

Innovative chemical and biological remediation processes for soil decontamination.



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Summary

1. Pollutants in Environment

1.1. Problems with hazardous compounds

1.2. Heavy metals and PAHs

1.3. Quantifying the problem in soils

2. Remediation technologies

2.1. Overview

2.2. Biological remediation

2.2.1. PAHs bioremediation

2.2.2. PAHs and metals phytoremediation

2.3. PAHs and metals electrokinetic remediation

Pollutants in Environment

Problems with hazardous compounds



- Definition

Adverse effects on individuals, species or ecosystems

- Classifications

- Origins natural/anthropogenic
- Effects health, growth rate of organisms, death...
- Properties volatility, water solubility...

- Particular problem with **toxic, non degradable/persistent** compounds



Pollutants in Environment

Problems with hazardous compounds



- Origins
 - By-products of human processes
 - Industrialized/urban areas - intensive agriculture zones
- Persistent contaminants travel long distances
 - Emissions in atmosphere (combustion processes), or improper disposal of chemicals
 - Transport by water
 - **Accumulation in sediments and soils**



Pollutants in Environment

Problems with hazardous compounds

- A long list of various persistent chemicals!

Inorganics		Organics
<ul style="list-style-type: none">• Heavy metals: Hg, Pb, Cd, Ba...• Metalloids: Sb, As...• Radionuclides: Th, U...	<ul style="list-style-type: none">• Organo-metallics: TBT, methylmercury ...	<ul style="list-style-type: none">• POPs Pesticides: DDT, dieldrin... Flame retardants: PCB... Dioxins, furans PAHs• Persistent pharmaceuticals, microplastics...• VOCs

Pollutants in Environment

Heavy metals and PAHs

- **Heavy metals: trace elements**

Occuring in the nature, not harmful at very small levels

- Essential metals:
involved in biological processes
Fe, Cu, Zn, Ni, Cr_{III}...

- Non essential metals: toxic even at low levels
Hg, Pb, Cd, Cr_{VI}...

- Considered as pollutants in high amounts

- Industrialization (mining, batteries...), fungicides

- High toxicity: poisons, reproductive/immune effects, neurotoxic, possible carcinogens...

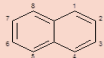




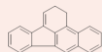


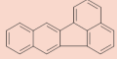
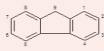

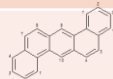


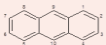

Periodic Table of the Elements

1	2											3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
1	H																			He									
2	Li	Be																	B	C	N	O	F	Ne					
3	Na	Mg											Al	Si	P	S	Cl	Ar											
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr											
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe											
6	Cs	Ba	*La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn											
7	Fr	Ra	+Ac	Rf	Ha	Sg	Ns	Hs	Mt	110	111	112	113																
			* Lanthanide Series																										
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu													
			+ Actinide Series																										
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr													

Pollutants in Environment

Heavy metals and PAHs

- **PAHs**: polycyclic aromatic hydrocarbons

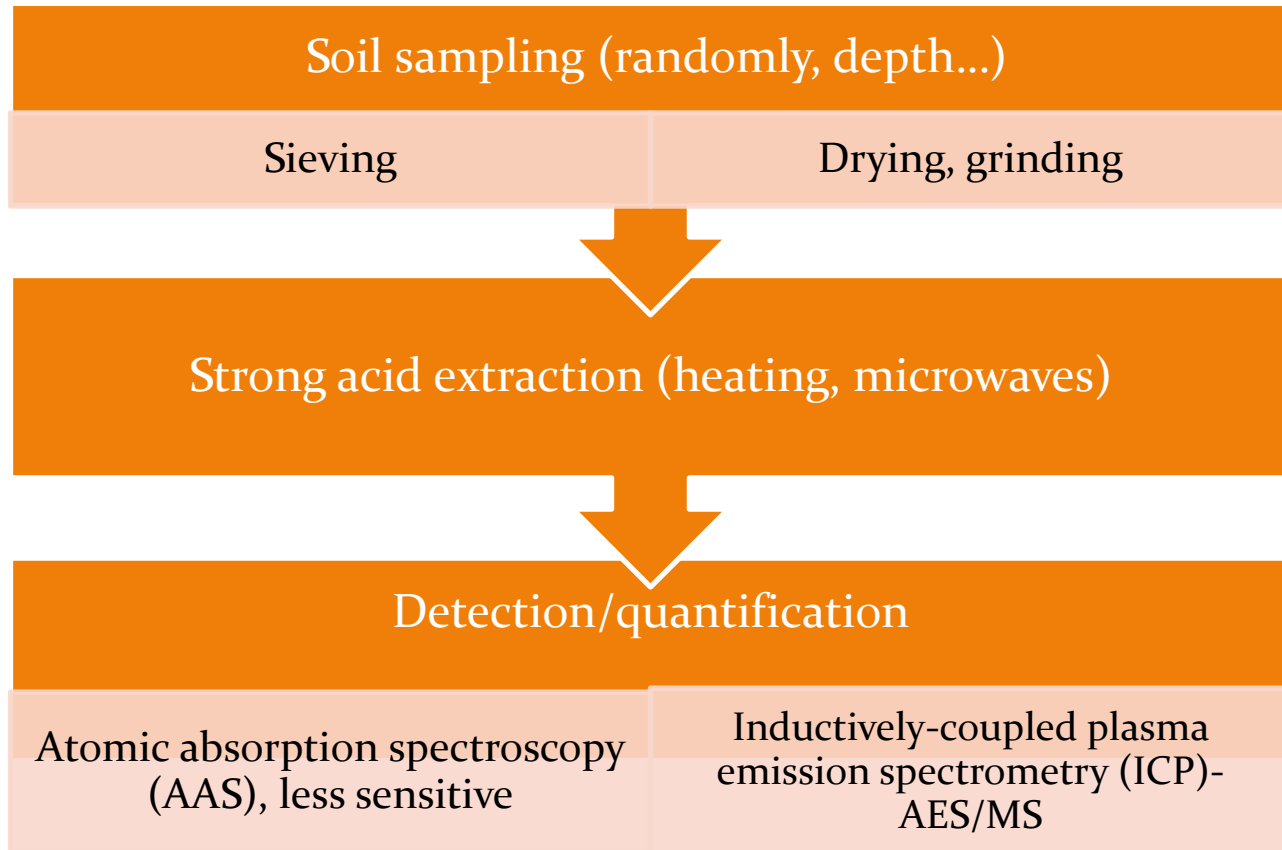
LMW PAHs <i>Vapor phase</i>		Vapor/particulate <i>phase</i>		HMW PAHs <i>Particulate phase</i>	
naphthalene		fluoranthene		Benzo[a]pyrene	
acenaphthylene		pyrene		Benzo[b]fluoranthene	
acenaphthene		chrysene		Benzo[k]fluoranthene	
fluorene		Benz[a]anthracene		Bibenz[a,h]anthracene	
phenanthrene				Indeno[1,2,3,cd]pyrene	
anthracene				Benzo[g,h,i]perylene	

- Natural or anthropogenic combustion processes (engines)/oil spills...
- Toxic, carcinogenic, mutagenic

Pollutants in Environment

Quantifying the problem in soils

metals



Pollutants in Environment

Quantifying the problem in soils

PAHs



Soil sampling (randomly, depth...)

Sieving

Drying <35°C, grinding



Solvent extraction



**Soxhlet,
ultrasound**

☹ long, high
solvent volumes

**Microwave
irradiation**

☺ short time,
low solvent
volumes

**Pressurized
heated solvent**

☺ short time,
low solvent
volumes

**Supercritical
CO₂**

☺ short time,
low solvent
volumes

Pollutants in Environment

Quantifying the problem in soils

PAHs



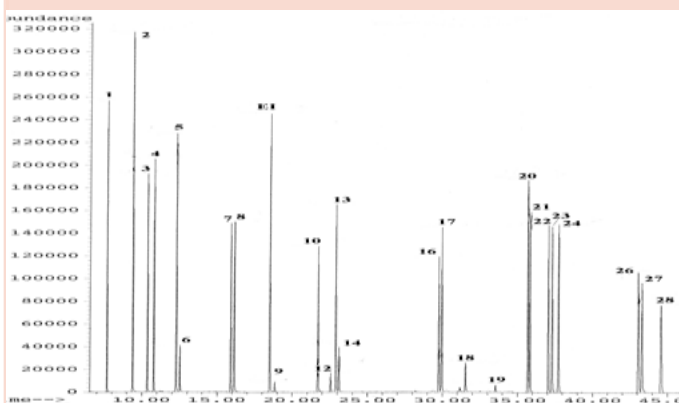
Purification/concentration
(silica gel columns, SPE)



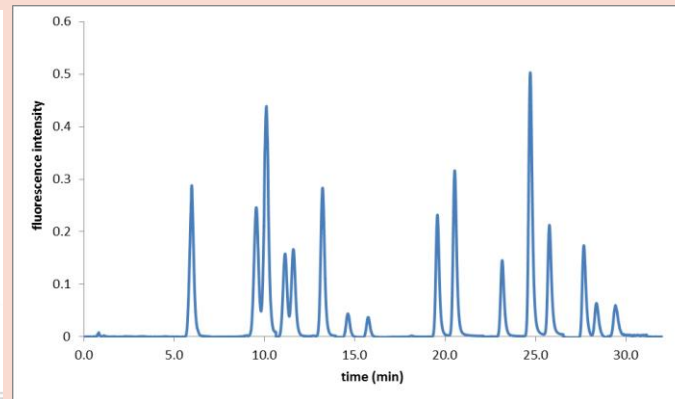
Detection/quantification



Gas chromatography FID/MS



Liquid chromatography UV/FLD



Pollutants in Environment

Quantifying the problem in soils

- Contaminants identified/quantified \Rightarrow potential threat assessed \Rightarrow **media must be treated!**
- No longer pose a threat for human health or ecosystems

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Remediation technologies

Overview

- Soils decontamination: variety of remediation processes
 - Decrease of contamination (< thresholds required by legislations)
 - Contaminant immobilization
- *Ex-situ/in-situ* implementation?
 - Treatment units: excavation+transport (high costs), short and reproducible
 - On-site: cost savings, longer and greater variability



Soil excavation for ex-situ treatment



Treatment in-situ

Remediation technologies

Overview

- **Thermal treatments** ⇒ Exposure to high temperatures
⇒ Soil quality affected

- Volatilization/Destruction

Heating ⇒ gas transported to other treatment systems

- Thermal desorption 90-560°C
- Incineration 450-800°C

- Immobilization

Very high temperatures ⇒ glassy materials chemically stable

- Vitrification 1600-2000°C



Remediation technologies

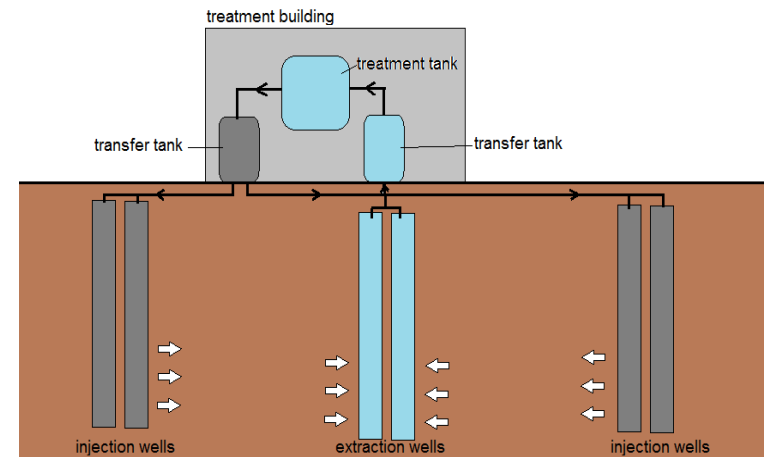
Overview

- **Physical-chemical treatments**

- **Physical**

- Water flushing: injection of water ⇒ pump and treat (P&T)
 - Air sparging: injection of air
 - Vapor extraction: vacuum applied to a zone ⇒ P&T
- ⇒ Not aggressive, too selective (volatile pollutants)

- Solidification: encapsulating semi-liquid wastes (cement)
⇒ restrict migration
⇒ Affect soil characteristics



Pump and treat P&T technology

Remediation technologies

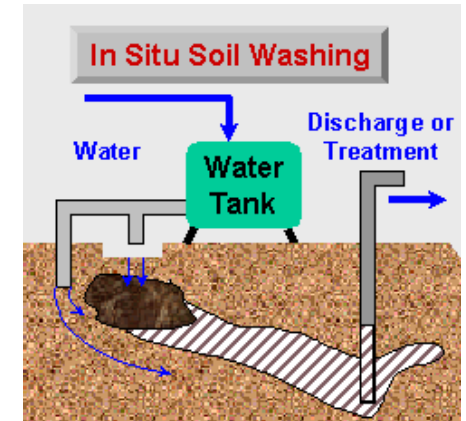
Overview

- **Physical-chemical treatments**

- **Chemical**

- Chemically enhanced flushing or soil washing : injection of solutions with additives (basic, acid, surfactants...) to enhance desorption/solubilization
- Oxidation/reduction: transformation by oxidants or reductants
- Solvent extraction : organic solvents as extractants

⇒ Aggressive treatments



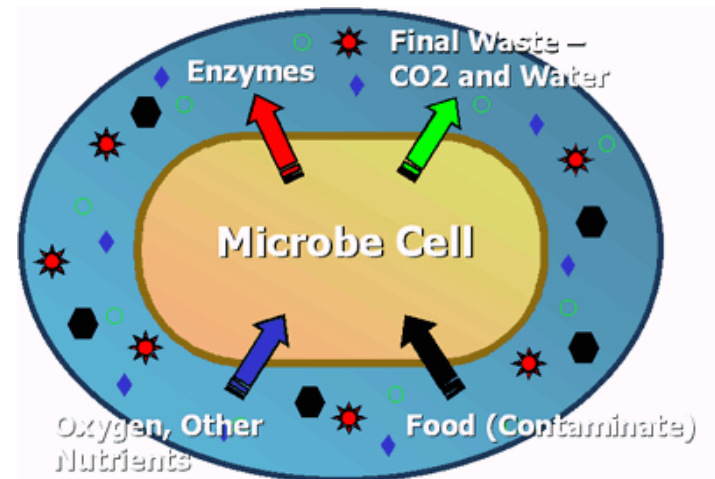
Remediation technologies

Overview

- **Biological treatments**

- **Bioremediation**

- **Monitored natural attenuation:** uses natural processes (microbes/fungi) to biodegrade ⇒ Not aggressive but very long
- **Biostimulation/Bioaugmentation:** introduction of nutrients or microorganisms ⇒ enhanced biodegradation
- **Bioreactors:** enhanced biodegradation in bioreactors



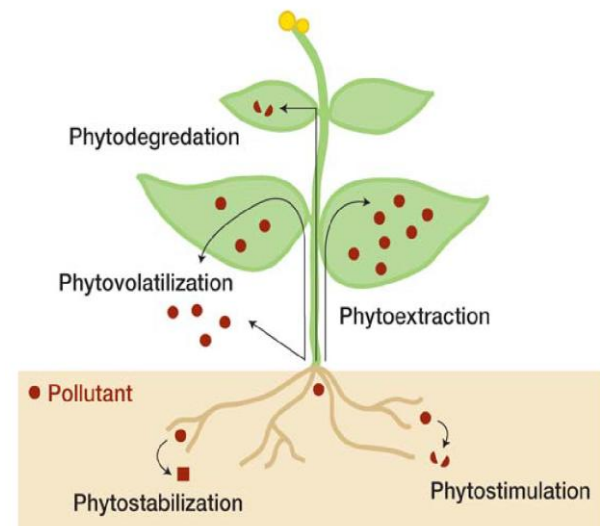
Remediation technologies

Overview

- **Biological treatments**

- **Phytotechnologies:** vegetation to remove/trap contaminants

- **Phytodegradation:** uptake and degradation by plants, or by associated microorganisms in roots
- **Phytoextraction** or phytostabilization: uptake and accumulation in plant tissue or immobilization in roots
 - ⇒ subsequent harvesting



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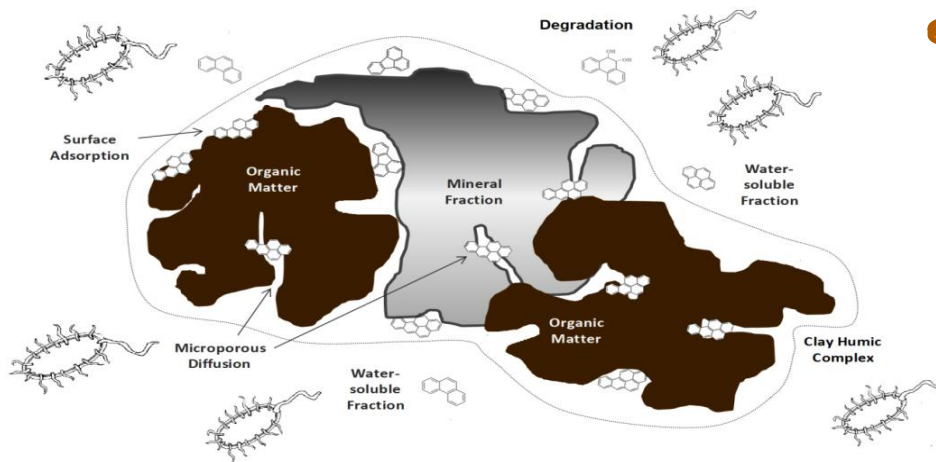
2.3. PAHs and metals electrokinetic remediation

Remediation technologies

Biological remediation

PAHs bioremediation

- Natural attenuation effective if
 - Accessible PAHs ?
 - Degrading microbes exist ?
- Problem of accessibility: sequestered vs labile PAHs
 - high bioaccessible fraction ⇔ natural attenuation effective
 - low bioaccessible fraction ⇔ natural attenuation not effective



- Necessary diagnostic:
Original method developed at
COBRA laboratory

Strong sorption of PAHs on clays and organic matter

Remediation technologies

Biological remediation

PAHs bioremediation

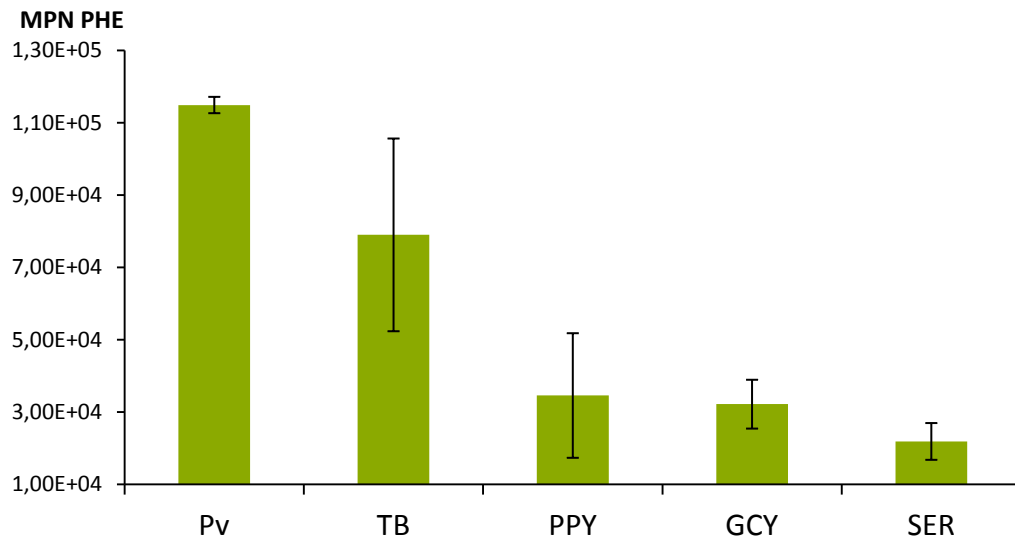
- Microbial characterization

- Total number of bacteria: not correlated to PAH degradation rates!

- ⇒ Number of **specific degrading bacteria** is more important

- Looking for the nature of degrading bacteria

- ⇒ Various biological techniques are available (*ex: DNA stable isotope probing*)



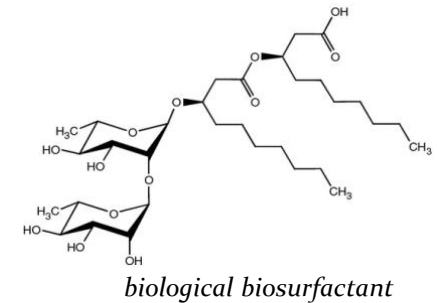
Most Probable Number of PHEN-degrading bacteria in different soils (Johnsen method, 2010)

Remediation technologies

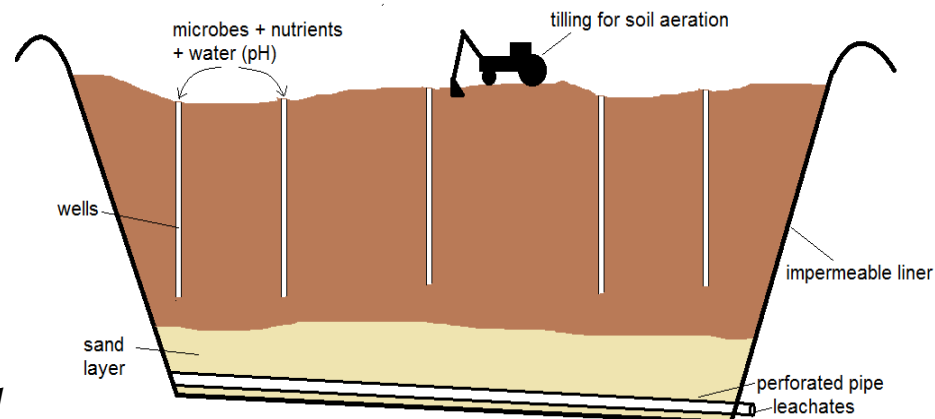
Biological remediation

PAHs bioremediation

- Low accessible PAH fraction?
 - ⇒ Amendments to enhance PAH desorption/solubilization
 - Ex: surfactants, soluble humic substances...
- Few degrading microorganisms ?
 - Biostimulation: amendment of nutrients
ex: O₂ (bioventing), carbon rich substrates
 - Bioaugmentation: amendment of specific microbes or fungi



Land farming

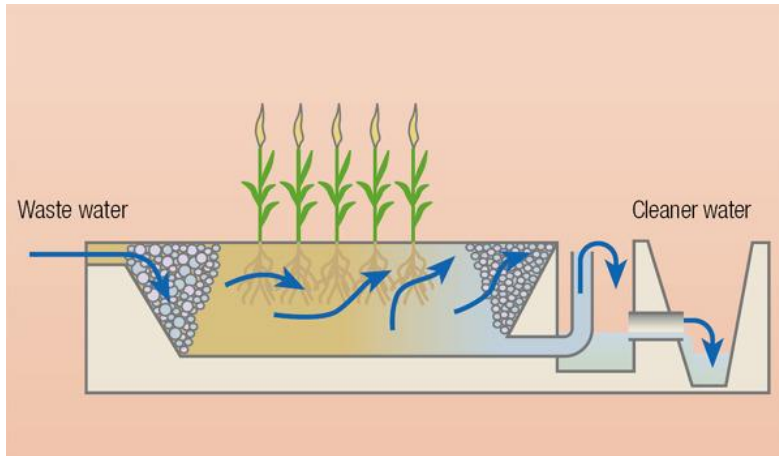


Remediation technologies

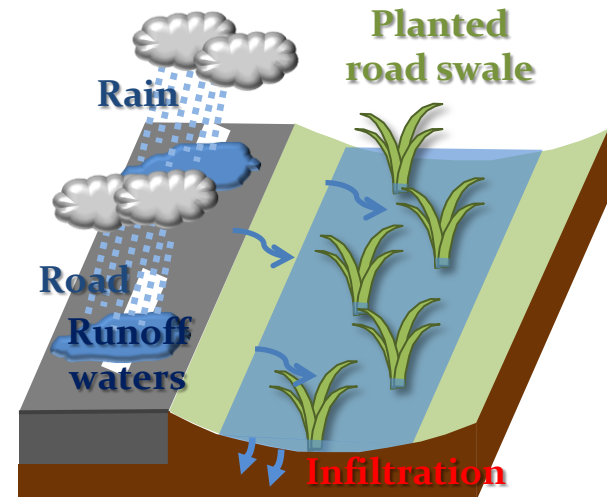
Biological remediation

PAHs/metals phytoremediation

- Phytoremediation: enhanced decontamination **by plants**
 - Main applications for metal removal, but also effective for PAHs
 - Main applications for waste waters decontamination



Use of plants in biofilters (sewage treatment plants)



Use of plants in urban green spaces (planted swales)

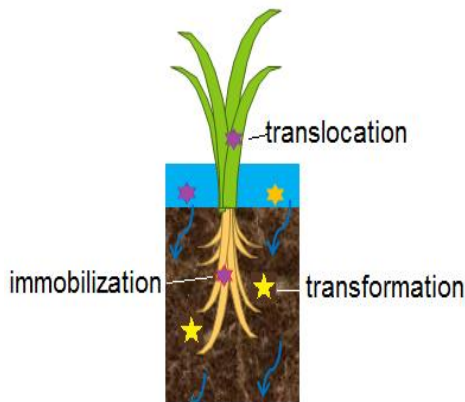
Remediation technologies

Biological remediation

PAHs/metals phytoremediation

- Different processes for organics/inorganics
 - **Phytodegradation** of PAHs: enhanced degradation by associated microorganisms in roots
 - **Phytoextraction** of metals: transfer to plant tissues (leaves, fruits)
 - ⇒ periodic harvesting for eliminating metals

- Which plants? ⇒ Tests in pots, mesocosms...



Different processes in plants

Indian mustard,
Sunflowers,
Rye-grass,
Poplar trees...

Grass mix
Iris Pseudacorus
Phalaris Arundinaceae
Juncus Effusus

tests in mesocosms



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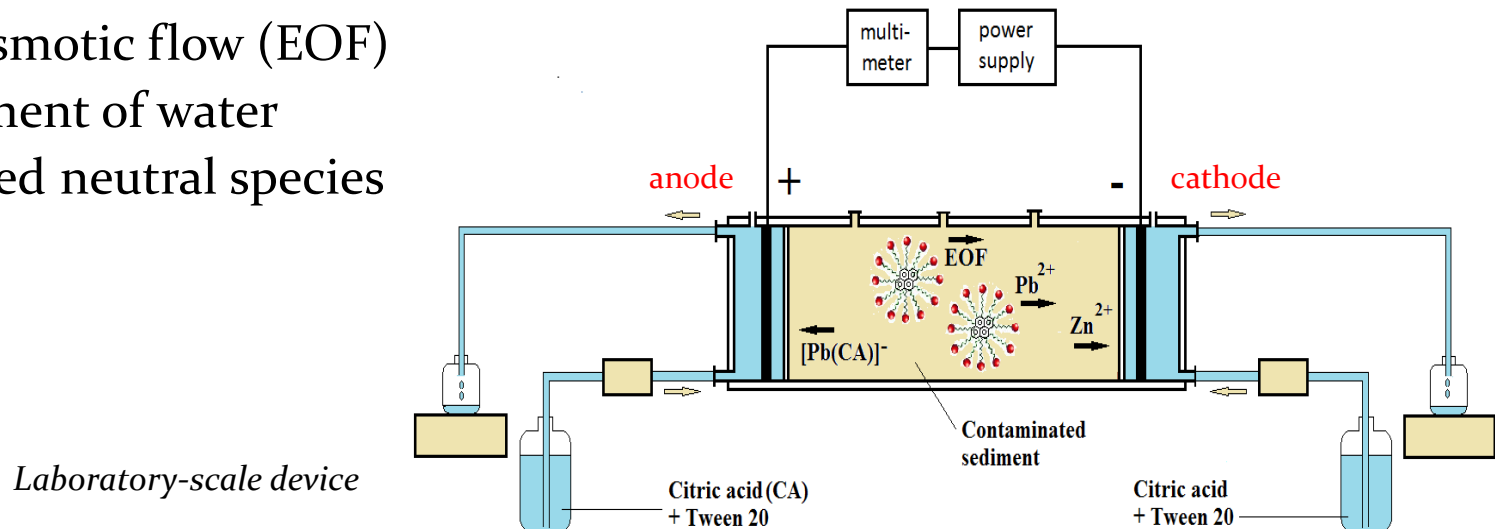
Remediation technologies

PAHs and metals electrokinetic remediation

- Electrokinetic (EK) migration of pollutants through soils/sediments
 - ⇒ Attenuation in large zones/concentration in restricted zones ⇒ P&T

➤ Principles:

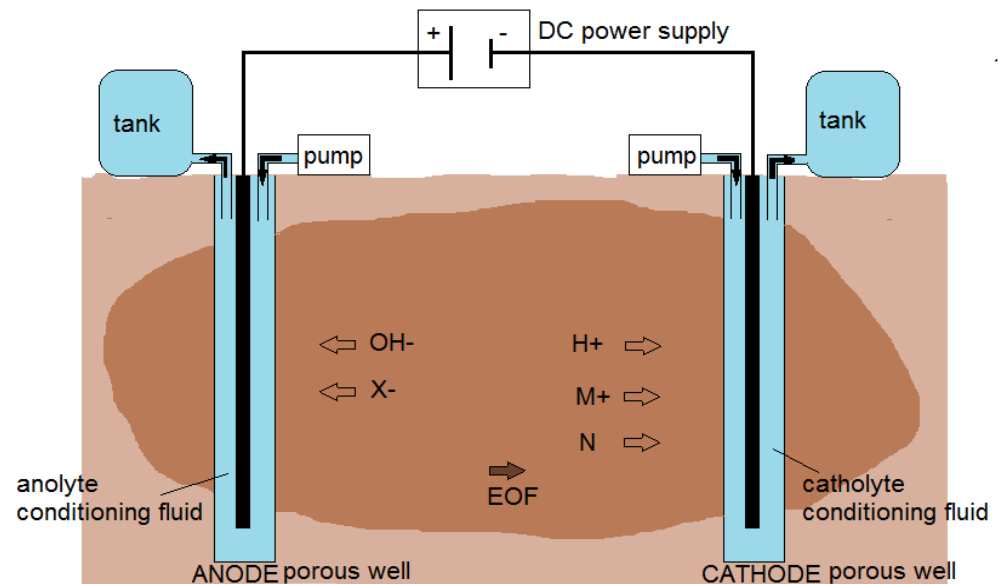
- Electric field applied via electrodes ⇒ electromigration of charged metals
- Electroosmotic flow (EOF)
 - ⇒ Movement of water
 - + dissolved neutral species



Remediation technologies

PAHs and metals electrokinetic remediation

- Advantages of EK treatment
 - Possible *ex-situ/in-situ* treatments
 - Possible for low-permeability soils (flushing impossible)
 - Faster than bioremediation (weeks rather months/years)
 - Not aggressive for soils (low current)
 - Multiple depollution: metals + PAHs together



In-situ field-scale EK treatment

Remediation technologies

PAHs and metals electrokinetic remediation

- Developments for *on-site* EK treatments

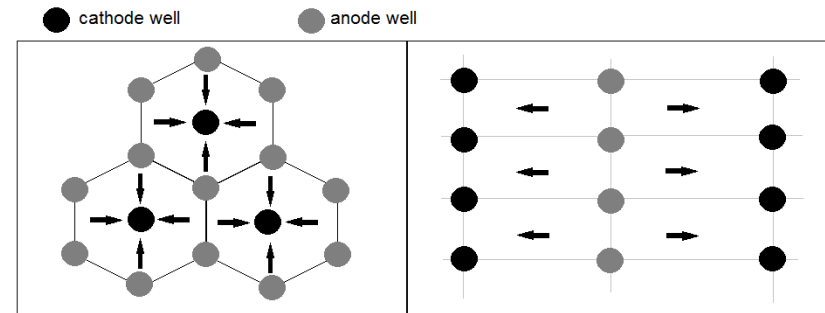
- Which configuration of electrodes?

- Combined technologies

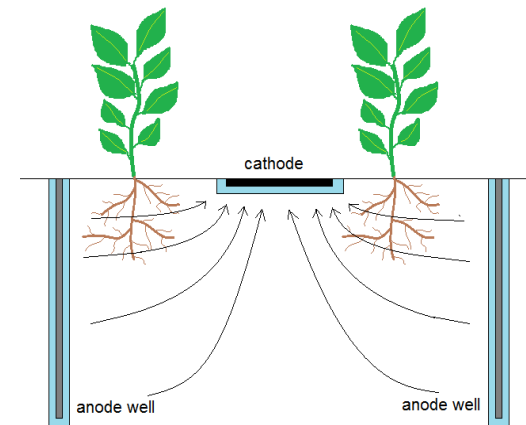
- EK + oxidation : accelerate degradation

- EK + bioremediation (microorganisms amendments):
accelerate degradation

- EK + phytoremediation:
accelerate degradation+extraction



Possible in-situ configurations of electrodes



EK-assisted phytoremediation

Thank you for your attention!

