USING ZERO-VALENT BIMETALS FOR THE DEGRADATION OF CHLORINATED SOLVENTS VAPORS IN THE UNSATURATED ZONE

Clarissa Settimi, **Daniela Zingaretti**, Iason Verginelli, Renato Baciocchi

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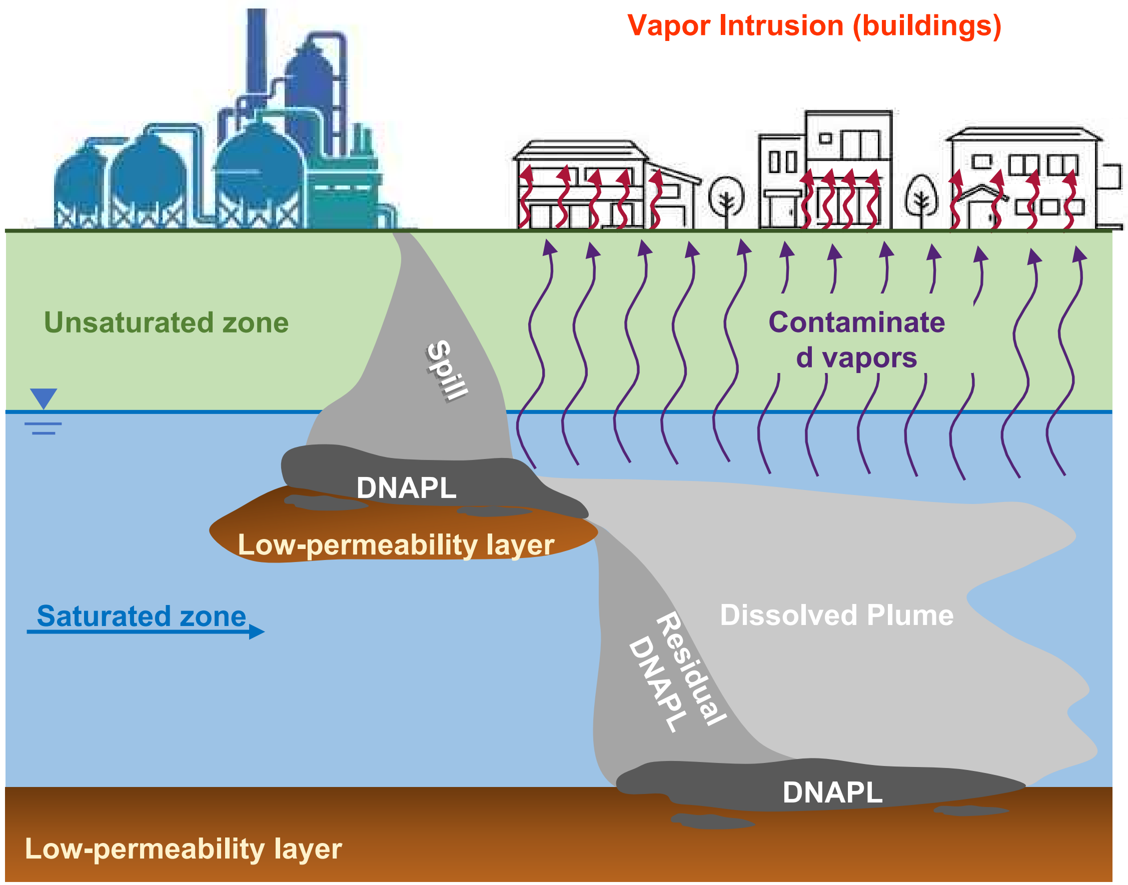
Chlorinated solvents: environmental behavior

CHLORINATED SOLVENTS such as trichloroethylene (**TCE**):

- Widely used in many applications
- Formation of Dense Non-Aqueous Phase Liquid (DNAPL)
- Large and diffuse contamination plumes
- Chemical Characteristics: volatile organic compounds (VOCs) and carcinogenic
- Critical pathway: Vapor Intrusion



Horizontal permeable reactive barriers (HPRB)

HORIZONTAL PERMEABLE REACTIVE BARRIER (HPRB) was proposed as vapor intrusion mitigation system

- ✓ Function: interrupt the volatilization pathway of contaminated vapors
- ✓ Filling material: Solid potassium permanganate
- ✓ Main findings:
  - Effective solution for treating TCE vapors
  - Problems due to leaching and dissolution


Journal of Environmental Management 163 (2015) 204–213

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Journal of Environmental Management

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Research article

Evaluation of a horizontal permeable reactive barrier for preventing upward diffusion of volatile organic compounds through the unsaturated zone

Mojtaba G. Mahmoodlu [a, d, *], S. Majid Hassanizadeh [a], Niels Hartog [a, b], Amir Raoof [a], Martinus Th. van Genuchten [a, c]

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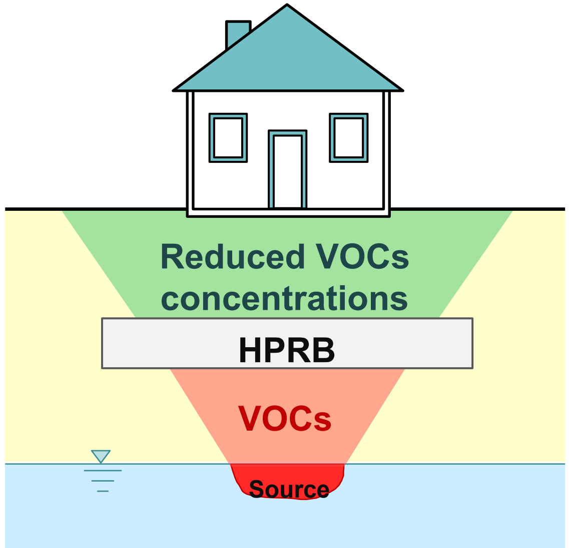

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HPRB with Zero Valent Iron

ALTERNATIVES PROPOSED BY OUR GROUP:

Use of ZERO VALENT IRON as filler for the HPRB for treating TCE vapors

Preliminary results :

- ✓ Zero-valent iron, partially saturated with water, proved to be effective
- ✓ A complete abatement of TCE in gas phase was achieved in **6 weeks**

Science of the Total Environment 647 (2019) 682–689

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Dehalogenation of trichloroethylene vapors by partially saturated zero-valent iron

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AIM OF THE RESEARCH: PHASE 1

Evaluation of the performances of several iron powders commercially available from different manufacturers and characterized by different specific surface areas

PHASE 1: Materials

ZVI samples

I.D.	PROCESS	MANUFACTURER	DIMENSION
Fe1	water atomization and sieving	iPutec	d< 63 µm
Fe2	n.a.	SIGMA-ALDRICH	d< 44 µm
Fe3	processing of annealing (H_2 furnace)	Pometon METAL POWDERS AND GRANULES	d< 425 µm
Fe4	water atomization and sieving	iPutec	d< 63 µm

Pre-Treatment

Washing with HCl 0.1 M, rinsing with N_2-purged water and drying in a N_2 atmosphere

Material characterization

- **Surface area:** Brunauer–Emmett–Teller (BET) method
- **Microstructure:** Scanning Electron Microscopy (SEM)
- **Mineralogy:** X-ray diffraction (XRD)

Journal of Contaminant Hydrology 234 (2020) 103687

Contents lists available at ScienceDirect

Journal of Contaminant Hydrology

journal homepage: www.elsevier.com/locate/jconhyd

ELSEVIER

Horizontal permeable reactive barriers with zero-valent iron for preventing upward diffusion of chlorinated solvent vapors in the unsaturated zone

Daniela Zingaretti[a], Iason Verginelli[a,*], Igor Luisetto[b], Renato Baciocchi[a]

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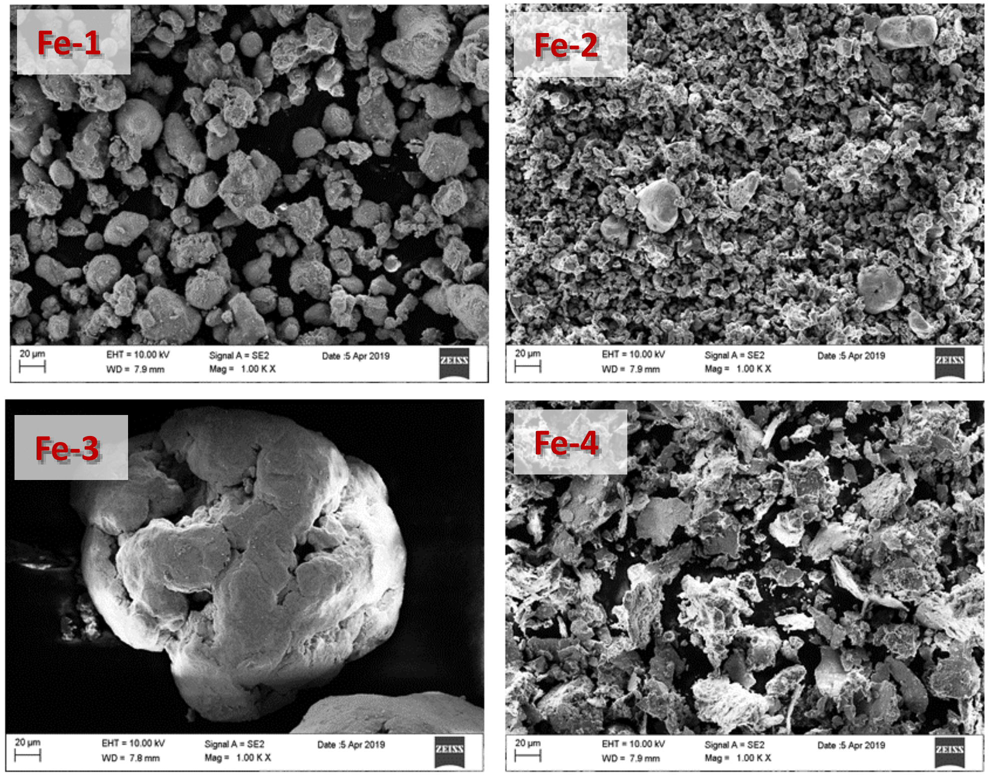
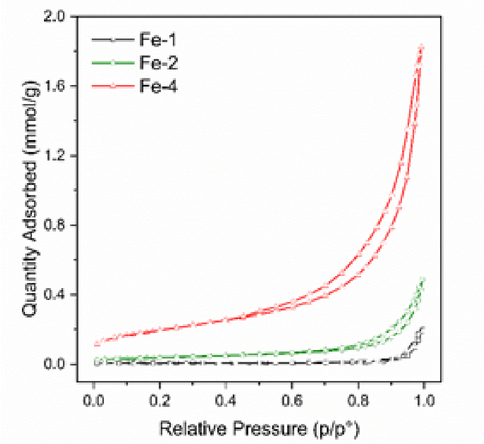
Materials characterization

Scanning Electron Microscopy analyses (SEM)



N_2 adsorption isotherm



BET method (specific surface area(SSA))

- **Fe-1: 0.69 m^2/g**
- **Fe-2: 3.10 m^2/g**
- **Fe-3**: below L.O.Q. (<0.01 m^2/g)
- **Fe-4**: **15.54 m^2/g**

✓ Fe3: higher particle diameter
✓ Fe2 and Fe4: Presence of flaky particles

✓ SSA values consistent with other commercial ZVI

Zingaretti et al.(2020). Journal of Contaminant Hydrology, 234, 103687

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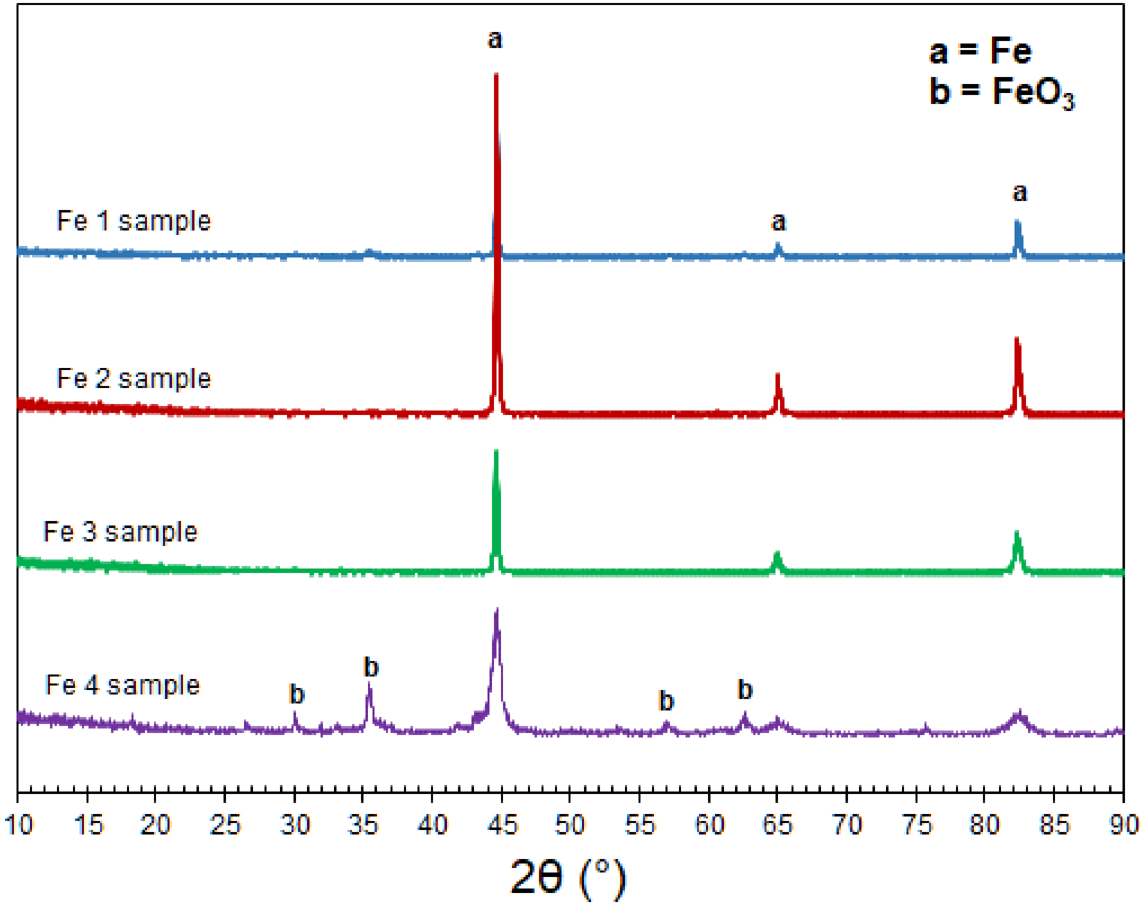
Materials characterization

X-Ray Diffraction (XRD)



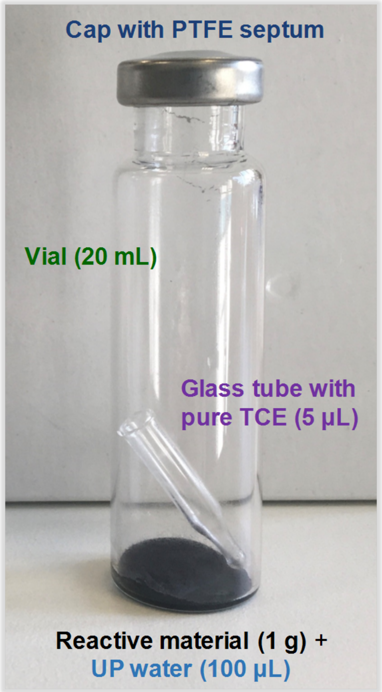
- ✓ Crystalline phases: iron (Fe) and iron oxides (FeO_3)
- ✓ Iron oxides detected on the Fe4 sample (ineffectiveness of acidic washing)

Zingaretti et al.(2020). Journal of Contaminant Hydrology, 234, 103687

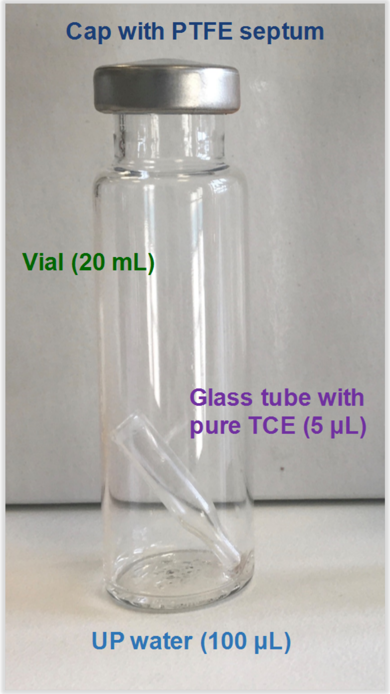
TCE removal experiments

- **TCE degradation tests:** with reactive material
- **Control tests:** without the reactive material, to assess vial losses contribution on TCE removal
- **Determination of the TCE residual concentration** in the gas phase at the end of the tests by GC-FID
- **Determination of by-products** in the gas phase by GC-MS

TCE degradation test



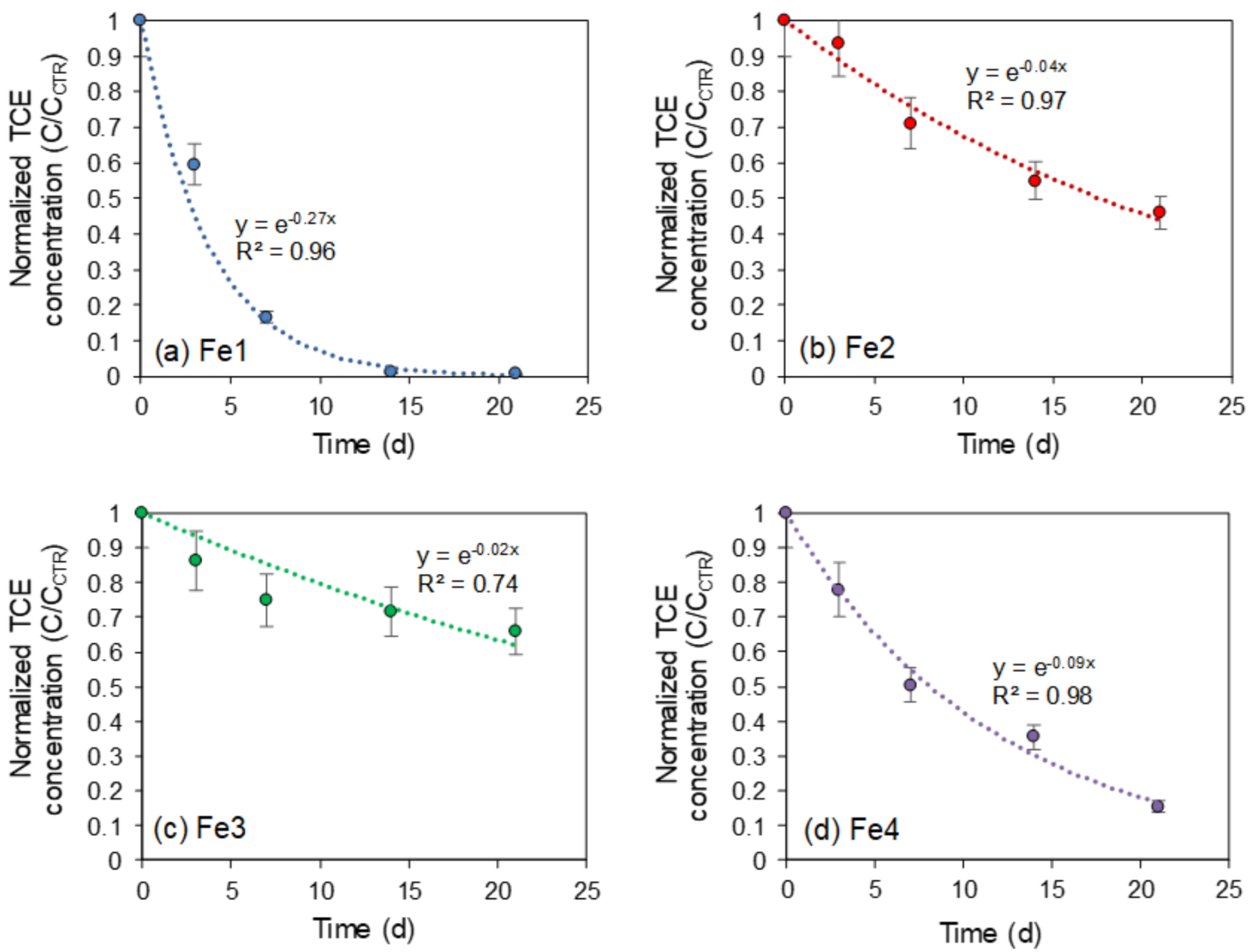
Control test



Operating conditions

- ✓ **$TCE_{initial}$:** 365 g m-3
- ✓ **Water:** 100 µL (10%wt.)
- ✓ **Reaction time**: 3, 7, 14, 21 days

TCE removal kinetics with different ZVIs



Iron Sample	SSA [m2 g-1]	TCE degradation rate (k) [d-1]
Fe1	0.69	0.27
Fe2	3.1	0.04
Fe3	<0.01	0.02
Fe4	15.54	0.09

- ✓ First order TCE degradation kinetics
- ✓ Poor correlation with iron SSA value
- ✓ Complete degradation of TCE for t>**3 weeks**
- ✓ Fe1 proved to be more reactive
- ✓ Faster passivation for Fe2 and Fe4

Zingaretti et al.(2020). Journal of Contaminant Hydrology, 234, 103687

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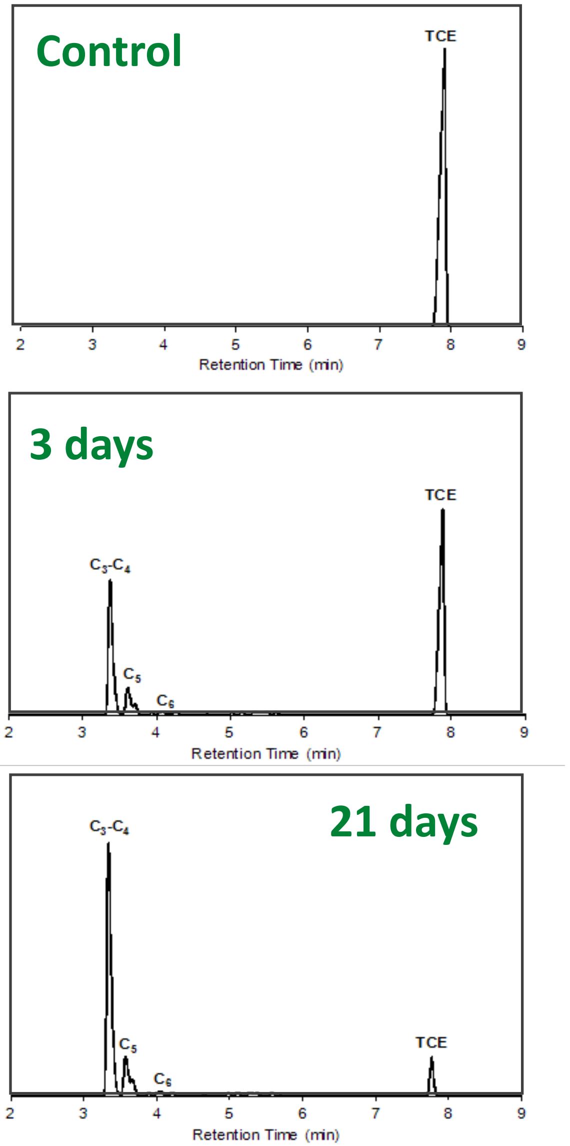
TCE By-products



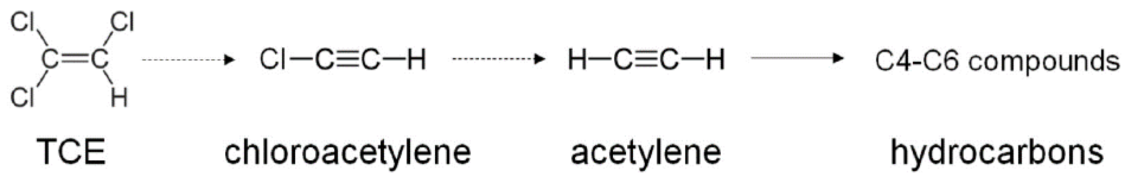
✓ Detectable Byproducts:

- C_3-C_4 hydrocarbons
- C_5-C_6 hydrocarbons (lower extent)

✓ The HC formation probably due to **carbon impurities in the iron (**Campbell et al. 1997; Schrick et al. 2002)

✓ Mechanism analogous to the **Fischer-Tropsch synthesis** of hydrocarbons

✓ Main degradation pathway: **β-elimination**



Zingaretti et al.(2020). Journal of Contaminant Hydrology, 234, 103687

Potential use of iron in HPRBs

Minimum HPRB thickness (d_{HPRB}*)

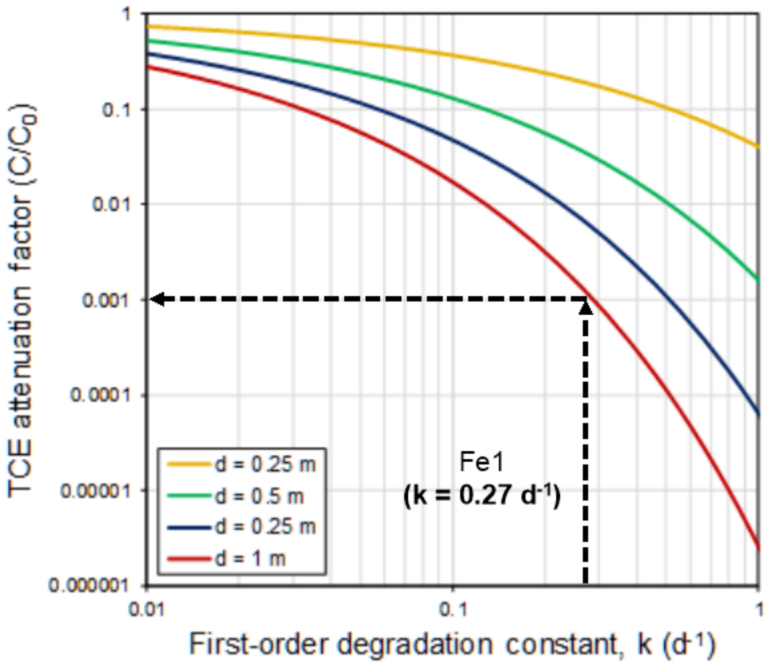
$$d_{HPRB}^{*} = L_R \ln\left(\frac{C_{HPRB,in}}{C_{target}}\right)$$

Hypothesis:

- Kinetic: First-order
- $C_{HPRB,in}$ (g m^{-3}): TCE entering into the barrier
- C_{target} (g m^{-3}): acceptable TCE concentration (risk-based)
- Reaction length (L_R)

$$L_R = \sqrt{(D_{HPRB} \cdot H)/(k \cdot \theta_{w,HPRB})}$$

- *k* is the first-order degradation rate constant,
- $\vartheta_{w,HPRB}$ the water-filled porosity in the HPRB,
- *H* the dimensionless Henry's law constant of the contaminant
- D_{HPRB} the effective porous medium diffusion coefficient through the HPRB (Millington and Quirk, 1961)



✓ 1 m-HPRB filled with Fe1 (k =0.27 d^{-1}) ensures 0,001 TCE attenuation (i.e. 99.9% TCE abatement)

Zingaretti et al. (2020). Journal of Contaminant Hydrology, 234, 103687

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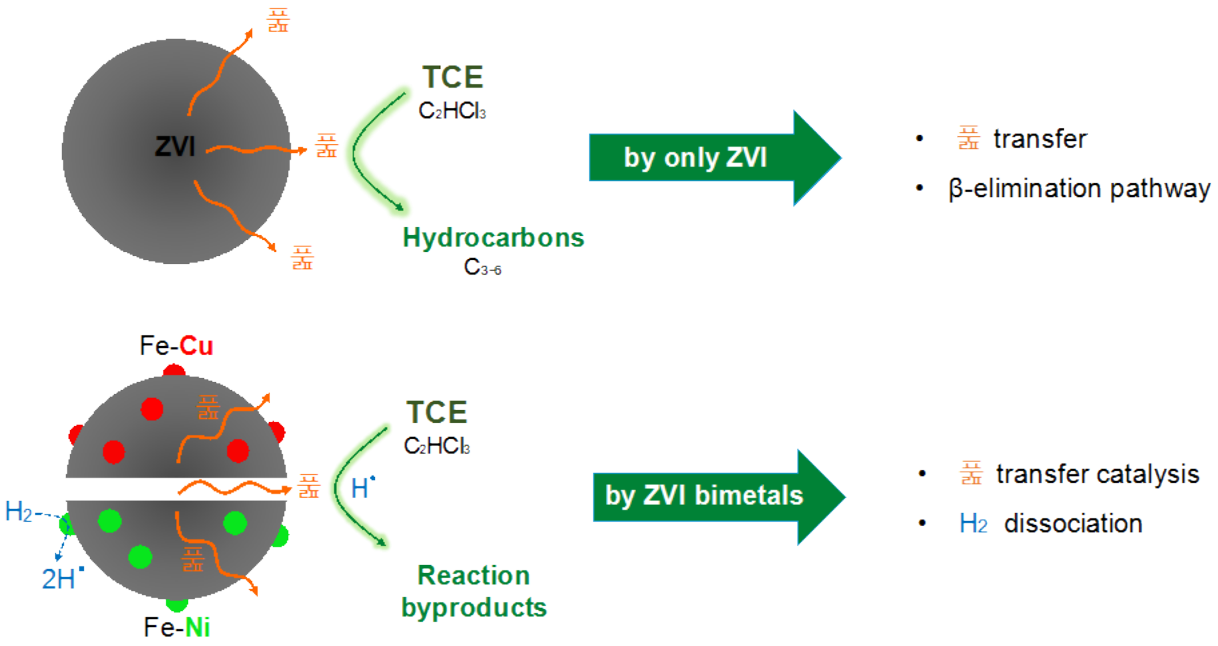
PHASE 2: HPRB performance enhancement

MATERIAL ENHANCEMENT

The addition of a secondary metal (e.g. Cu or Ni) could catalyze the TCE degradation



AIM OF THE STUDY

Investigate the feasibility of using **ZVI bimetals** by adding Cu or Ni on ZVI to catalyze the degradation reactions (*Settimi et al. 2022; 2023*)

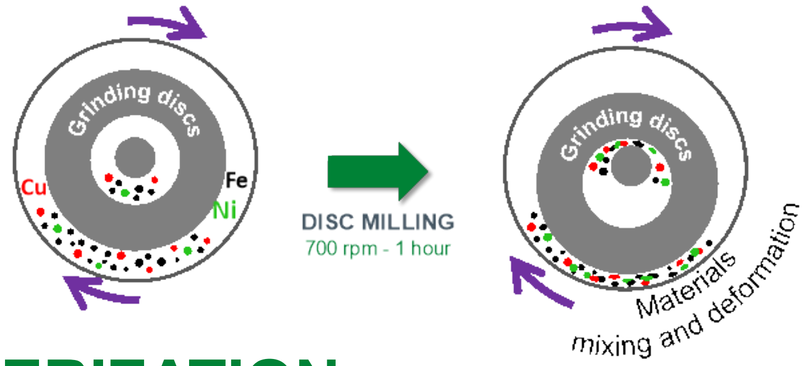
EXPERIMETAL ACTIVITIES

- Bimetals production from raw powders
- Characterization of the materials
- TCE degradation tests

Materials Production and Characterization

RAW POWDERS

- Iron powder Fe1 (iPutec GmbH, 0-63 µm)
- **Copper powder** (Sigma Aldrich, < 75 µm)
- **Nickel powder** (Sigma Aldrich, < 75 µm)



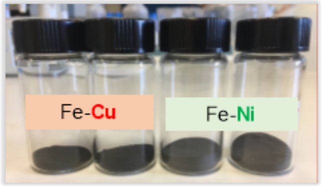
MATERIALS PRODUCED

Fe-**Cu** bimetals

Fe + { 1%, 5%, 20% } **Cu**

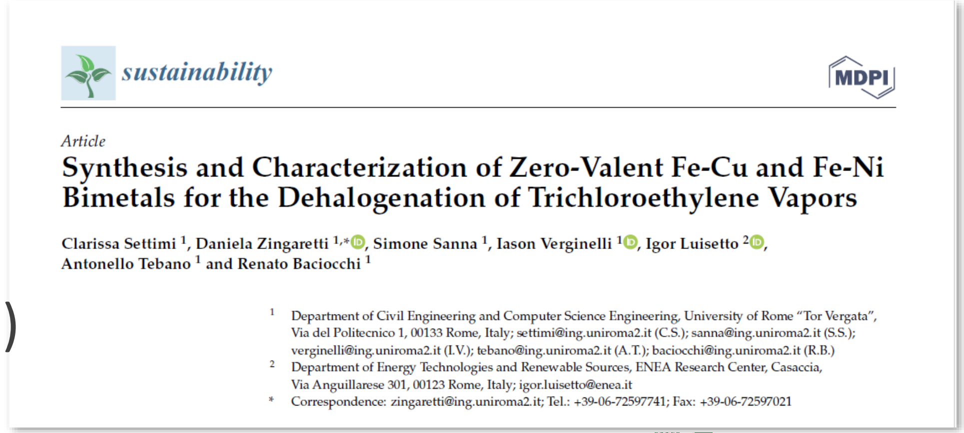
Fe-**Ni** bimetals

Fe + { 1%, 5%, 20% } **Ni**



CHARACTERIZATION

- **Specific Surface area:** Brunauer–Emmett–Teller (BET) method
- **Microstructure:** Scanning Electron Microscopy (SEM-EDS)
- **Mineralogy:** X-ray diffraction (XRD)



sustainability MDPI

Article

Synthesis and Characterization of Zero-Valent Fe-Cu and Fe-Ni Bimetals for the Dehalogenation of Trichloroethylene Vapors

Clarissa Settimi [1], Daniela Zingaretti [1,*], Simone Sanna [1], Iason Verginelli [1], Igor Luisetto [2], Antonello Tebano [1] and Renato Baciocchi [1]

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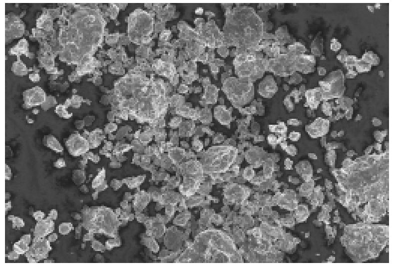
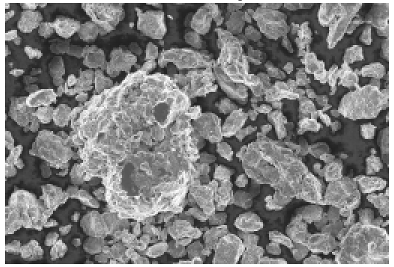
Results – materials characterization

Scanning Electron Microscopy analyses (SEM)

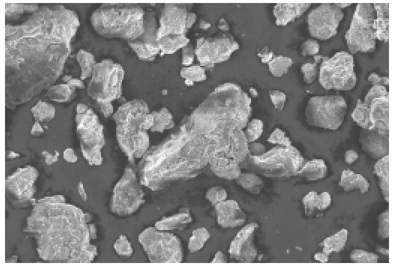
Bimetal Fe-1%**Cu** - 5-60 µm



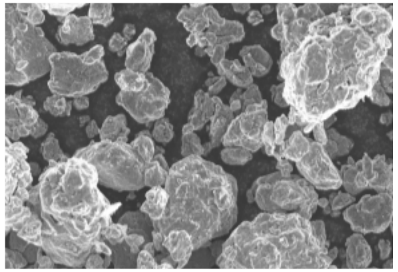
Bimetal Fe-5%**Cu** - 30-100 µm



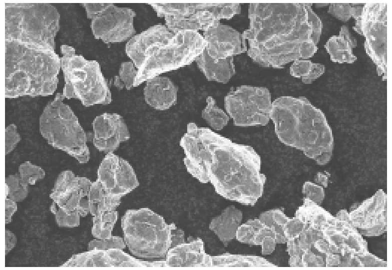
Bimetal Fe-20%**Cu** - 20-90 µm



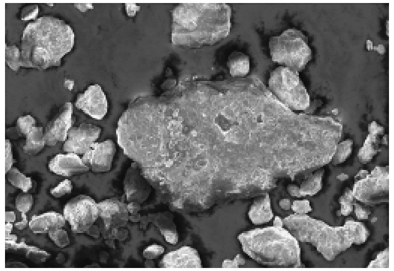
Bimetal Fe-1%**Ni** - 5-60 µm



Bimetal Fe-5%**Ni** - 20-90 µm



Bimetal Fe-20%**Ni** - 10-100 µm



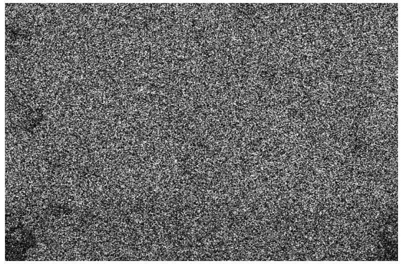
10 µm

✓ micrometric dimensions suitable for HPRBs to avoid problems of particle aggregation

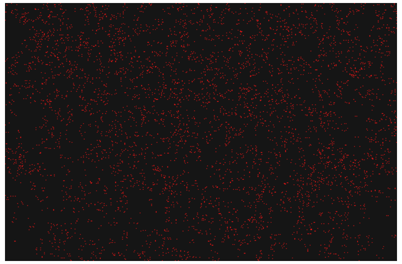
Elemental Mapping (EDS)

EDS%

95.3%Fe



4.7%Cu



10 µm

✓ homogeneous distribution of the secondary metal

Settimi et al. (2022). Sustainability, 14(13), 7760.

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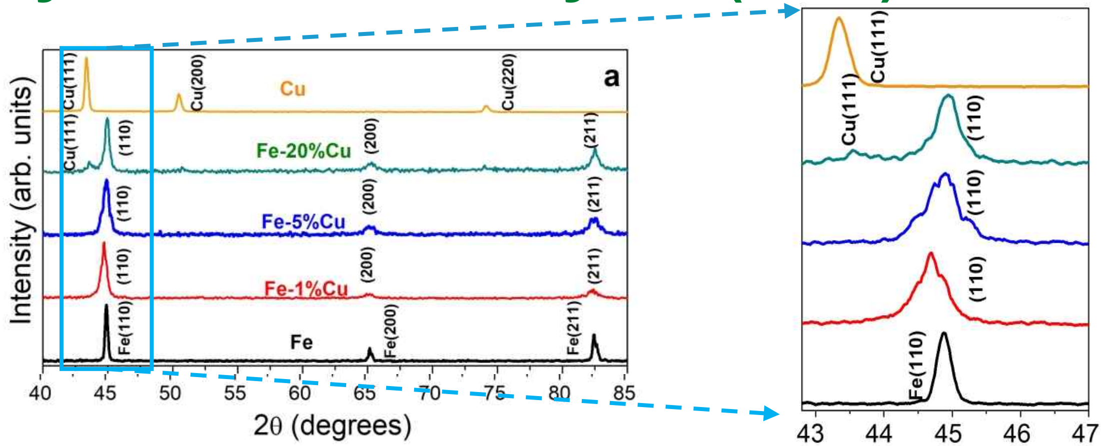
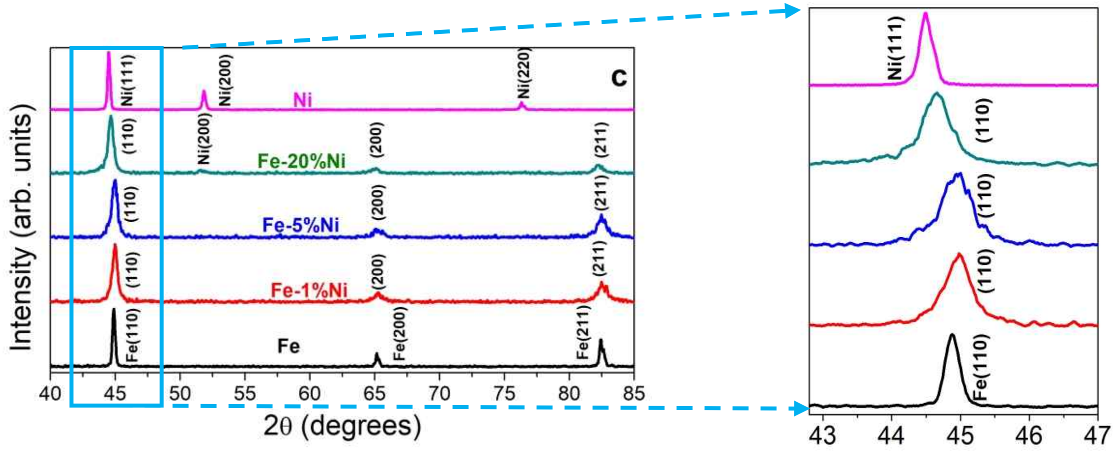
Results – materials characterization

X-Ray Diffraction Analyses (XRD)

Fe-Cu bimetals



Fe-Ni bimetals



✓ Bimetal formation (Fe peak shift)

Specific Surface Area (SSA) using Brunauer-Emmett-Teller method (BET)

Bimetallo	SSA (m^2/g)
Fe-1%Cu	0.7
Fe-5%Cu	<LOQ
Fe-20%Cu	0.5
Fe-1%Ni	0.3
Fe-5%Ni	0.3
Fe-20%Ni	0.2

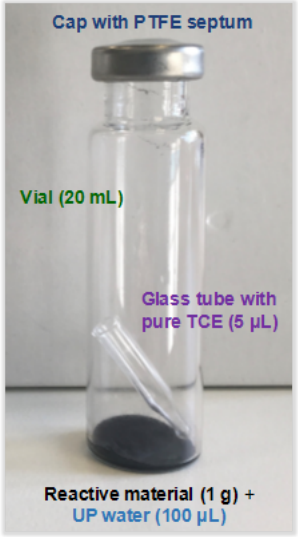
✓ Similar SSA values among the produced bimetals

Settimi et al. (2022). Sustainability, 14(13), 7760.

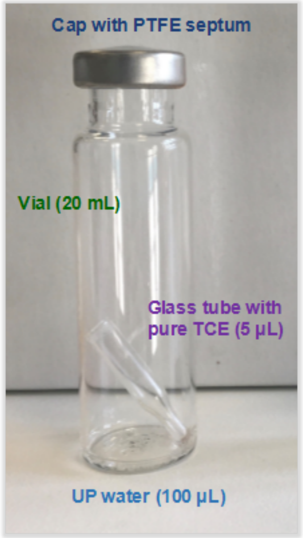
TCE Degradation tests

- **Pre-Treatment**: acidic washing
- **TCE degradation tests** with bimetals
- **Control tests** without the reactive material
- Determination of the **TCE residual concentration** in the gas phase by GC-FID
- Determination of **TCE degradation by-products** by GC-MS

TCE degradation test



Control test




Journal of Contaminant Hydrology 257 (2023) 104204

Contents lists available at ScienceDirect

Journal of Contaminant Hydrology

journal homepage: www.elsevier.com/locate/jconhyd

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Degradation of trichloroethylene vapors by micrometric zero-valent Fe—Cu and Fe—Ni bimetals under partially saturated conditions

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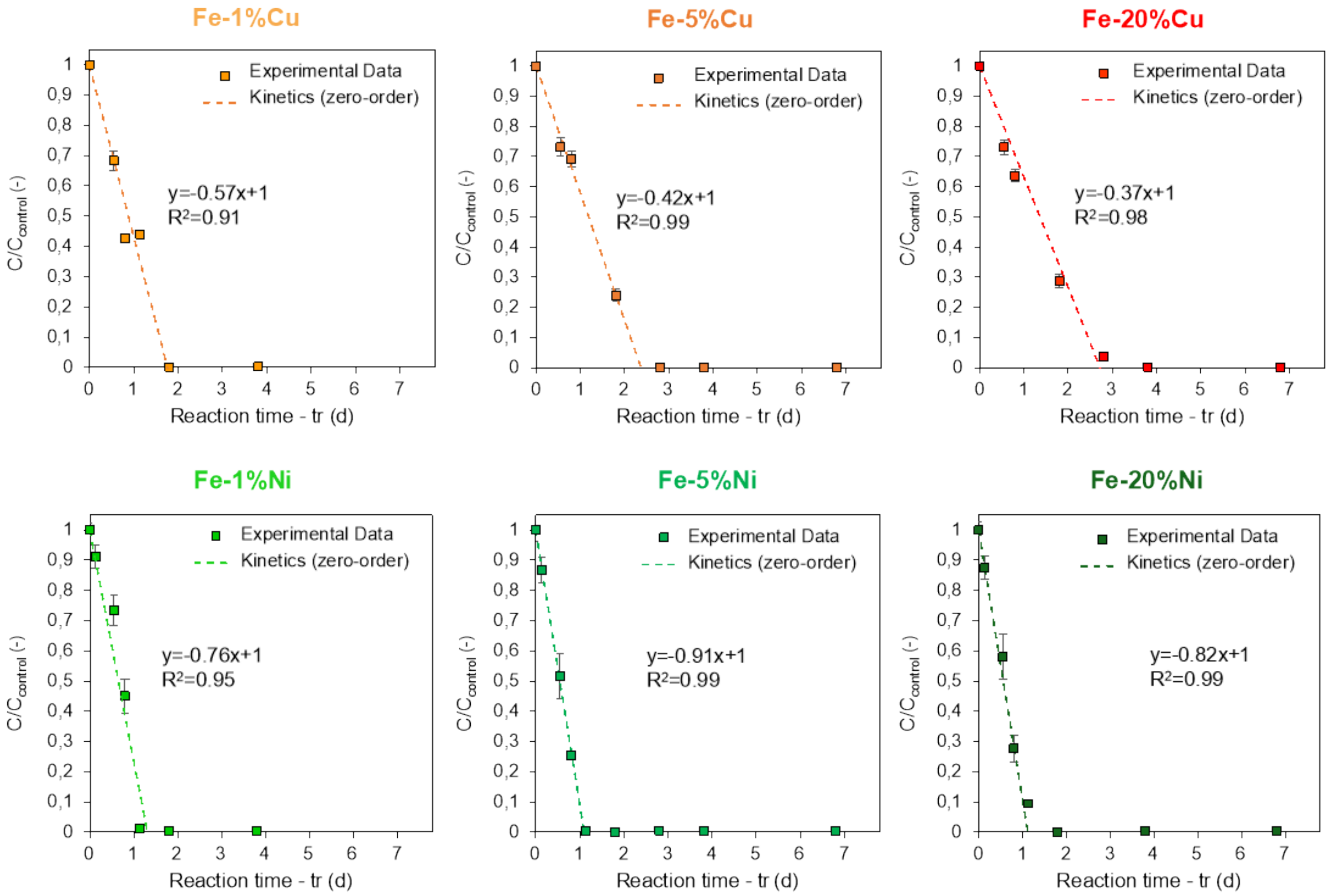
TCE degradation tests using bimetals



Bimetals	K_0 (g $m_{air}^{-3}d^{-1}$)	SSA (m^2g^{-1})	k_{SSA} (g $m^{-2}d^{-1}$)
Fe-1%Cu	207	0.7	5.7E-03
Fe-5%Cu	153	<LOQ	-
Fe-20%Cu	134	0.5	5.8E-03
Fe-1%Ni	278	0.3	1.9E-03
Fe-5%Ni	332	0.3	2.7E-02
Fe-20%Ni	300	0.2	2.7E-02

- ✓ **Fe-Cu bimetals:** Up to 99.9% TCE vapors degradation in **4 days**
- ✓ **Fe-Ni bimetals:** Up to 99.9% TCE vapors degradation in **2 days**

Degradation kinetics (zero-order):

$$\frac{C(t)}{C_{Control}} = -\frac{k_0}{C_0}t_r + 1$$

Settimi et al. (2023). Journal of Contaminant Hydrology 257, 104204.

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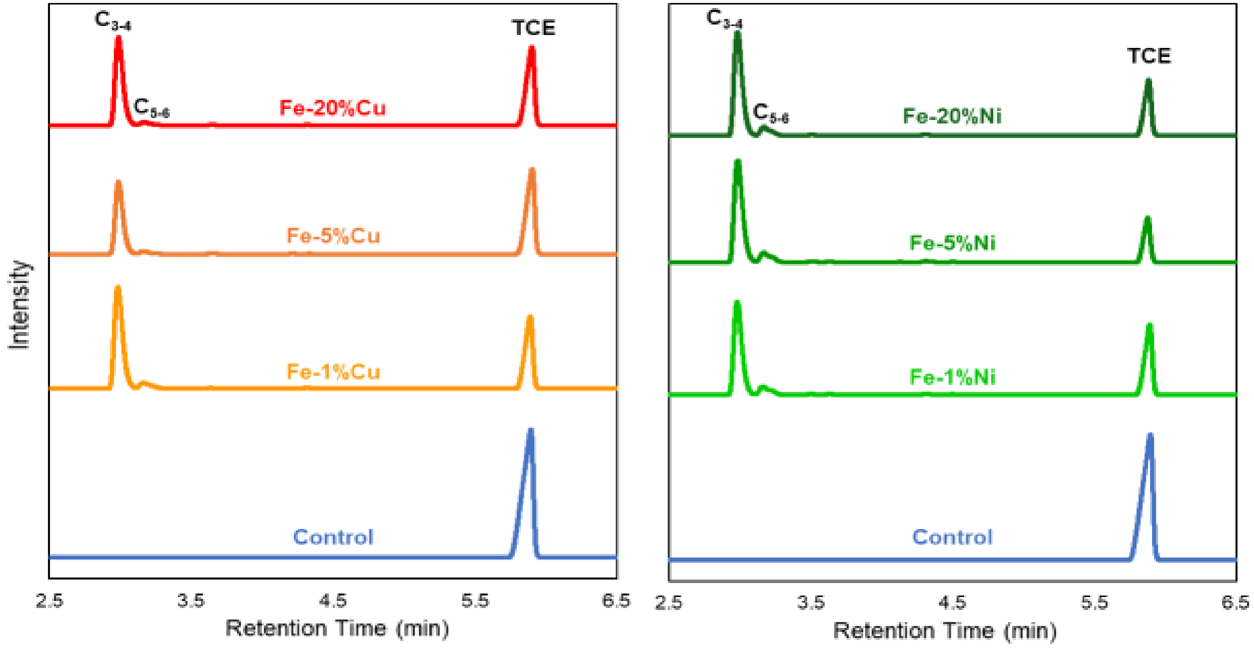
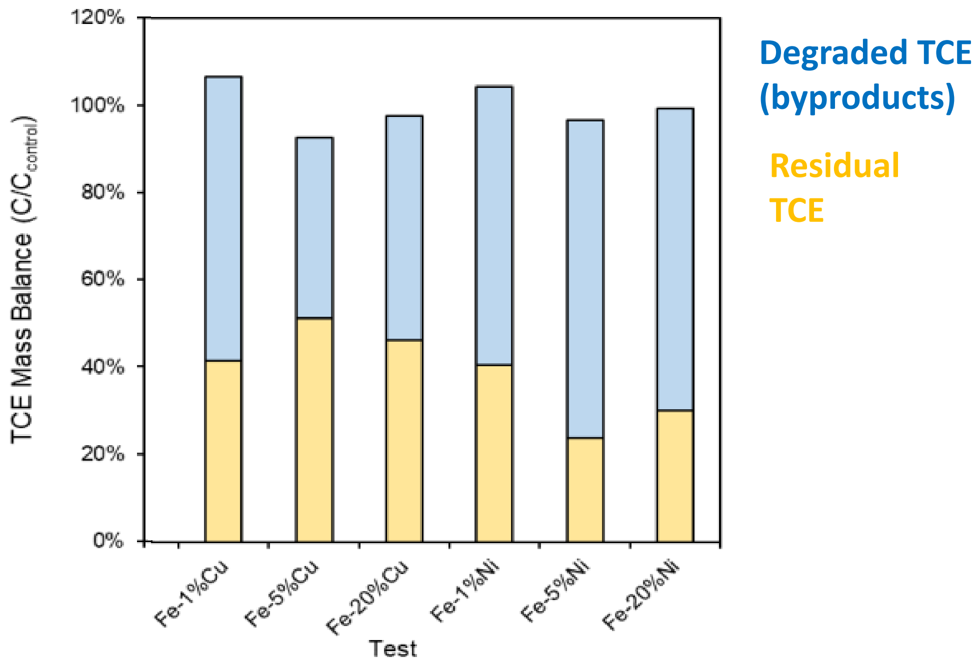
Reaction byproducts and TCE mass balance

Chromatograms at the end of the tests (1 day of reaction time)



TCE Mass Balance at the end of the tests (1 day of reaction time)



- ✓ C_3-C_6 hydrocarbon byproducts
- ✓ No VC and DCE detected
- ✓ Main degradation pathway: β-elimination

- ✓ Removal of TCE due to the reduction in byproducts (mass balance≈100%)
- ✓ Other effects (i.e. adsorption) negligible

Settimi et al. (2023). Journal of Contaminant Hydrology 257, 104204.

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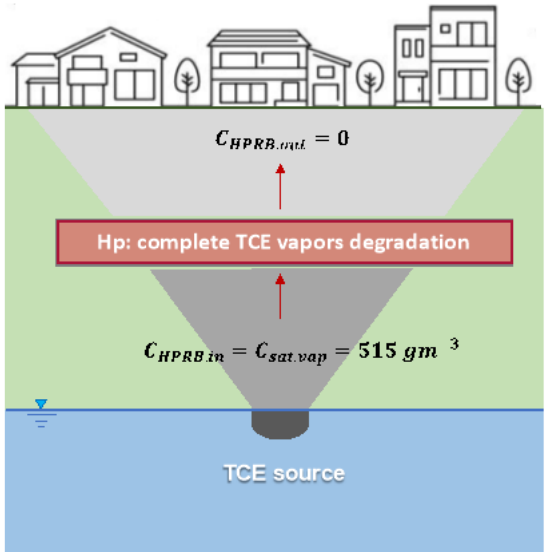
HPRB minimum thickness

HPRB minimum thickness to complete remove TCE (*d**)



$$d_{HPRB}^{*} = \sqrt{2D_{HPRB}\frac{C_{HPRB,in}}{k_0}}$$

Hypothesis:

- zero order kinetic
- $C_{HPRB,in}$ (g m^{-3}): TCE entering into the barrier
- k_0: degradation kinetic constant (g m^{-3}d^{-1})
- D_{HPRB}: Diffusion coefficient in the HPRB (m^{2}d^{-1})

Settimi et al. (2023). Journal of Contaminant Hydrology 257, 104204.

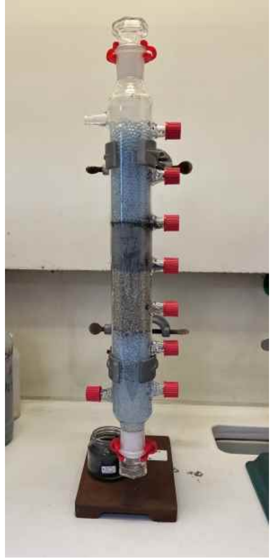
Materiali	d*
Fe[a]	1 m
Fe-1%Cu	0.15 m
Fe-5%Cu	0.17 m
Fe-20%Cu	0.18 m
Fe-1%Ni	0.13 m
Fe-5%Ni	0.12 m
Fe-20%Ni	0.12 m

[a] *Zingaretti et al. 2020*

Reduced thickness (~ 15 cm)

Ongoing activities

PROCESS SCALE -UP

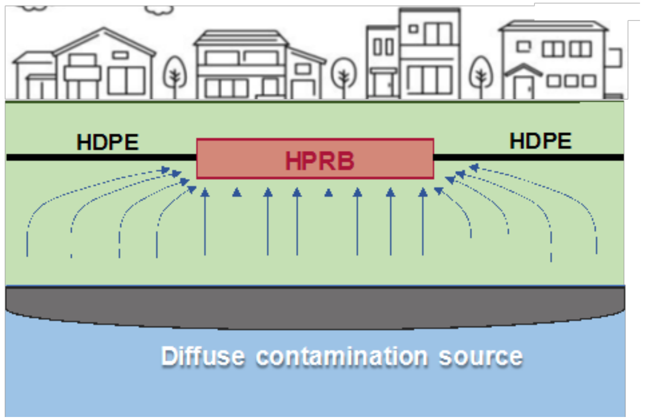


Column Diffusion test

MATERIAL PASSIVATION

Long-term batch tests

FIELD APPLICATION



Design of the configuration for in situ applications (e.g. brownfields)

Thanks!

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