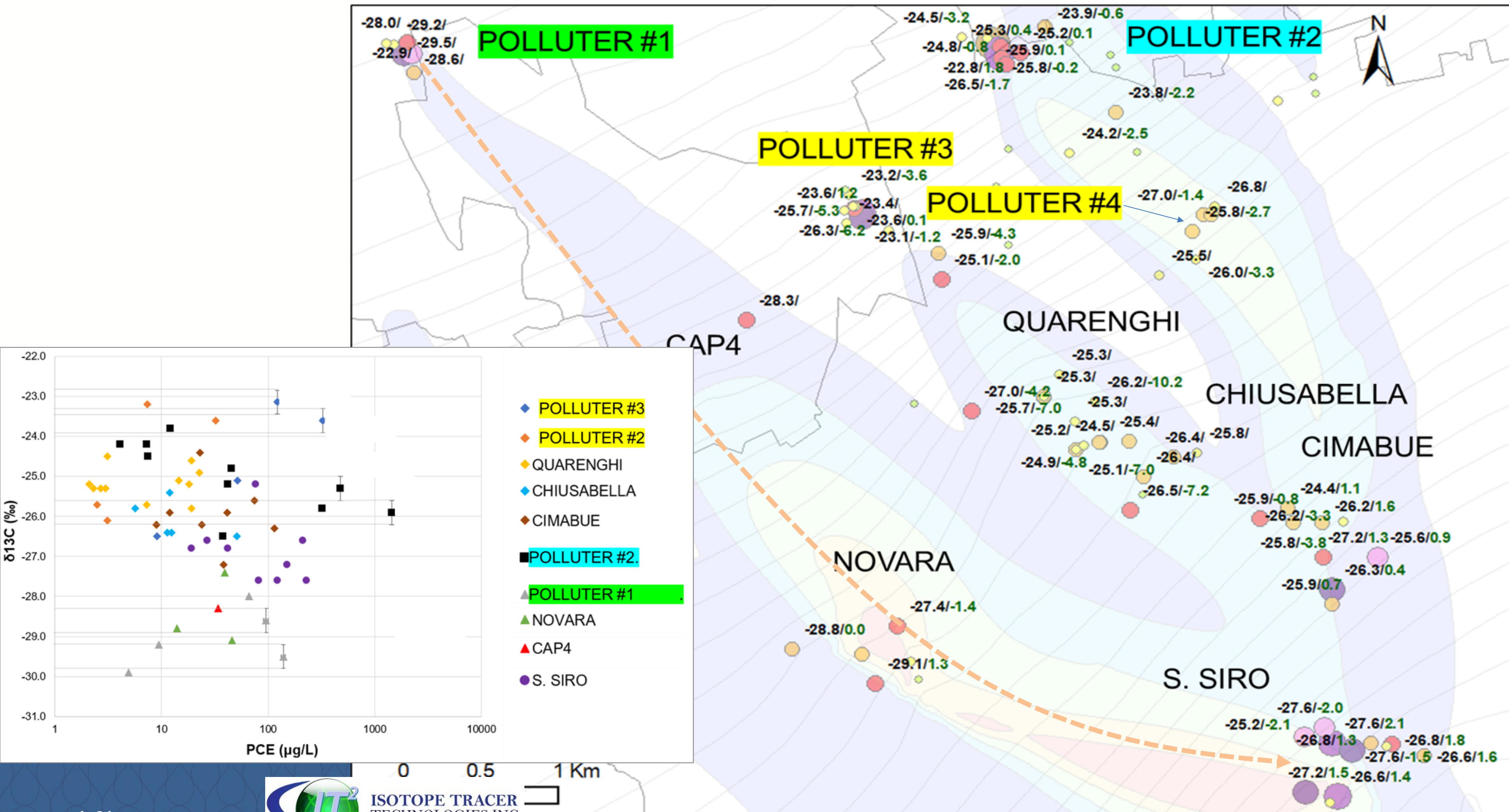


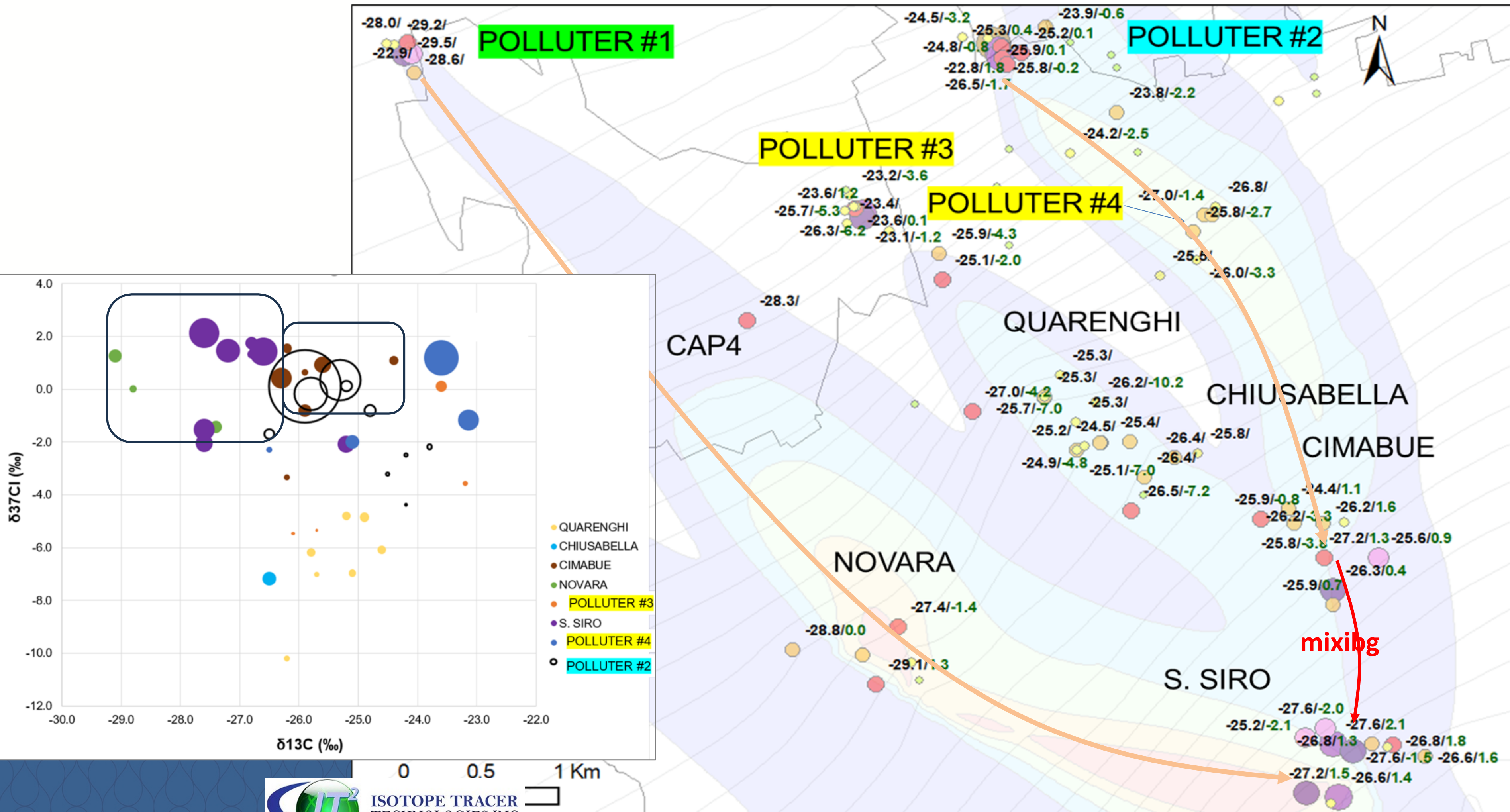
LARGE FUA SCALE APPLICATION

LARGE FUA SCALE / WSP









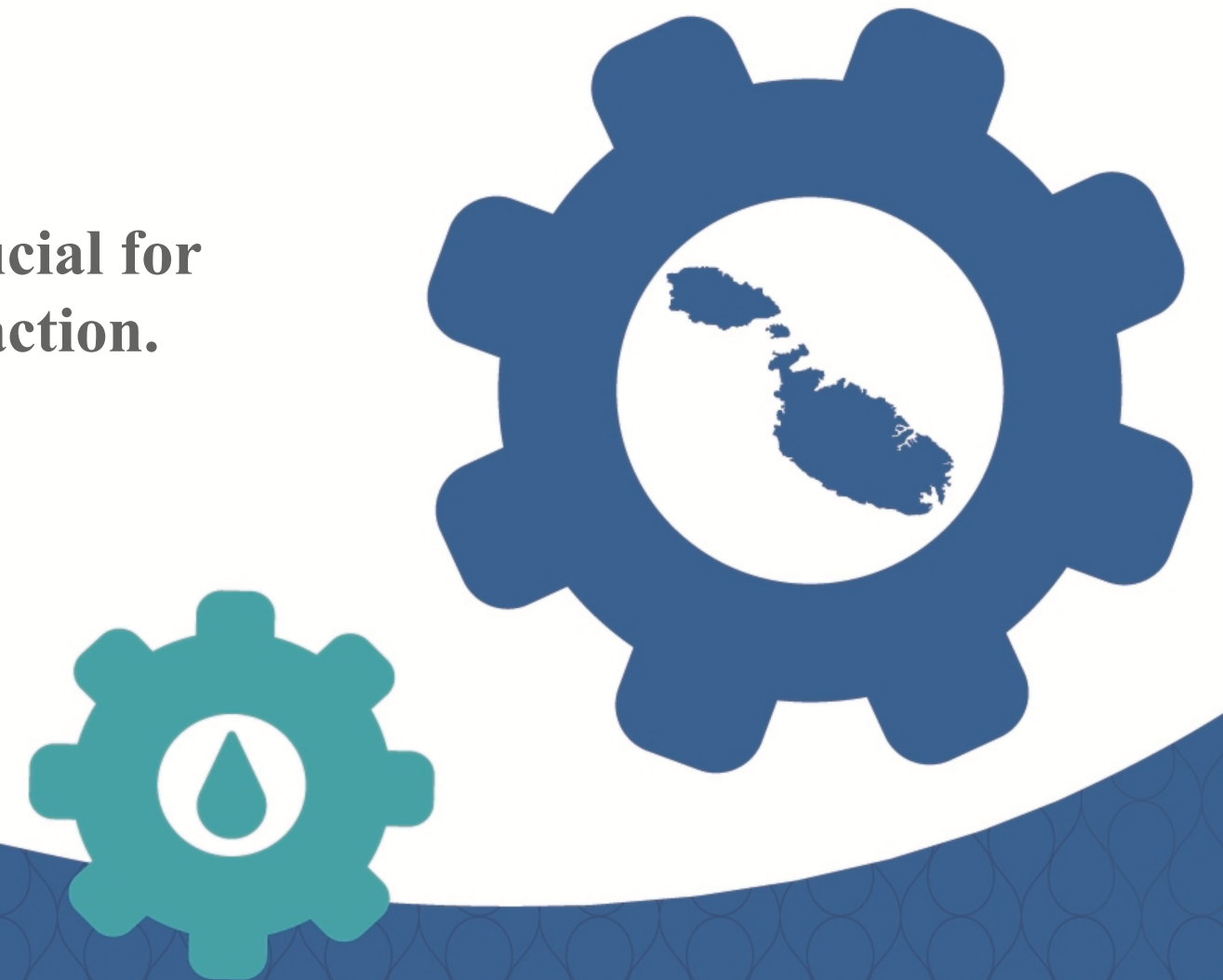
OUTCOMES

The utilization of CSIA enabled the identification of contamination sources

Helps in better understanding processes.

Identifies transformation mechanisms.

Distinguishing between diffuse and local/point source contamination is crucial for assigning responsibilities accurately and identifying the correct course of action.





Thank you for your attention



Orfan Shouakar-Stash

Email: orfan@it2isotopes.com

www.it2isotopes.com



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