

New technology for monitoring the efficiency of in situ chemical oxidation (ISCO) treatments with persulfate

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Grup MAiMA - Isòtops estables i Mineralogia -

Departament de Mineralogia, Petrologia i Geologia Aplicada
Facultat de Ciències de la Terra
Universitat de Barcelona

MAiMA: Who we are?

MAiMA is a research group from the University of Barcelona that applies the **latest technology in stable isotope analysis, mineralogy and geochemistry**.

MAiMA counts with a multidisciplinary team of specialists, with complementary background in: **Geology, Environmental Sciences, Earth Sciences, Chemistry, Biology** and previous experiences abroad and in private consultancies.



MAiMA Team: 21 people

7 Senior Researchers (UB)

3 Post-Doc Researchers

4 PhD Students

2 Scientific Project Managers RDI

1 European Project Manager

1 Coordinator MSc Hydrogeology & Modelling

1 Laboratory Manager

2 Laboratory Technicians

MAiMA: Who we are?

+30 Years

Recognized experience in
mineralogy and isotope
geochemistry



More than 25 national projects
8 European projects and more
than 200 scientific publications



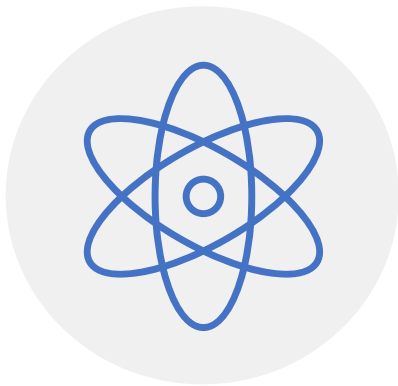
Tecnio Accreditation

Strong commitment in knowledge
transfer, participating in more than
100 R&D&I projects

CCiTUB

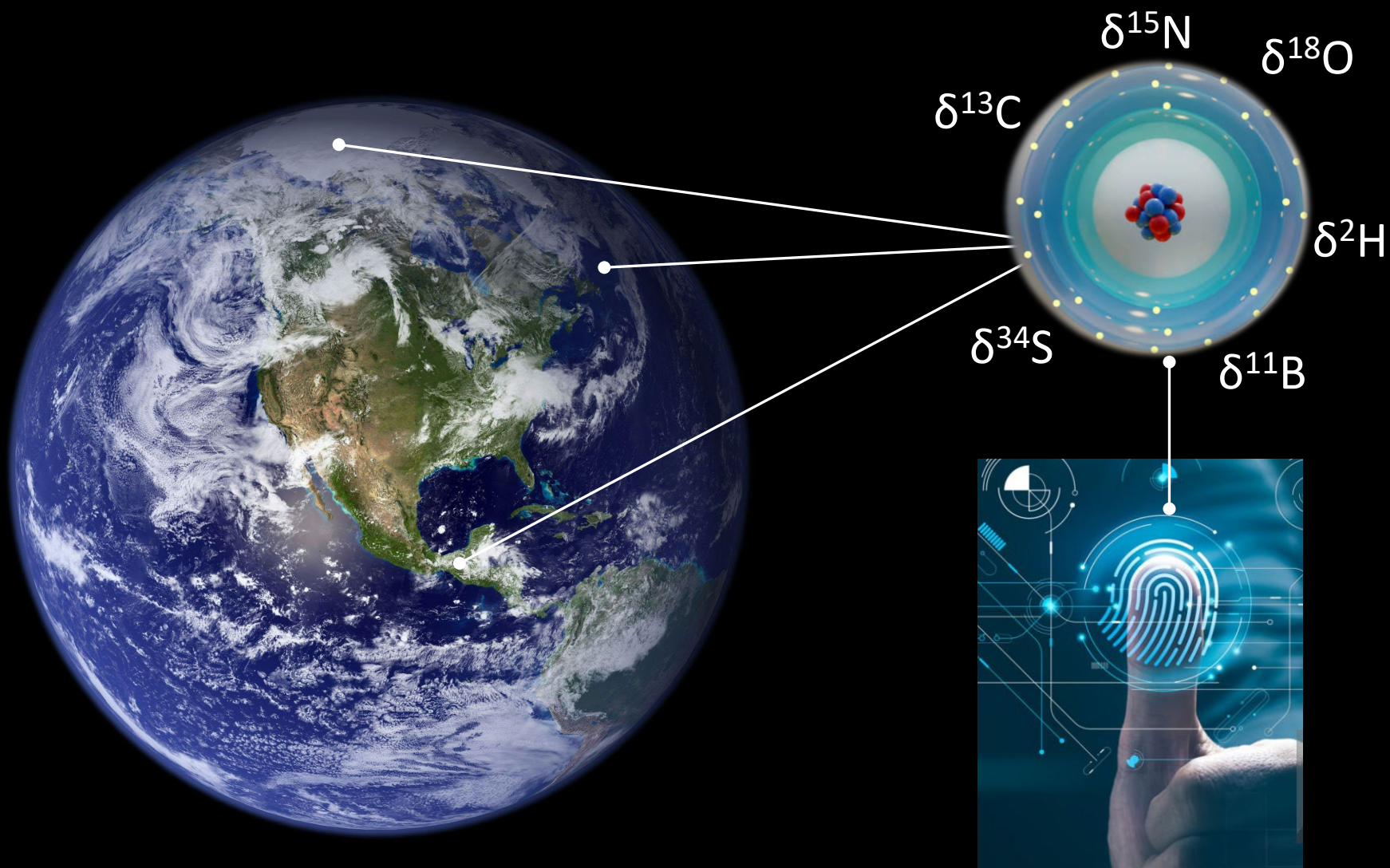
Technological Platform

Equiped with last generation
scientific instrumentation.
ISO 9001: 2015 Accreditation



Stable isotopes

for environmental pollution diagnosis



Isotopic fingerprint

Stable isotopes for environmental pollution diagnosis

Fingerprinting



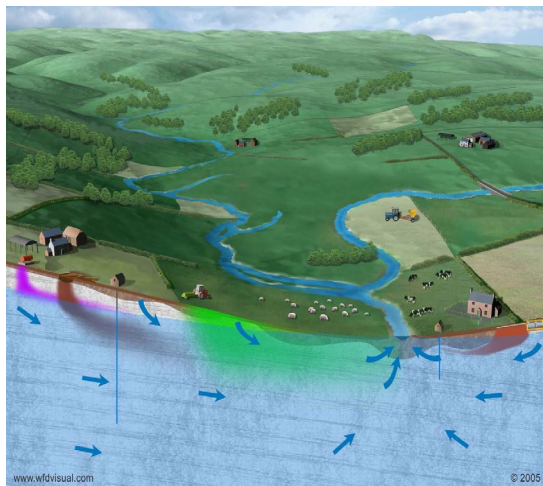
- Identify **sources**
- Single vs. **multiple** sources
- **Contribution** from different sources

Degradation Assessment

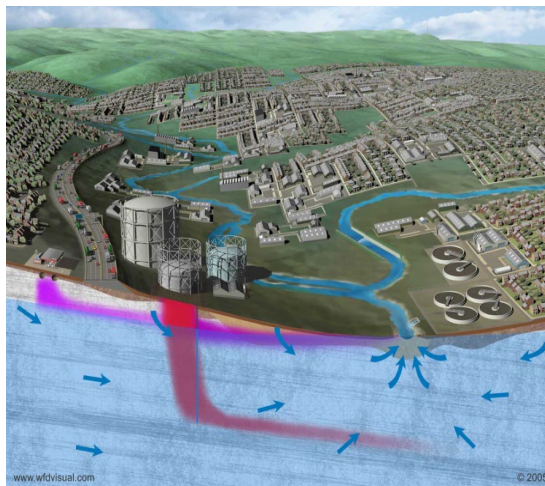


- Direct **evidence** of degradation
- Degradation **extent**
- Degradation **pathways** and mechanisms

Agriculture and Livestock



Industrial



Mining



Contaminants/tracers:

- Nitrates, ammonium
- Sulfates
- Boron
- Water
- Micropollutants: pesticides

Isotopes:

$\delta^{15}\text{N}_{\text{NO}_3^-}$, $\delta^{18}\text{O}_{\text{NO}_3^-}$, $\delta^{15}\text{N}_{\text{NH}_4^+}$
 $\delta^{34}\text{S}_{\text{SO}_4^{2-}}$, $\delta^{18}\text{O}_{\text{SO}_4^{2-}}$, $\delta^{34}\text{S}_{\text{H}_2\text{S}}$
 $\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{13}\text{C}_{\text{DOC}}$
 $\delta^2\text{H}_{\text{H}_2\text{O}}$, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$
 $\delta^{11}\text{B}$
CSIA: $\delta^{13}\text{C}$, $\delta^{37}\text{Cl}$

Contaminants:

- Chlorinated VOCs
- Petroleum hydrocarbons (BTEX)
- Fuel oxygenates (MTBE, ETBE)
- Polycyclic Aromatic Hydrocarbons (PAHs)
- Lindane (HCHs)

Isotopes:

Chlorinated VOCs: $\delta^{13}\text{C}$, $\delta^{37}\text{Cl}$
BTEX, MTBE, ETBE, PAHs, HCHs: $\delta^{13}\text{C}$, $\delta^2\text{H}$

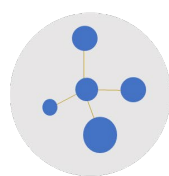
Contaminants/tracers:

- Nitrates
- Sulfates
- Water

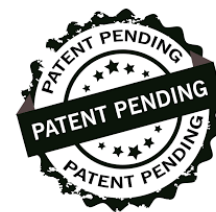
Isotopes:

$\delta^{15}\text{N}_{\text{NO}_3^-}$, $\delta^{18}\text{O}_{\text{NO}_3^-}$
 $\delta^{34}\text{S}_{\text{SO}_4^{2-}}$, $\delta^{18}\text{O}_{\text{SO}_4^{2-}}$
 $\delta^2\text{H}_{\text{H}_2\text{O}}$, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$

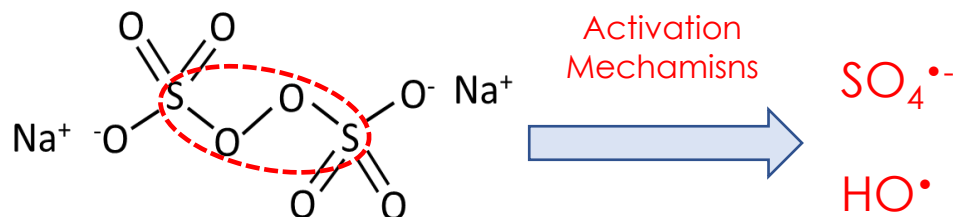
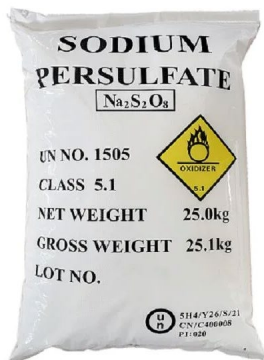
New technology for monitoring the efficiency of **in situ chemical oxidation (ISCO)** treatments with persulfate



IscoTracer
Stable Isotope Analysis



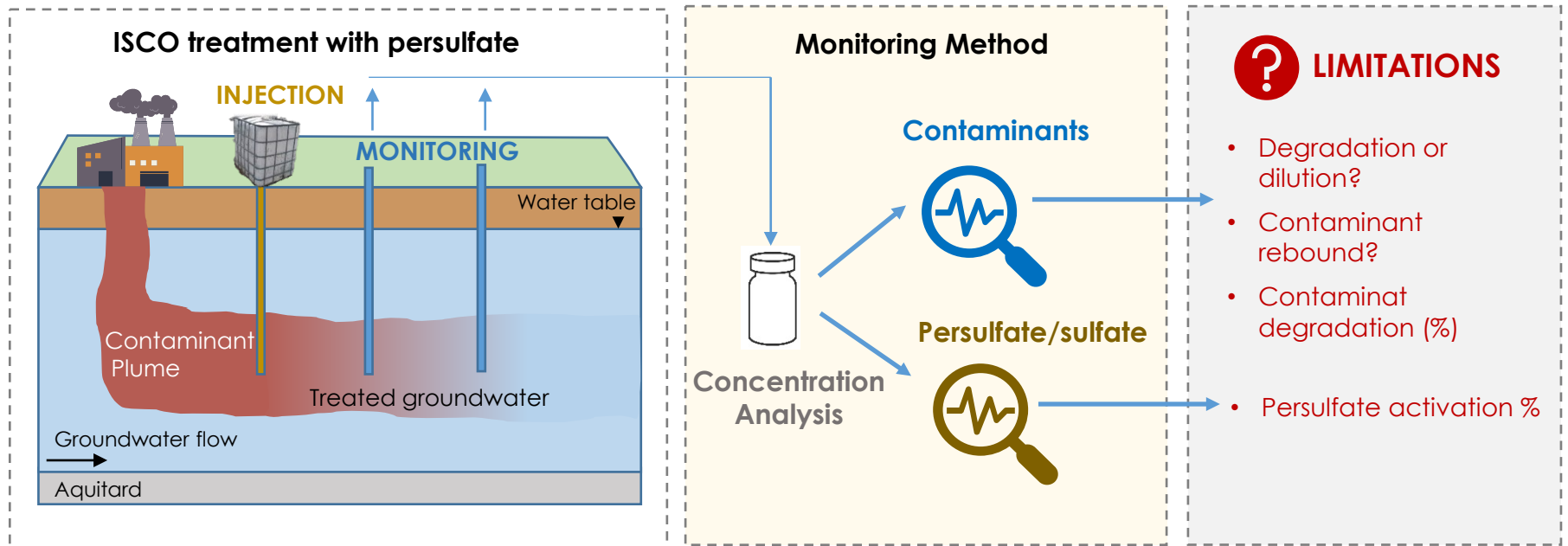
PERSULFATE (sodium peroxodisulfate)

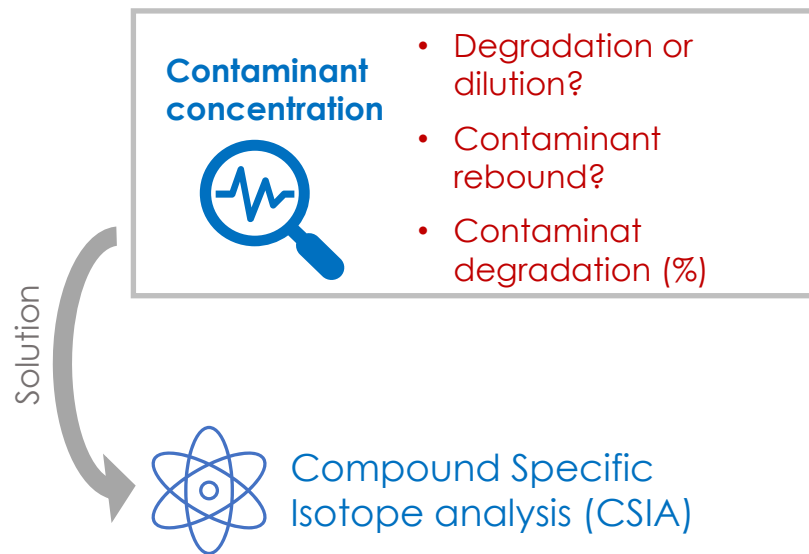


Standard reduction potentials E° (V)

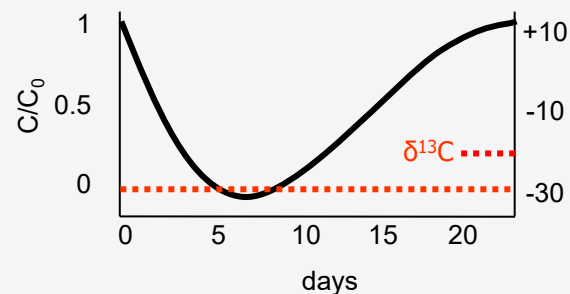
$\text{S}_2\text{O}_8^{2-} + 2\text{e}^- \rightarrow 2\text{SO}_4^{2-}$	+2.01 V	Peroxodisulphate
$\text{SO}_4^{\bullet-} + \text{e}^- \rightarrow \text{SO}_4^{2-}$	+(2.6 – 3.1) V	Sulphate radical
$\text{OH}^{\bullet} + \text{H}^+ + \text{e}^- \rightarrow \text{H}_2\text{O}$	+2.76 V	Hydroxyl radical

Bennedsen et al. *Chemistry of Advanced Environmental Purification Processes of Water*, 2014

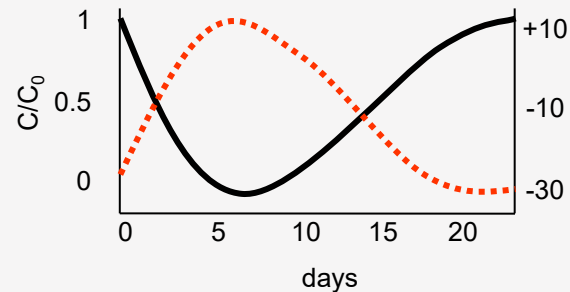




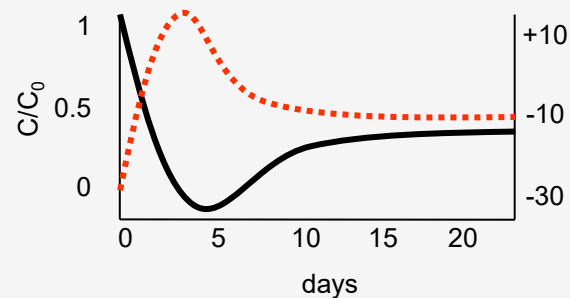
Compound Specific Isotope analysis (CSIA) of contaminants



Dilution/
Displacement



Degradation +
Rebound



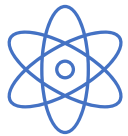
Degradation

Contaminant concentration

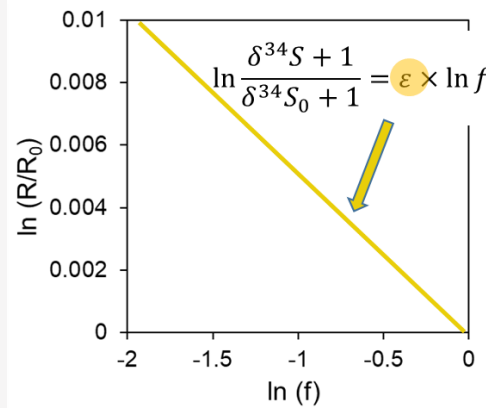


- Degradation or dilution?
- Contaminant rebound?
- Contaminant degradation (%)

Solution



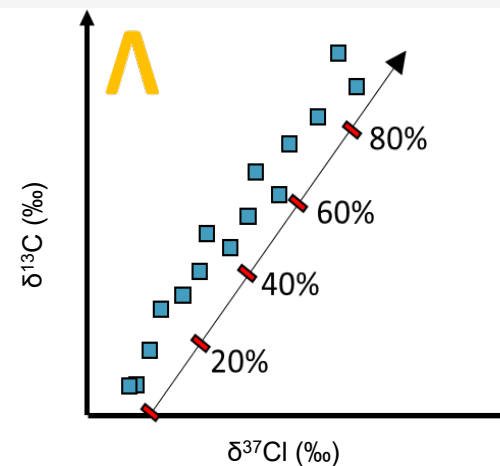
Compound Specific Isotope analysis (CSIA)



Fraccionament isotòpic (ϵ)

$$D[\%] = \left[1 - \left(\frac{\delta^{13}C_t + 1000}{\delta^{13}C_0 + 1000} \right)^{\left(\frac{1000}{\epsilon} \right)} \right] \times 100$$

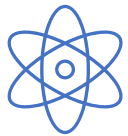
2-D Isotòpic anàlisis



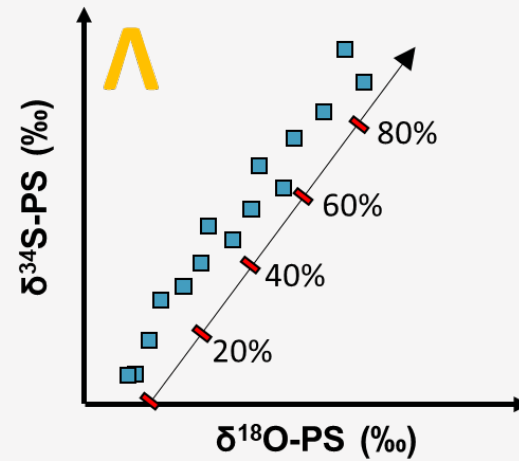
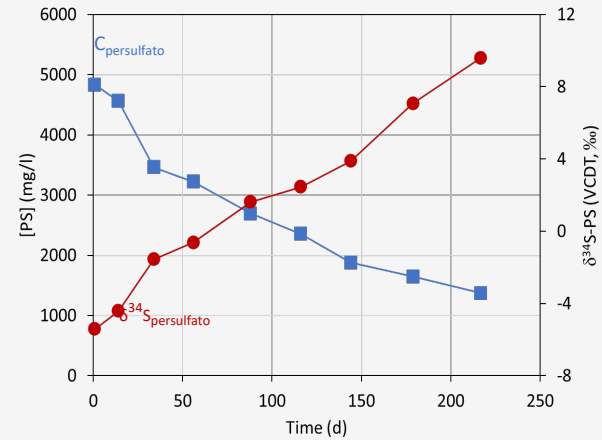
Concentració
 Persulfat/sulfat • Persulfate activation %



Solution



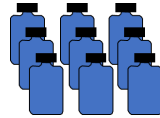
Compound Specific
Isotope analysis (CSIA)



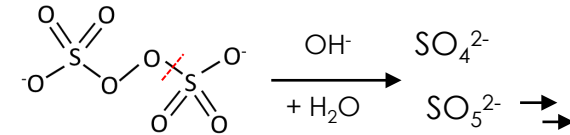
Persulfate (PS) Activation experiments

Alkaline activation

[PS] = 5 g/L (26 mM)
[NaOH] = 1 M pH ~ 13

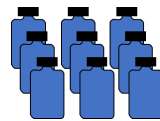


25 °C

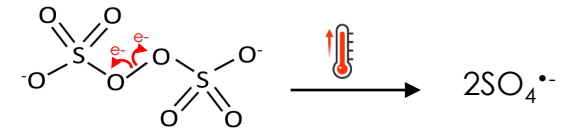


Thermolysis

[PS] = 5 g/L (26 mM)
pH ~ 6.5
(Phosphate buffer 3 mM)



50 °C

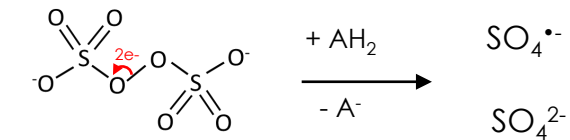


Activation with organic acid

[PS] = 5 g/L (26 mM)
Ascorbic acid
[AH₂] = 2 – 24 mM



25 °C



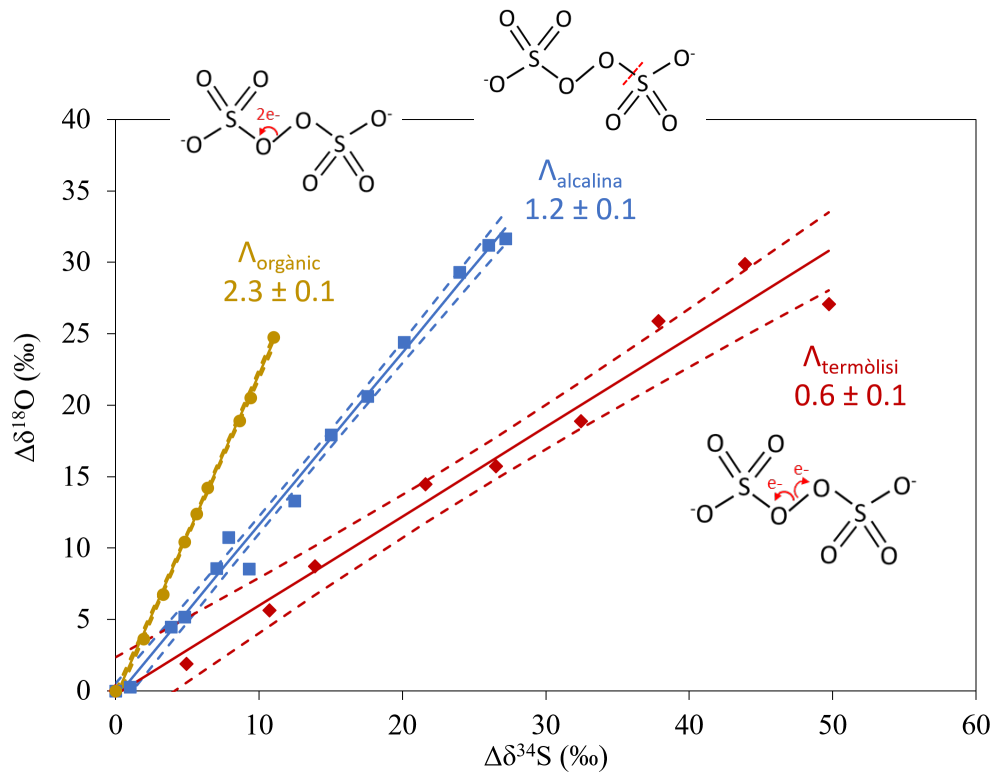
PS remanent ($\text{S}_2\text{O}_8^{2-}$)



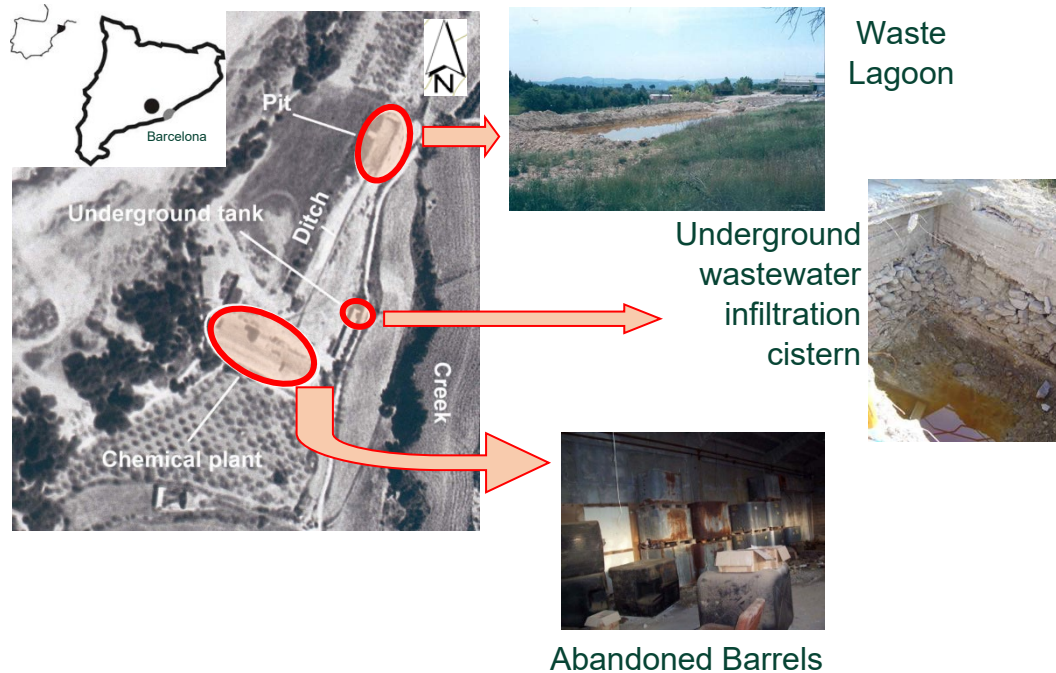
Concentració (Espectrofotometria)

$\delta^{18}\text{O}$ EA-TC-IRMS
 $\delta^{34}\text{S}$ EA-IRMS





- ➡ **Significant S and O isotope fractionation** of PS occurs across all activation mechanisms.
- ➡ The dual-isotope slopes (Λ) differ depending on the activation mechanism. It is possible to **identify the processes controlling PS activation**.
- ➡ Isotope fractionation during PS activation allows for the calculation of the **activation %**.



Former factory of phytosanitary products

Very complex site (*Palau et al., 2014*)

- Fractured aquifer
- Mixture of chlorinated organic compounds
- Various sources of contamination



Installation (2006)



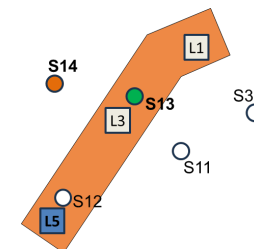
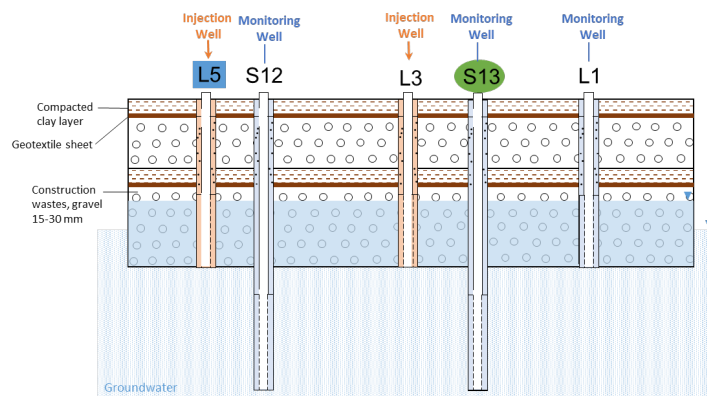
**Construction
wastes
(concrete)**



pH alkaline 11.5 ± 0.2

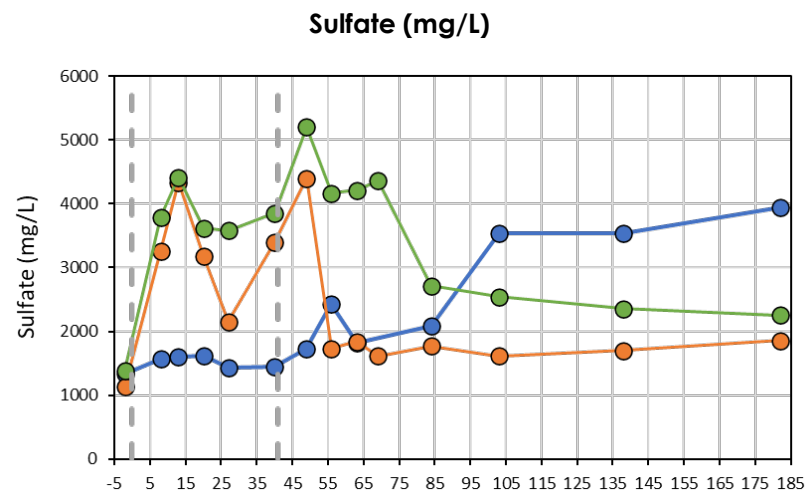
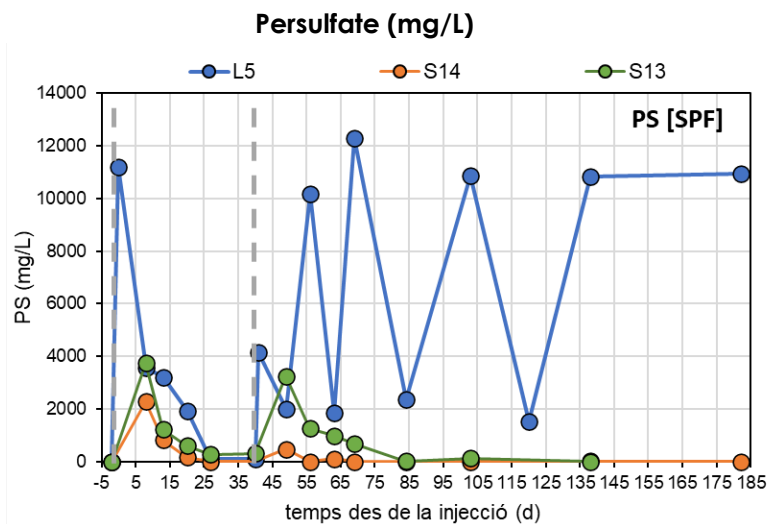
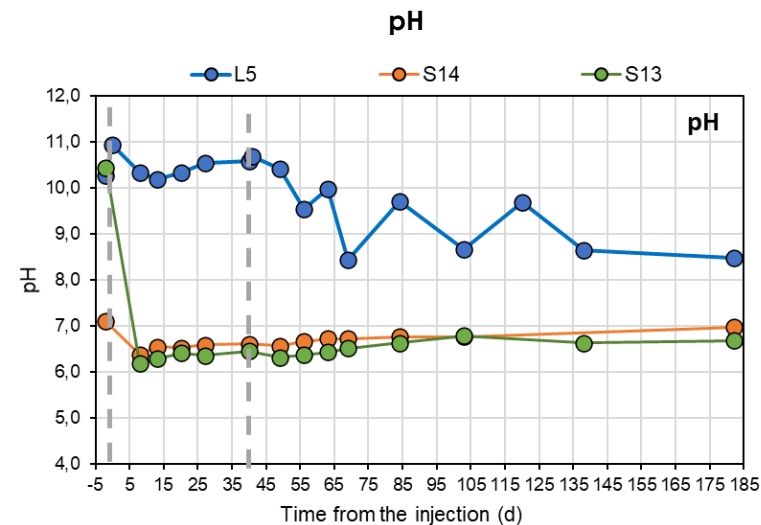
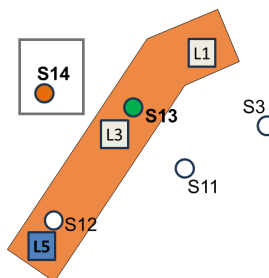
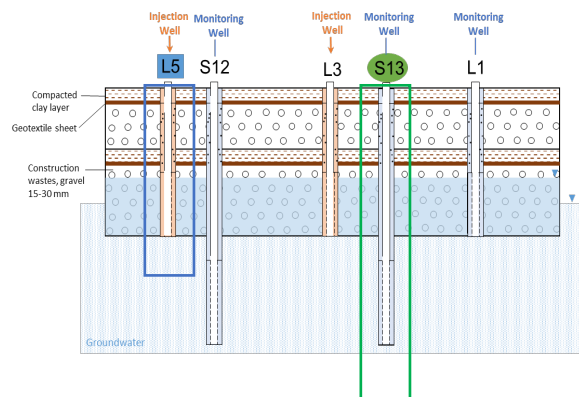


Permeable reactive barrier in the non-saturated zone

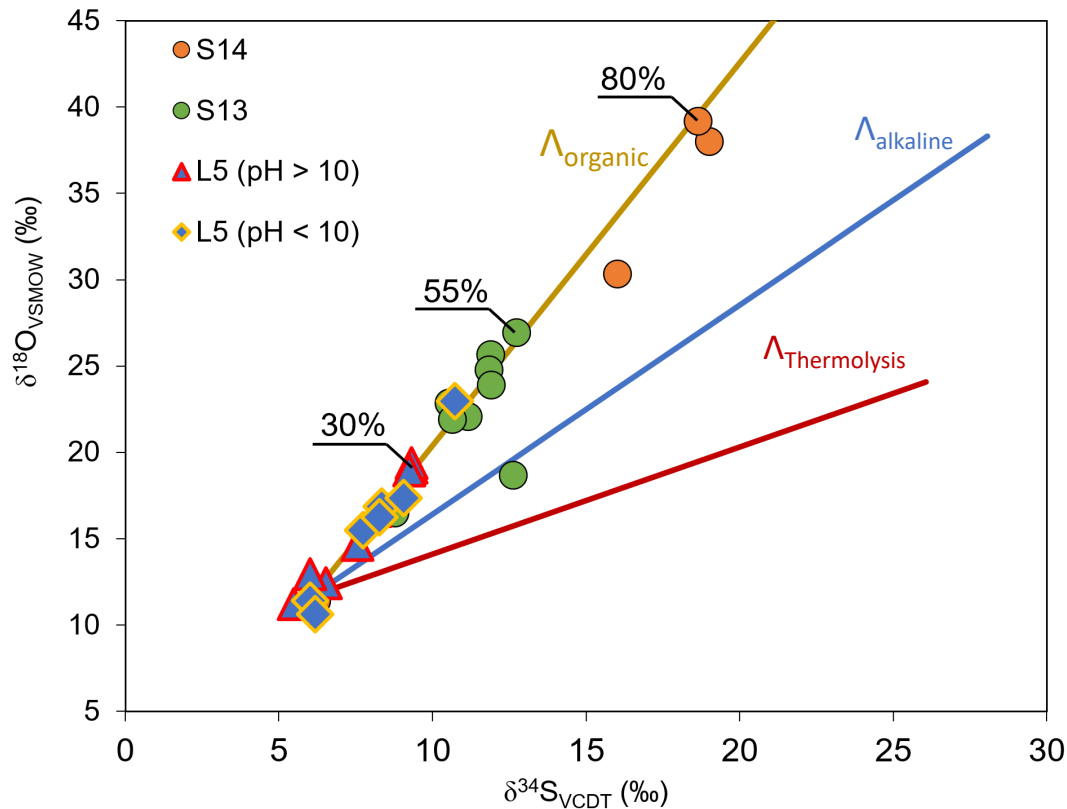


- **Two injections:** **March and April 2024**
- **Oxidant:** **diluted $\text{Na}_2\text{S}_2\text{O}_8^{2-}$** (200 kg KLOZUR®, Evonik Industries AG in 700L of downstream groundwater)
- **Flow rate:** **4 L/min**
- **Injection wells:** **L5** and **L3**

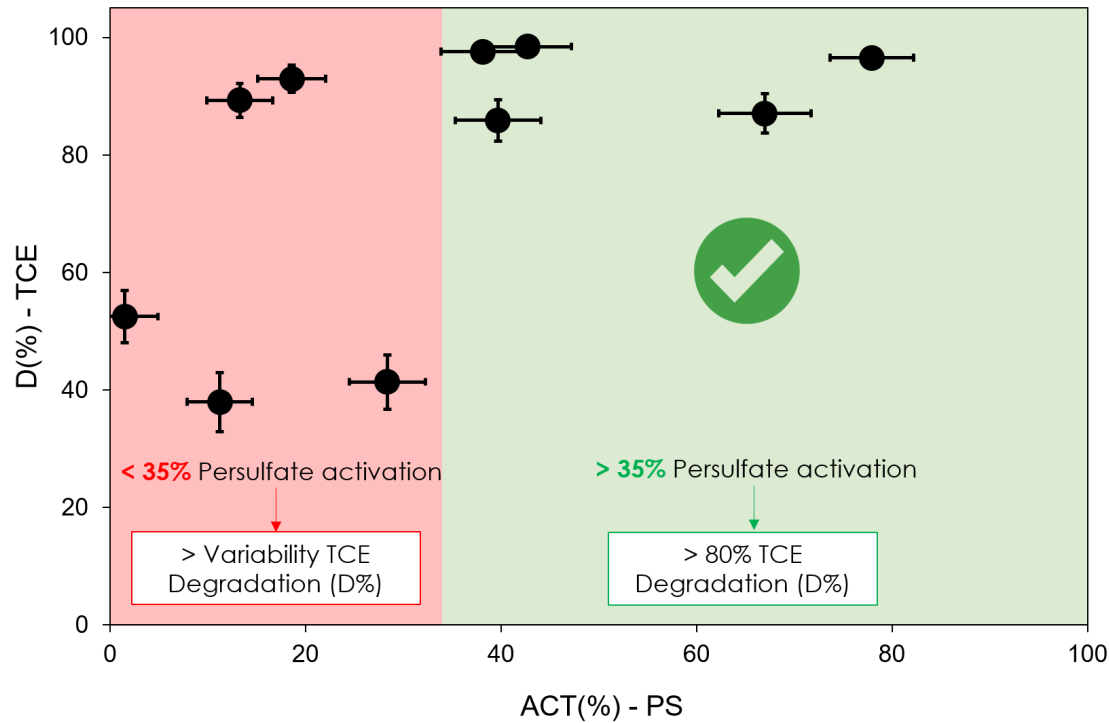
Classic monitoring parameters



Anàlisi de la composició isotòpica del S i O del persulfat



- It has been possible to identify **the persulfate activation mechanism in the field.**
- Alkaline activation does not play an important role, the main activation mechanism is **activation with an organic substrate.**
- It has been possible to calculate the **percentage of persulfate activation in the field.**



➡ The representation of the % of persulfate activation vs. the % of contaminant degradation, provides a **robust tool to assess ISCO efficiency in the field**

BENEFITS IscoTracer



Key information for ISCO monitoring:

- **Oxidant:** Percentage of persulfate activation.
- **Contaminants:** extent of degradation of each contaminant.



Optimization of oxidant further injections: Better dose calculation, better planning of spatial and temporal distribution of injections.



Decision-making support tool: whether the ISCO treatment needs adjustment.



Time and cost savings: More efficient ISCO application.





Validated at
laboratory
Scale



Validation at field
scale (2 sites)
Undergoing



Patent
pending





Thanks for your attention!

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