"Remediacion de suelos por tratamientos de oxidacion quimica in situ (ISCO)"

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https://www.ucm.es/inproquima

Potential and Identified Contaminated Sites in EU

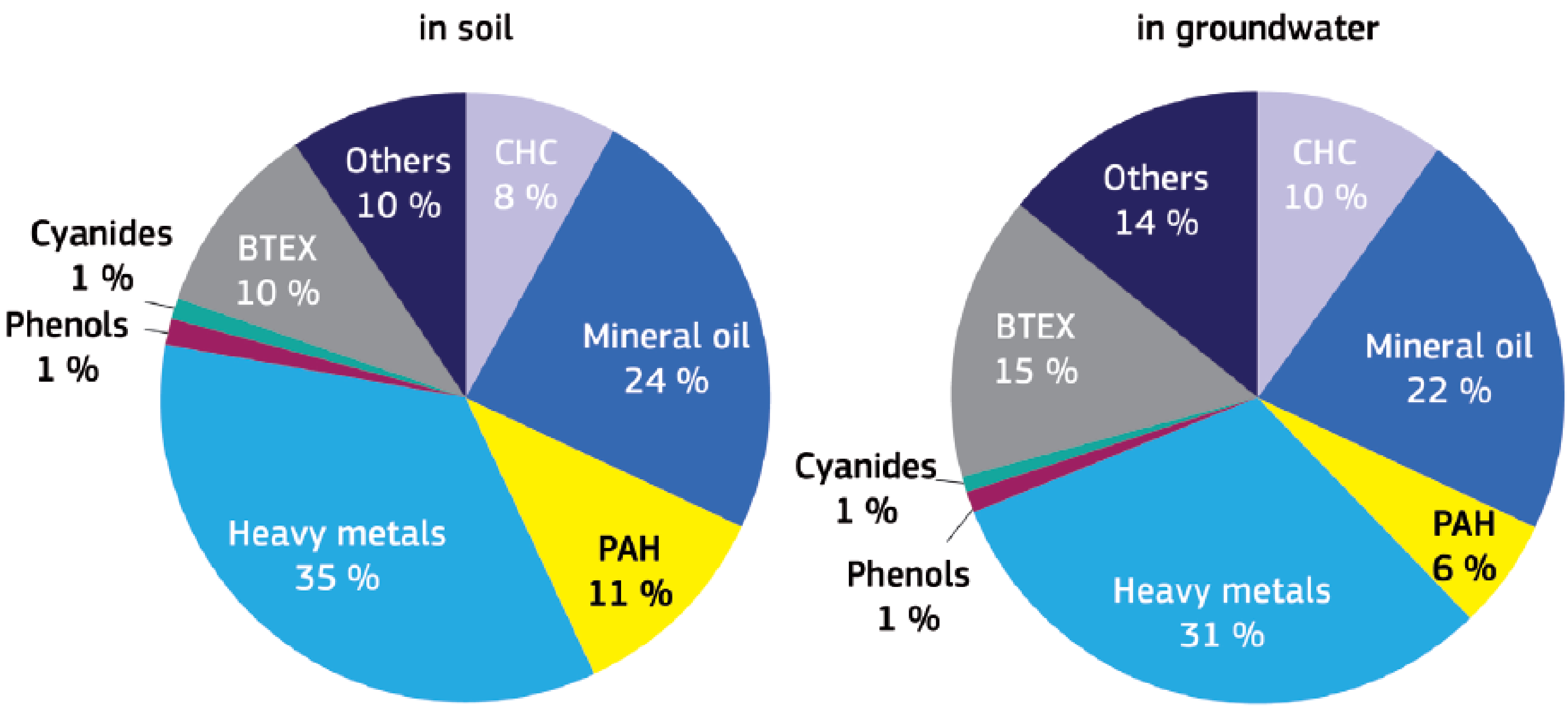
Estimated extent of local soil contamination in Europe

2.5 million Potentially Contaminated Sites. About 14 % (340,000 sites) are expected to be contaminated and likely to require remediation

Identified and remediated local soil contamination versus future work load

about 1,170,000 Potentially Contaminated Sites have been identified to date (45% of possible) About 1/3 of the estimated total of 340,000 CS for the EEA-39 have already been identified and about 15 % of the estimated total have been remediated.

Most frequently applied occurring contaminants



REMEDIATION OUTCOMES

Complete or substantial destruction/degradation of the pollutants.

Extraction of pollutants for further treatment or disposal.

Stabilisation of pollutants in forms less mobile or toxic.

Separation of non-contaminated materials, and their recycling, from polluted materials that require further treatment.

Containment of the polluted material to restrict exposure of the wider environment

BIOTREATMENT

CHEMICAL TREATMENT
- OXIDATION
- REDUCTION

- Type of contaminants
- Extension of the contaminated area
- Type of soil (chemical composition, pH, Organic matter)

In situ

treat the contaminants in place

Ex situ

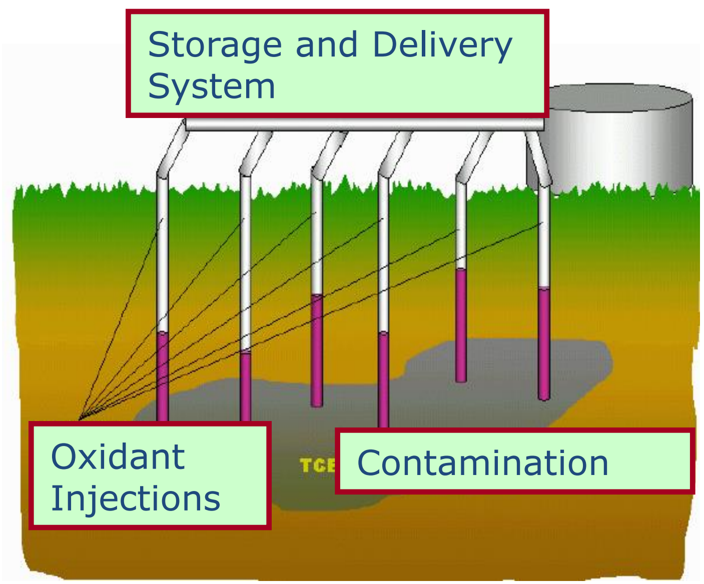
require the excavation of the soil. Treatment "off site" or "on site"

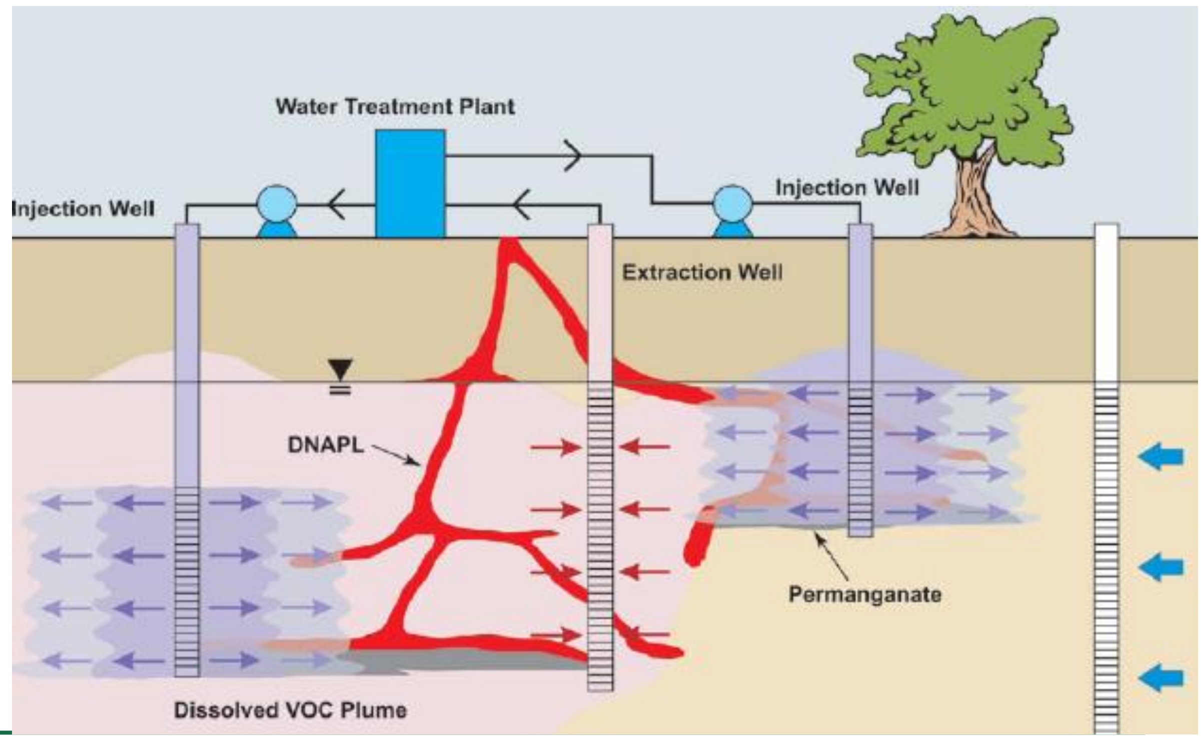
IN SITU CHEMICAL OXIDATION

In-situ chemical oxidation involves the **introduction of a chemical oxidant into the subsurface** for the purpose of transforming ground-water or soil contaminants into less harmful chemical species.

INJECTION WELLS

EXTRACTION WELLS ?
(WATER TREATMENT PLANT)





Contaminants amenable to treatment by ISCO include the following:

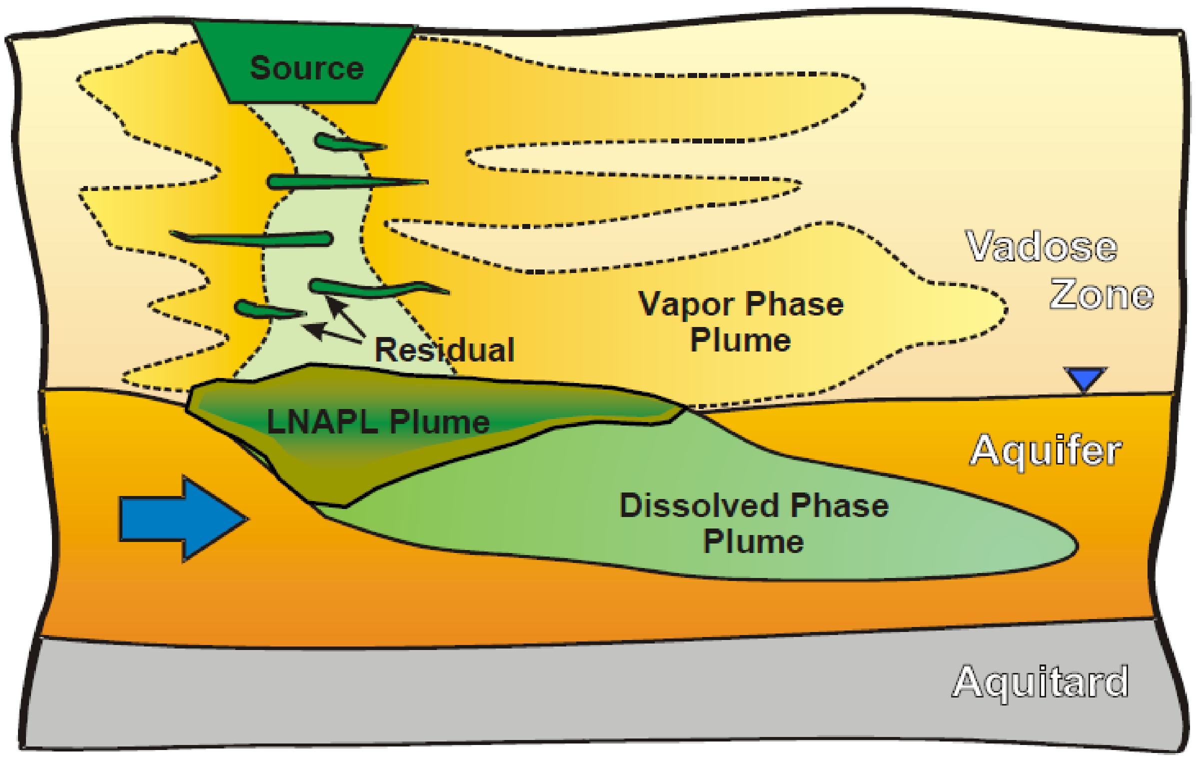
- benzene, toluene, ethylbenzene, and xylenes (BTEX);
- methyl *tert*-butyl ether (MTBE);
- total petroleum hydrocarbons (TPH);
- chlorinated solvents (ethenes and ethanes);
- polyaromatic hydrocarbons (PAHs);
- polychlorinated biphenyls (PCBs);
- chlorinated benzenes (CBs);
- phenols;
- organic pesticides (insecticides and herbicides); and
- munitions constituents (RDX, TNT, HMX, etc.).
- Emergent pollutants? (PFCs, etc)

MOST are PRESENT as NON AQUEOUS LIQUIDS PHASES (NAPLS)

- Light
- Dense

NAPLs

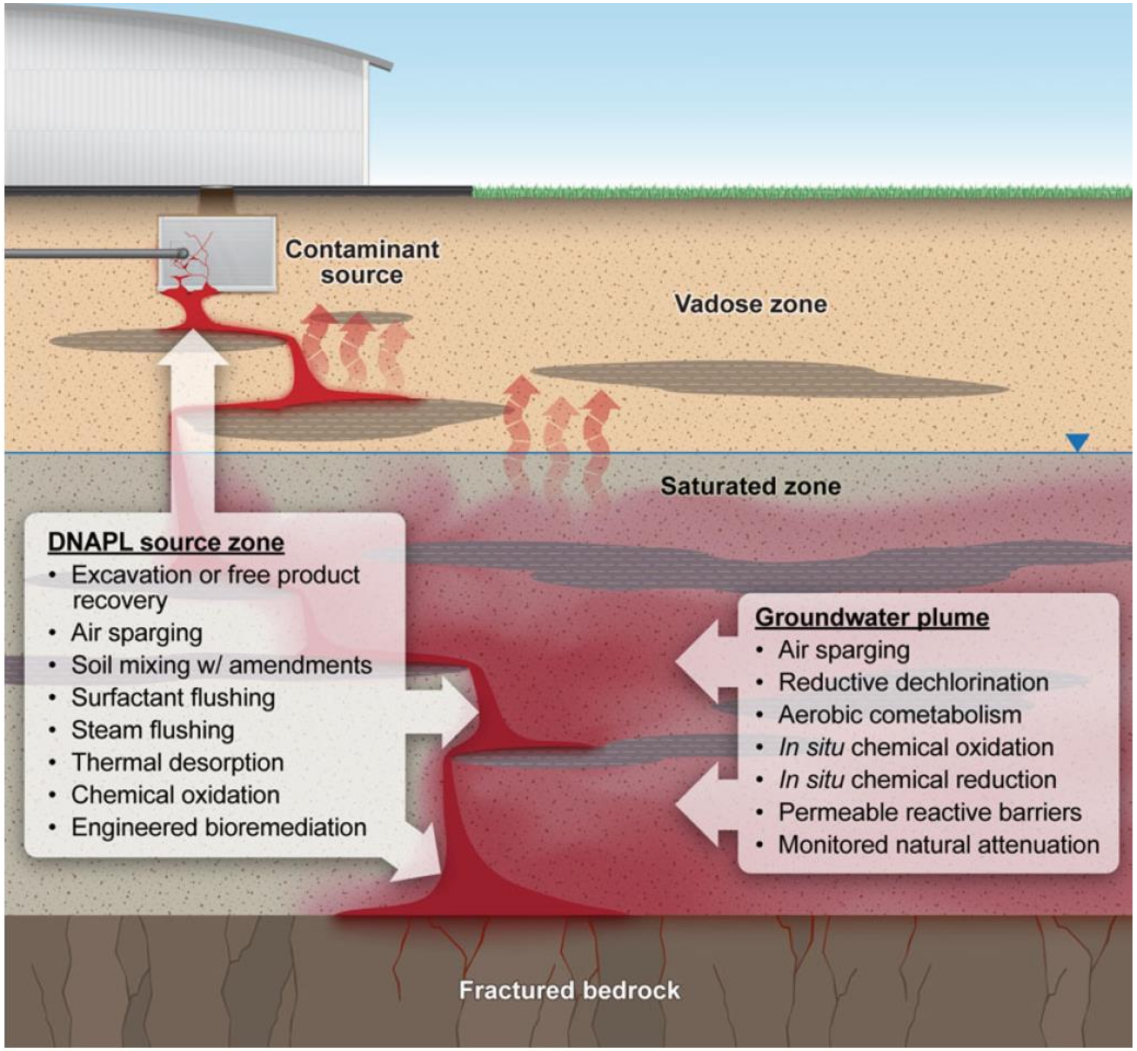
Light NAPLs (LNAPLs)**: L**ubricants and gasoline, pollutants often associated with leaking gasoline or oil storage tanks. ***Relatively insoluble in water*** and **less dense than water**



Vadose Zone

Aquifer

DNAPLs



Dense NAPLs (DNAPLs) **:** Chlorinated hydrocarbons used in dry cleaning and industrial degreasing**, etc**
Density> Water density

In Situ Chemical Oxidationvfor Groundwater Remediation. Ed L. Siegrist, M.Crimi and T.J. Simpkin. Springer Science+Business Media, LLC 2011

ISCO Advantages:

- Applicable to a wide range of contaminants.
- Contaminants are destroyed in-situ.
- In-situ treatment may reduce costs incurred by other technologies such as pump and treat, MNA (monitored natural attenuation), etc.
- Aqueous, sorbed, and non-aqueous phases of contaminants are transformed.
- Enhanced mass transfer (enhanced desorption and NAPL dissolution).
- Heat from oxidation reactions enhances mass transfer, reaction rates, and microbial activity.
- Potentially enhances post-oxidation microbial activity and natural attenuation.
- Cost competitive with other candidate technologies.
- Relatively fast treatment.

ISCO Disadvantages:

- Oxidant delivery problems due to reactive transport and aquifer heterogeneities.
- Natural oxidant demand may be high in some soil/aquifers.
- Short persistence of some oxidants due to fast reaction rates in the subsurface.
- Health and safety issues regarding the handling of strong oxidants.
- Potential contaminant mobilization.
- Potential permeability reduction.
- Limitations for application at heavily contaminated sites.
- Contaminant mixtures may require treatment trains.

ISCO. Introduction

Most commonly oxidants that have been frequently used for in situ chemical oxidation

- **Hydrogen peroxide** and **catalyzed hydrogen peroxide** (CHP) also referred to as modified **Fenton´s reagent.**
- **Ozone.**
- **Permanganate.**
- **Persulfate** and **activated persulfate (metal, heat).**

Oxidants can generally be group to

radical
non-radical

depending on whether they propagate the formation of free radicals. Persulfate and hydrogen peroxide can function both directly and through radical formation. Permangante doesn't form radicals.

CRITICAL ISSUES

CHEMISTRY OF THE OXIDANTS
SELECTION OF THE OXIDANT DOSE
SELECTION OF OXIDANT DELIVERY METHOD
DEVELOPMENT POTENTIAL and TREATMENT TRAINS

ISCO: What is needed..

- Development of new oxidants that are safer/easier to handle, such as solid peroxides
- Development of new activation aids, more effective iron chelates, innovative heating methods, recently alkaline activation.
- New delivery methods for the oxidants in order to overcome low permeability and diffusion constraints
- New methods of delivering the activation aids timely and in the targeted area.
- Treatment train approaches:

  Pre- or simultaneous treatment to prime the site for accepting the oxidant (e.g. fracturing, surfactant flushing, thermal)

  Post treatment is used as a polishing step (often bioremediation)

Hybrid Technologies

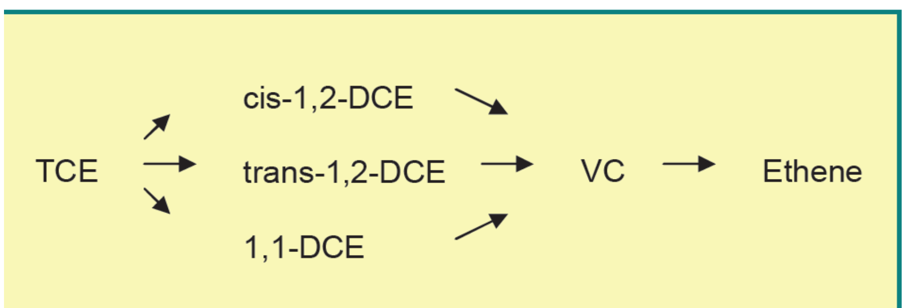
- **Application of persulfate ISCO after thermal treatment** could be employed as a cost effective way of achieving heat activation of persulfate.
- Other chemical treatments such as **the introduction of a surfactant can also be used together with ISCO: increase the solubility of sorbed contaminants (S-ISCO).**
- **ISCO** can be combined with a **subsequent natural or stimulated bioremediation to be used as a polishing step for rebound/intermediate contamination**. This can assist in a cost effective remediation by limiting the amount, area and period of applying expensive oxidizing reagents to the subsurface.

What Is In Situ Chemical Reduction?

In situ chemical reduction, or “ISCR,” uses chemicals called “reducing agents” to help change contaminants into less toxic or less mobile forms. It is described as “in situ” because it is conducted in place, without having to excavate soil or pump groundwater above ground for cleanup.

ISCR can clean up several types of contaminants dissolved in groundwater. It can also be used to clean up DNAPLs

ISCR is most often used to clean up the metal chromium and the industrial solvent trichloroethene, or “TCE,” which is a DNAPL



Rreductor employed: Zero Valent Iron (ZVI)

How Does It Work?

Reactive Barriers
Direct Injection (nano-micro particles)

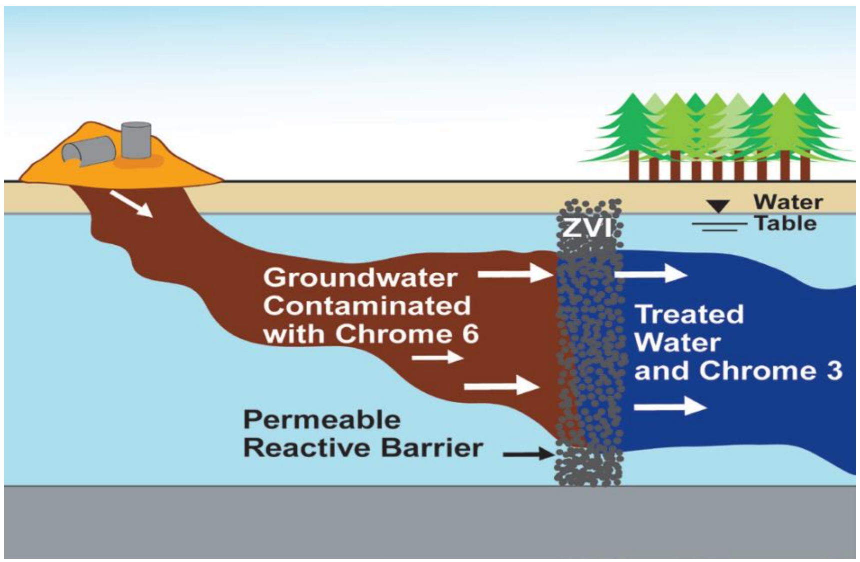


Illustration of the treatment of contaminated water with a PRB made of ZVI.

Contaminants

http://www.nanoiron.cz/en/contaminants

Group	Contaminant name	Contaminant other names
Chlorinated methanes	Dichloromethane	Freon 30, DCM
	Tetrachloromethane	Freon 10, Halon 104
	Chloroform	Freon 20, TCM
	Chloromethane	Freon 40, Methyl chloride
Trihalomethanes	Bromodichloromethane	Dichlorobromomethane
	Tribromomethane	Bromoform
	Dibromochloromethane	Chlorodibromomethane
Chlorinated ethanes	1,1-Dichloroethane	1,1-DCA,ethylidene dichloride
	1,1,1-Trichloroethane	TCA, Methyl chloroform
	1,1,1,2-Tetrachloroethane	
	1,1,2,2-Trichloroethane	
	1,1,2,2-Tetrachloroethane	PCA

Contaminants

http://www.nanoiron.cz/en/contaminants

Group	Contaminant name	Contaminant other names
Chlorinated ethenes	Tetrachloroethene	PCE, Perchlorethene, Perc
	Trichloroethene	TCE
	1,1-Dichloroethene	DCE
	Trans-1,2-Dichloroethene	t-DCE
Chlorinated benzenes	Chlorobenzene	Phenyl chloride
	Dichlorobenzene	
	Trichlorobenzene	
Other organic contaminants	Trichlorofluoroethane	Freon 11
	1,2-Dibromoethane	
	1,1,2-Trichlortrifluorethane	Freon 113
	1,2-Dichloropropane	Propylene dichloride
	1,2,3-Trichloropropane	
	Nitrobenzene	Nitrobenzol

Contaminants

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Group	Contaminant name	Contaminant other names
Inorganic	Arsenic	As
	Barium	Ba
	Cadmium	Cd
	Chromium	Cr
	Copper	Cu
	Lead	Pb
	Mercury	Hg
	Nickel	Ni
	Nitrates	
	Perchlorates	
	Selenium	Se
	Sulphates	$(SO_4)^{2-}$
	Uranium	U

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	Nitrates	
	Perchlorates	
	Selenium	Se
	Sulphates	$(SO_4)^{2-}$
	Uranium	U

How Long Will It Take

ISCR may take as little as a few months to clean up a source area using direct injection, and PRBs may take several years.

ISCR will take longer where:

- The source area is large, or contaminants are trapped in hard-to reach areas like fractures or clay.
- The soil or rock does not allow the reducing agent to spread quickly and evenly or reach contaminants easily.
- Groundwater flow is slow

INPROQUIMA: INFRAESTRUCTURAS

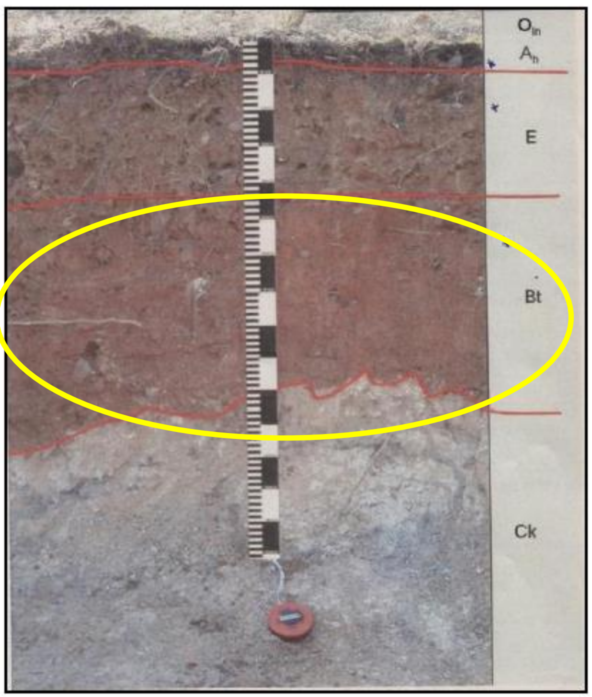
- ***ANALYSIS:***
- 1 gas chromatograph coupled with mass detector, GC-MS.
- 1 gas chromatograph with MS-HS-SPME.
- 2 gas chromatographs with FID detector.
- 1 ionic chromatograph.
- 1 HPLC chromatograph with UV-vis diode-array detector
- 1 micro GC with TCD detector.
- 1 tube furnace for TPD tests.
- 1 UV-vis spectrophotometer.
- 1 carbon analyzer for liquid and solid samples and total nitrogen analyzer in liquid samples.
- 1 Surface measurement apparatus, BET.
- 1 Microwave plasma atomic emission spectrometer for metals measurement.
- 1 Unit for COD measurements.
- 1 Unit for BOD5 measurements.
- 1 Unit for ecotoxicity measurement, Microtox.
- 1 Titration Equipment.

INPROQUIMA : INFRASTRUCTURES

- ***OTHER:***
- Automatized measurement system for conductivity, pH, and selective ions for the analysis of soil effluent of soil columns in continuous full length studies.
- 2 Orbital refrigerated shakers for soil remediation studies carried out in discontinuous.
- 4 Soxhlets and Microwave Sample Preparation
- Software COSMO.
- Supporting research services of UCM: Microscopy, elemental analysis, HPLC-MS and ICP-Plasma.

EJEMPLO: REMEDIACION DE SUELOS CONTAMINADOS POR NAPLs

SUELO TRATADO
(Arganda del Rey)



Materia orgánica del suelo %		0.365
Carbono orgánico total %		0.196
Fracciones materia orgánica del suelo %	Fracción lábil I	0.114
	Fracción lábil II	0.012
	Recacitrante	0.07
Carbono total %		0.198
Carbono inorgánico %		0.002
pH		7.22
Área BET $m^2 \cdot g^{-1}$		23
Volumen de poro $cm^3 \cdot g^{-1}$		0.031
[Mn] $mg \cdot g^{-1}$		0.170
[Fe] $mg \cdot g^{-1}$	Total	18.2
	Amorfo	0.525
	Cristalino	6.710

Suelo arcilloso-arenoso
Horizonte BT
- Bajo contenido en materia orgánica
- Alto contenido en Fe

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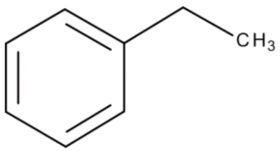
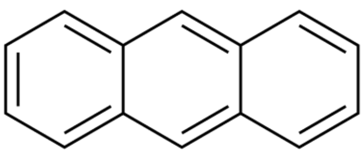
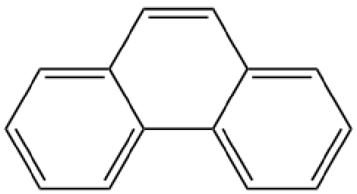


Etilbenceno (gasolinas)

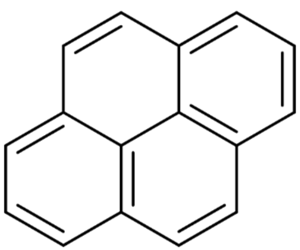
Antraceno



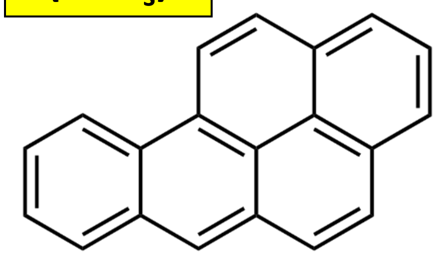
Fenantreno



Pireno

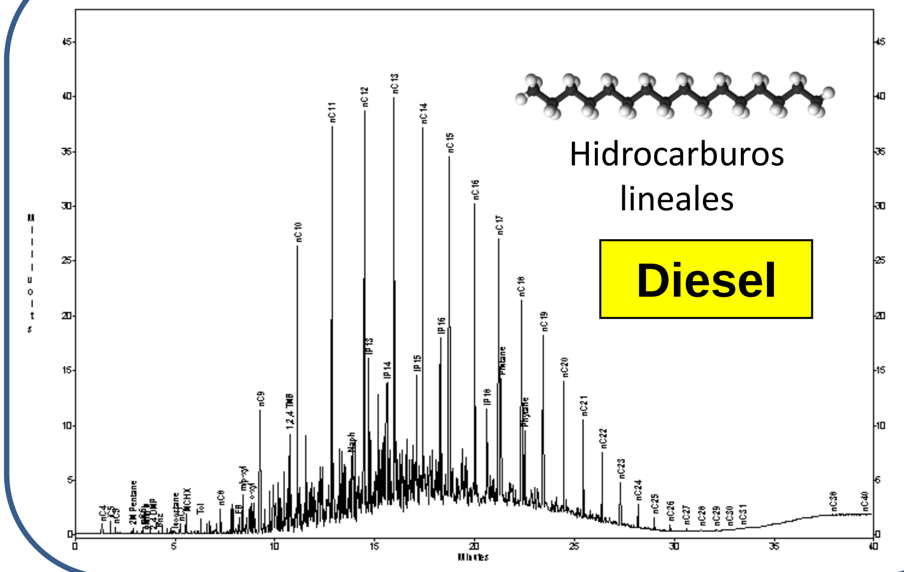


(PAH_s)



Benzo[a]pireno

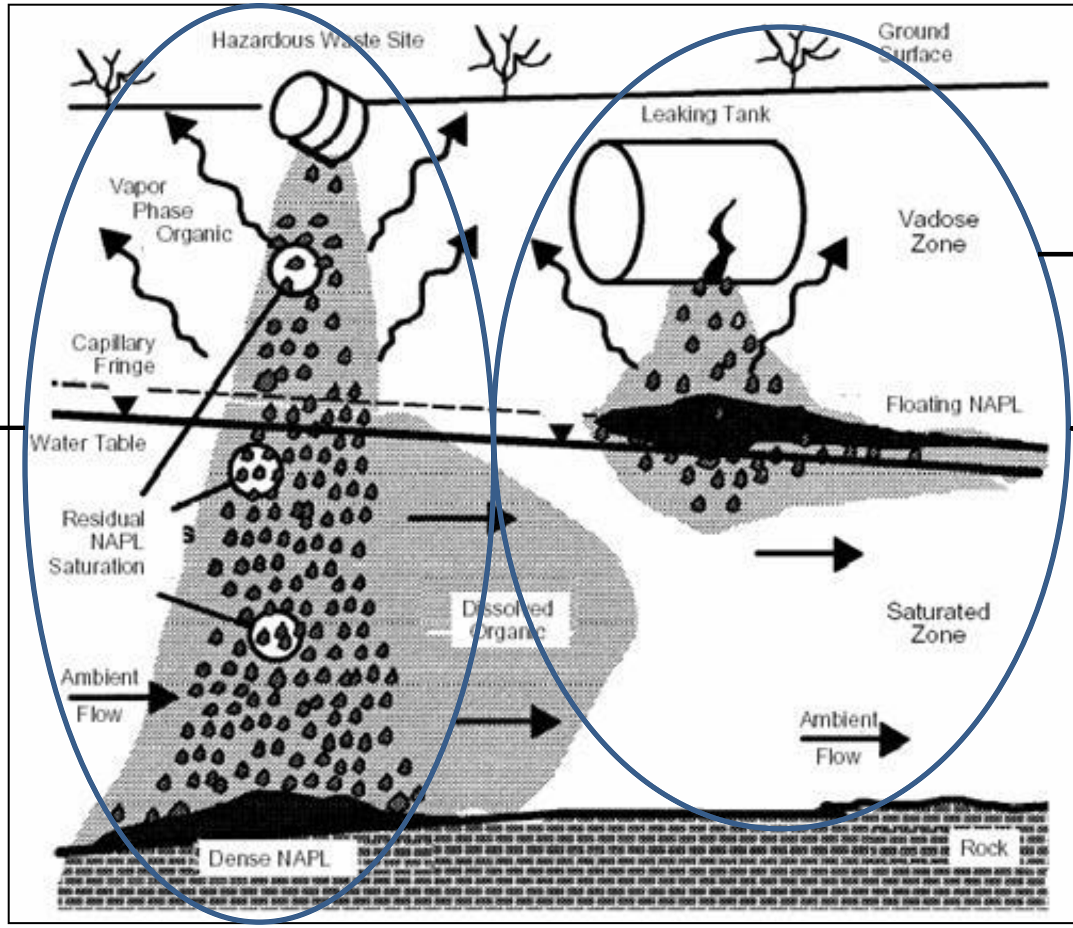
CONTAMINANTES



- Solubilidad prácticamente nula en agua.
- Tóxicos
- Muy poco biodegradables.
- Interaccionan fácilmente materia orgánica del suelo
- Contaminantes frecuentes en suelos contaminados a niveles muy por encima de los permitidos.

EJEMPLO: REMEDIACION DE SUELOS CONTAMINADOS POR NAPLs

QUÉ SUCEDE EN EL SUELO?



Diesel

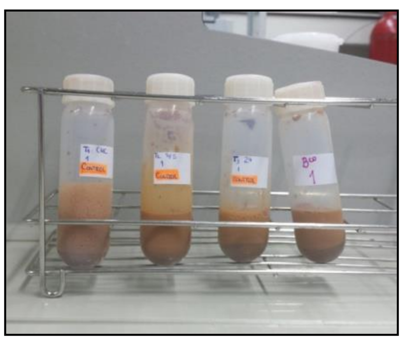
(PAH_s)

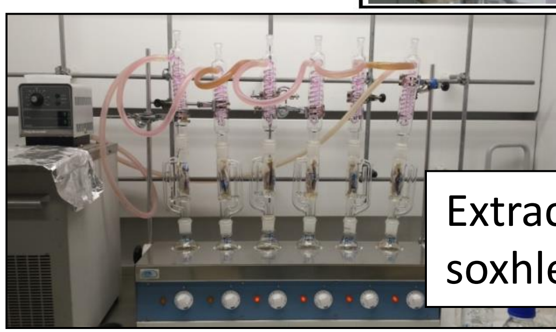
Etilbenceno (gasolinas)

EJEMPLO: REMEDIACION DE SUELOS CONTAMINADOS POR NAPLs

DISPOSITIVO EXPERIMENTAL

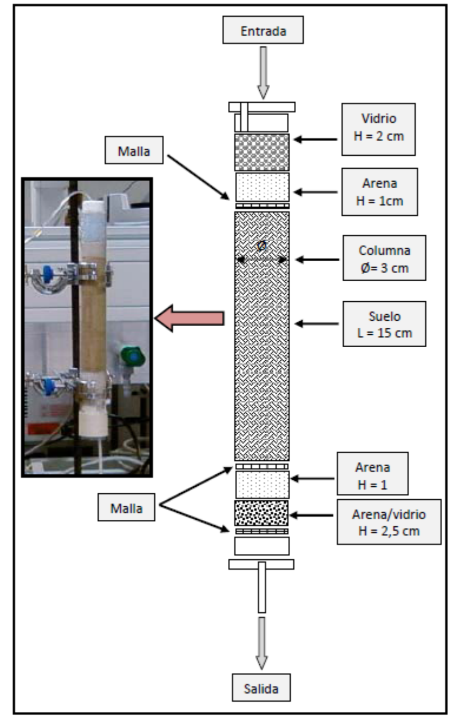
Experimentos en discontinuo





Extractores soxhlet

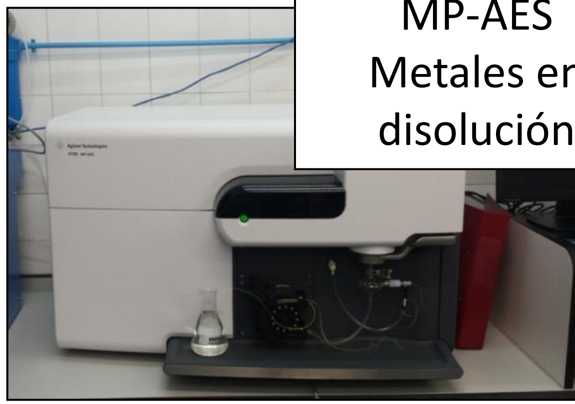
Experimentos en columna



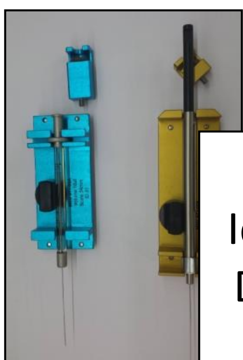
EJEMPLO: REMEDIACION DE SUELOS CONTAMINADOS POR NAPLs

EQUIPOS DE ANÁLISIS

HPLC – PAH
Y Etilbenceno



MP-AES
Metales en
disolución



GCMS –
Identificación fracciones
Diesel/identificación de
intermedios

GCMS –
Cuantificación de Diesel
(TPH)

EJEMPLO: REMEDIACION DE SUELOS CONTAMINADOS POR NAPLs

RESULTADOS OBTENIDOS

Contaminante	T (ºC)	Técnica Aplicada	[Contaminante] (mg·kg^{-1})	C_{OX}/C_{CONT} Molar exp	C_{OX}/C_{CONT} Molar esteq	Catalizador/ Activador	[Activador] (mM)	C_{OX}/C_{Fe}	X_{CONT}
Etilbenceno (Gasolinas)	20	Fenton modificado (citrato sodio)	1000	156	21	Fe (III)	5	294	**98%**
Diesel	20	Fenton	1000	432	49	Fe (III)	5	400	**61%**
		Fenton modificado (citrato de sodio)	1000	432	49	Fe (III)	5	400	**30%**
		Persulfato activado	1000	43.2	49	Fe (II)	5	40	**30%**
			1000	43.2	49	Fe 0 granular	5	40	**56%**
			1000	43.2	49	Fe 0 nanopart.	5	40	**62%**
PAH	20	Fenton	100 (cada PAH)	212	33-45	Fe (III)	5	76	**>99 %**
			100 (cada PAH)	212	33-45	Fe 0 nanopart.	5	76	**57%**
		Persulfato activado	100 (cada PAH)	111	33-45	Fe (III)+ ácidos húmicos	5	40	**80%**
			100 (cada PAH)	111	33-45	Fe 0 granular	5	40	**90%**
			100 (cada PAH)	111	33-45	Fe 0 nanopart.	5	40	**93%**

EJEMPLO: REMEDIACION DE SUELOS CONTAMINADOS POR NAPLs

- Pardo, F., Rosas, J., Santos, A., & Romero, A. (2014a). Remediation of a biodiesel blend-contaminated soil by using a modified Fenton process. *Environmental Science and Pollution Research, 21*(21), 12198-12207, doi:10.1007/s11356-014-2997-2.
- Pardo, F., Rosas, J. M., Santos, A., & Romero, A. (2014b). Remediation of soil contaminated by NAPLs using modified Fenton reagent: application to gasoline type compounds. *Journal of Chemical Technology and Biotechnology*, n/a-n/a, doi:10.1002/jctb.4373.
- Pardo, F., Rosas, J. M., Santos, A., & Romero, A. (2014c). Remediation Of a Biodiesel Blend-Contaminated Soil with Activated Persulfate By Different Sources of Iron. *Water, air & soil pollution*: 10.1007/s11270-014-2267-4) – Aceptado, pendiente de publicación.