Inorganic Pollutants

Origin – Distribution – Behavior – Analysis

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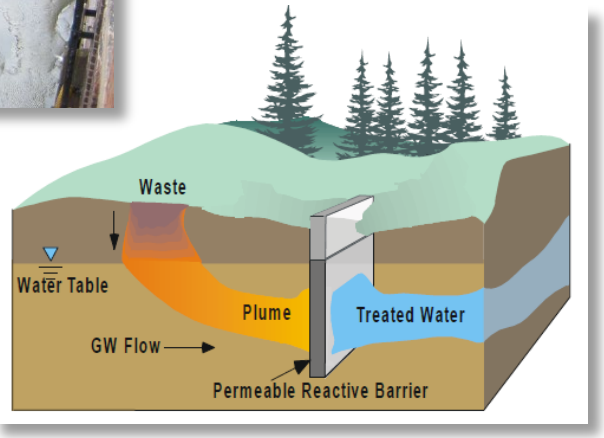
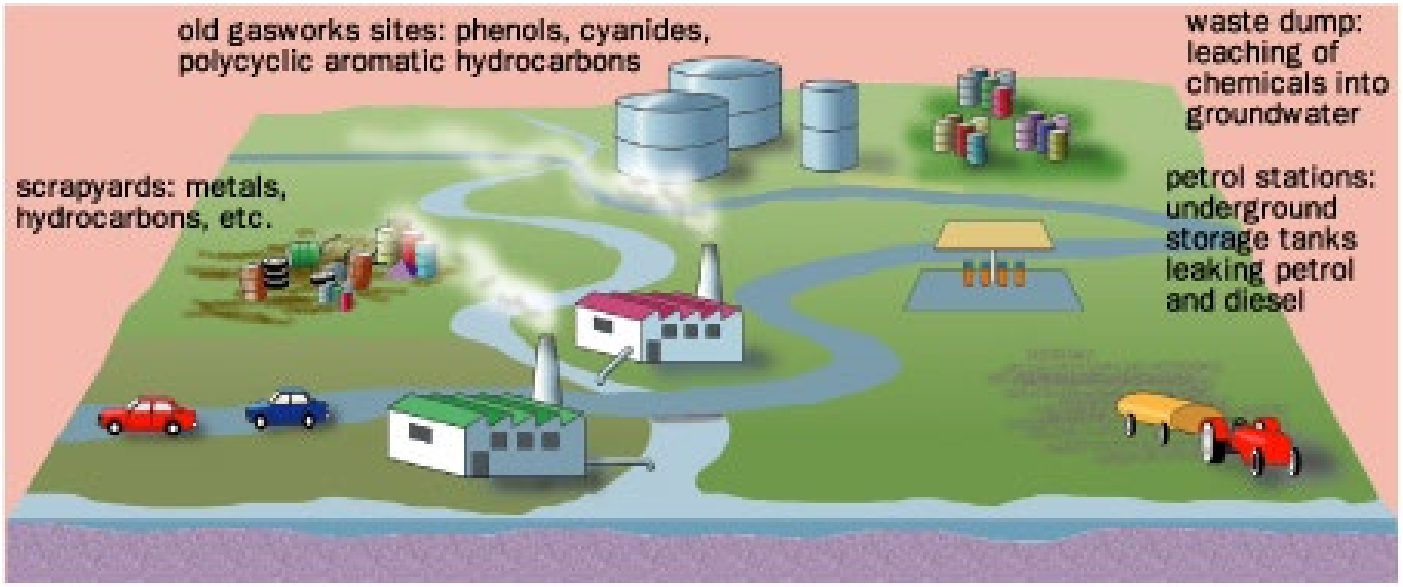
Inorganic Pollutants – Remediation of Inorganic Contaminants



Contaminated Sites



Contaminated sites emerge from:

- **wrong/no arrangements for environmental protection (within/outside of legal limits)**
- **careless handling of hazardous materials in the industry**
- **uncontrolled waste streams (effluents, smoke stack emissions, deposits)**
- **war damage / accidents / assaults**

Contaminated Sites

Worldwide production rates:

Metal		10^6 t per year	main use
Calcium	(as CaO, lime)	~ 300	cement/concrete, fertilizer, road de-icing salts
	(other)	~ 150	
Sodium	(as NaCl)	~ 270	table salt, road de-icing salts, chem. industry
Potassium	(as K_2O)	~ 39	fertilizer (95%)
Iron		1575	iron & steel industry
Aluminum		58	light alloy, electrical wires
Copper		20	electrical wires, alloys, pipes, sheets
Zinc		11	alloys, plating
Chromium (as Cr_2O_3)		13	plating, stainless steel
Lead		10 (6)	batteries, pigments
Titanium		7	TiO_2, white pigment
Nickel		2	alloys, stainless steel, batteries
SO_2		160	coal/oil burning, ore processing, emission to atmosphere
CO		380	coal/oil burning, ore processing, emission to atmosphere
		10^3 t per year	
Tin		340	plating, welding electrodes, solder
Arsenic		35	wood preservative, solid state devices, solar cells
Cadmium		26	plating, alloys, batteries
Tungsten		85	hard metall, bulbs, catalysis
Mercury		4	electronics, batteries, tooth filling, preservatives

coal and petroleum: 11,400 10^6 t per year

- wood treatment (As)
- leather production (Cr)
- electroplating (Cr, Cd, Zn)
- chemical industry
- pigment production
- battery production (Cd, Ni, Pb)
- mining & smelting

+ coal ash dumps

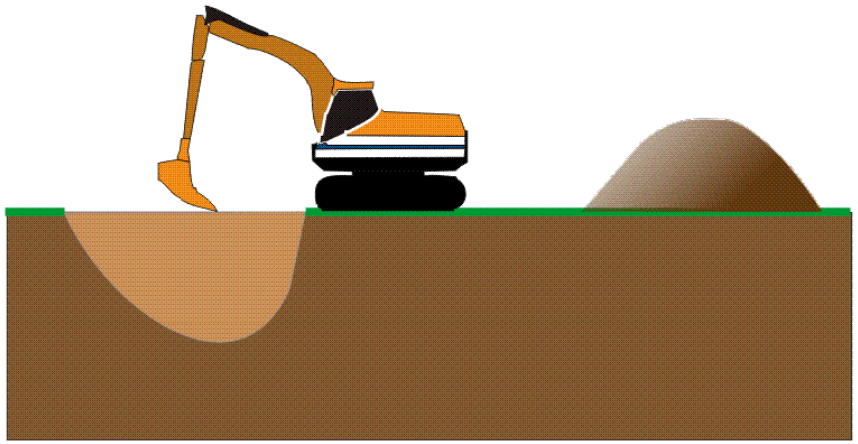
(110 mio tons/year in the US)

+ tailings from coal mining

+ waste deposits
+ tailings from mining
+ abandoned mine effluents

Source: diverse - 2018

Remediation (clean-up) options



dig and dump ?

+ removal of the contaminant
+ proof of removal
+ safe treatment (off site) or safe disposal
+ often comparably fast

+ high costs for low but wide-spread contamination

Alternatives?

→ huge problem & multi billion business → myriads of technologies were proposed

→ Often work well in the lab and in small scale or with a very specific problem (e.g. only one metal addressed)

→ alternatives to complete removal (dig & dump) of the contaminated materials must prove to be technically & economically competitive

Remediation (clean-up) options

It is important to know the behaviour of metals
for selecting /developing the remediation technique

Behaviour in the environment? **Remediation process & procedure**

Fate of the contaminant ?

Distribution between phases
Reactivity
Transport
Speciation/Transformation

How do environmental conditions change

the behaviour of contaminants?

Knowing the behavior & toxicity to

- assess the situation on a contaminated site
- identify current and future problems

- assess the risks emerging from the site situation
- rank the risks

- select best technique for remediation

Remediation (clean-up) options

It is important to know the behaviour of metals
for selecting /developing the remediation technique

Behaviour in the environment? — **Remediation process & procedure**

Fate of the contaminant ?

Distribution between phases
Reactivity
Transport
Speciation/Transformation

How do environmental conditions change
the behaviour of contaminants?

Knowing the behavior to develop alternative remediation techniques

Experiments in the lab

applicability
feasibility
proof of principle
+ cost evaluation

Scale-up
+ feasibility
+ cost analysis

Testing (large scale / field)

Remediation (clean-up) options

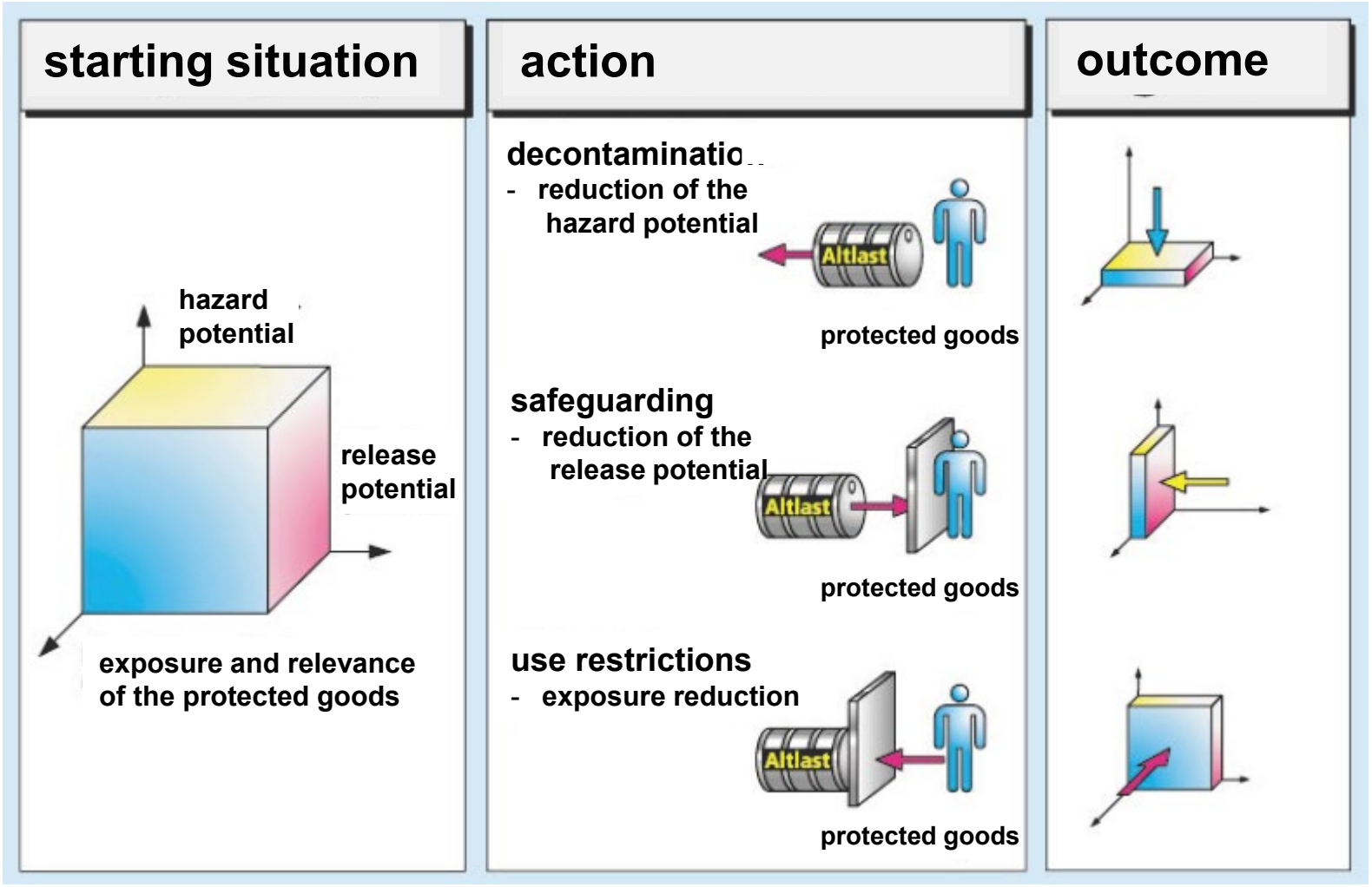
Properties of metals and related processes suitable for a remediation action

Persistence	→	**No biological degradation**
	→	**Enrichment in sinks like soils and sediments**
	→	**Sinks can turn into sources**
Fixation	→	**Ion exchange**
	→	**Precipitation (pH, Redox, Sulphides…)**
	→	**Sorption**
	→	**Complexation (org. subst.)**
Mobilisation	→	**Complexation (DOC, Cl^-)**
	→	**Bound to colloids or nanoparticles**
	→	**Transformation (Methylation, Redox)**
	→	**Ion exchange**
	→	**Dissolution / Desorption (pH, Redox)**
Speciation	→	**Oxidation state, complexation**
	→	**binding**

→ **all depend on environmental conditions !**

Site Assessment
Treatment techniques
Remediation techniques

3-options concept of remediation



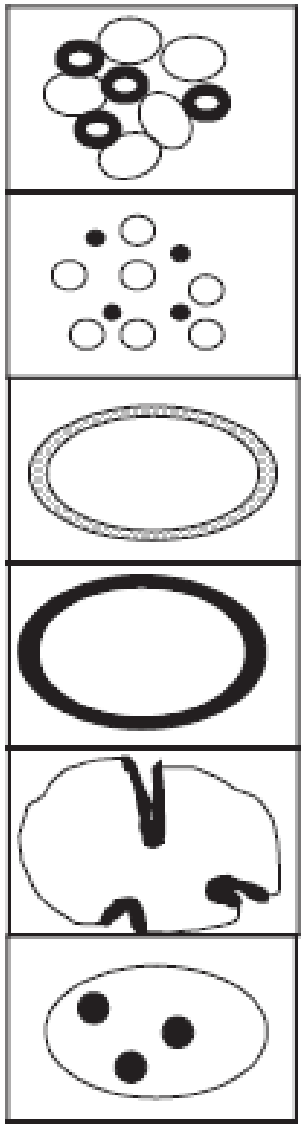
http://www.umwelt-schweiz.ch/

Overview

- Prominent Remediation Techniques:
  - Soil Washing
  - Soil Flushing
  - Soil Stabilisation or Solidification
  - Electro-kinetic Techniques
  - Chemical Oxidation
  - Thermal Desorption
  - Encapsulation, Capping, Reactive Walls
  - Phytoremediation
  - Nanotechnology

https://frtr.gov/

Contaminant Association with Soil & Sediment



(a) Adsorbed contamination - the contaminants preferentially sorb on specific particles such as clays and peaty matter

(b) Discrete particles – the contaminants occur as individual particles.

(c) Liquid or semi -liquid coatings - oily or tarry contaminants which coat the outside of soil particles

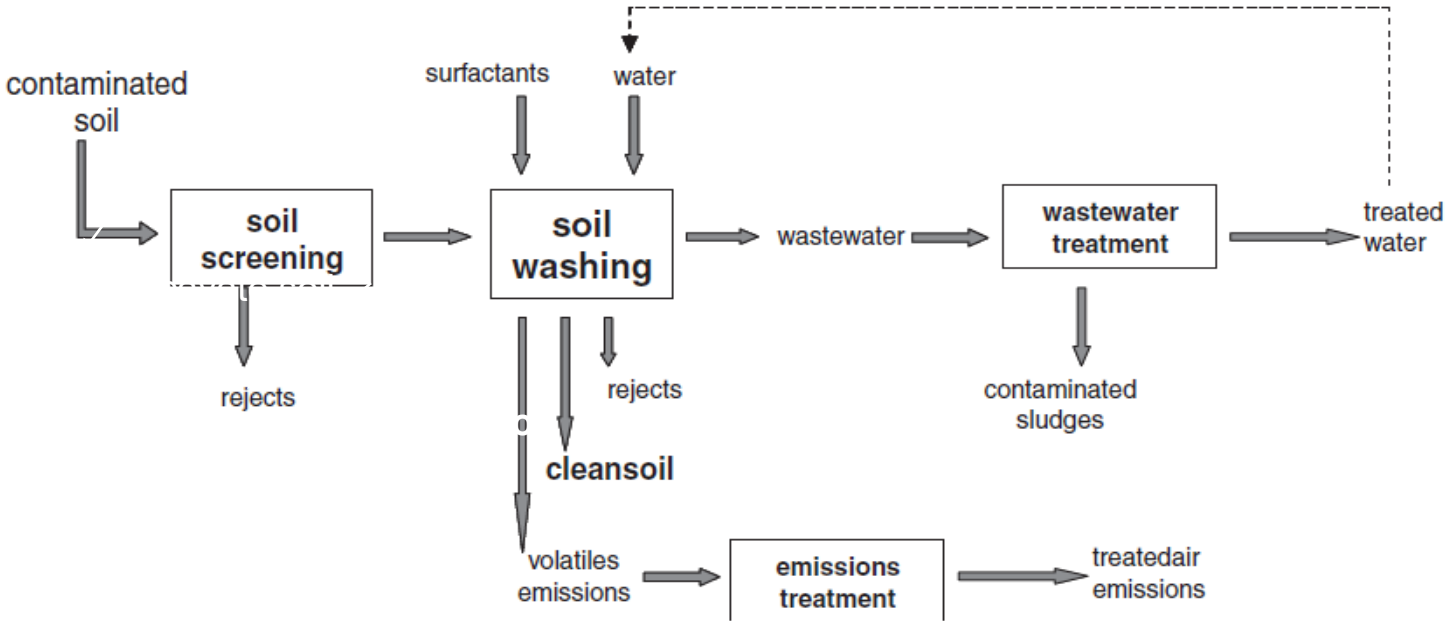
(d) Chemically precipitated coatings - many inorganic contaminants coat the outer surface of soil particles

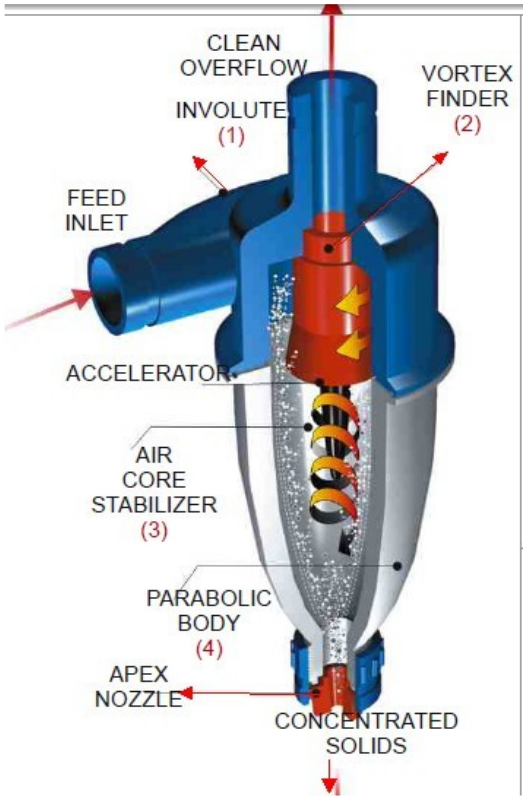
(e) Coatings on pore walls - similar to (b) and (c) but the soil particles are porous

(f) Internal contamination - larger grains with inclusions of contaminants

EPA CL:AIRE bulletin

Soil Washing



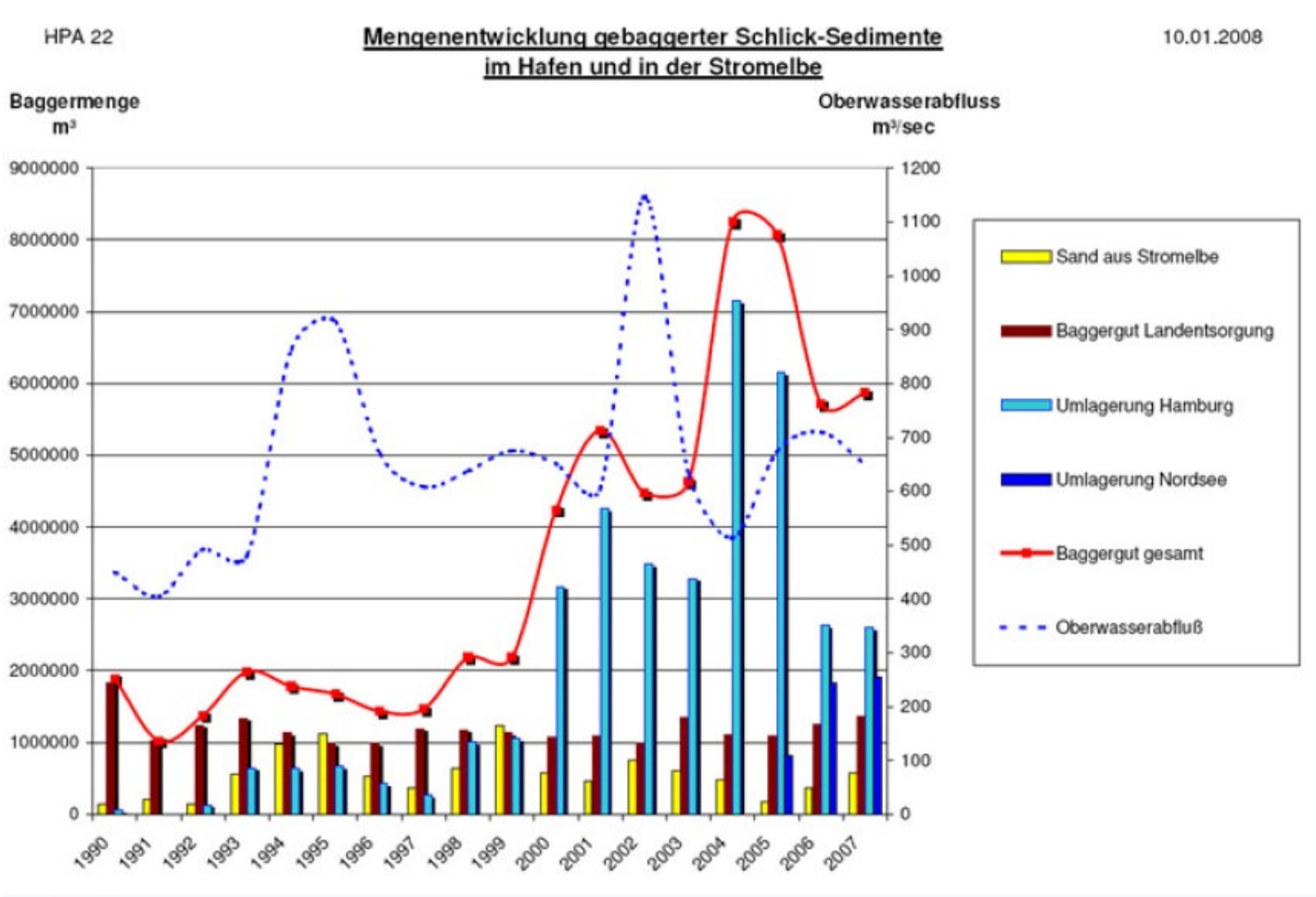


http://gn-solids-control.typepad.com

Physical	Chemical
Metal particles or **metal contaminated particles**: • By size (screening, hydrocyclone) • Density (settling velocity → flotation) • Magnetism • Electrostatic separation (aerosols → filters)	**Exchangeable metals** or **Fe/Mn oxide associated** • Acids (H^+ exchange, dissolution eg. carbonate particles) • Salts or high Cl^- (exchange & Cl-complexes) • Chelating agents (solubilize by complexation) • Surfactants (detach particles, desorb M) • Redox agents (increase mobility, dissolve FeOx & MnOx)

Example: harbor-sludge treatment METHA (Hamburg)

- **Harbor: Sediment trap for the SPM transported in the river**
- **Contains various contaminants**
- **Fine fraction holds most of the contamination (surface area !)**
- **Hamburg: ~ 6,000,000 m³ per year**



Relation of particle size with pollutant load and surface area

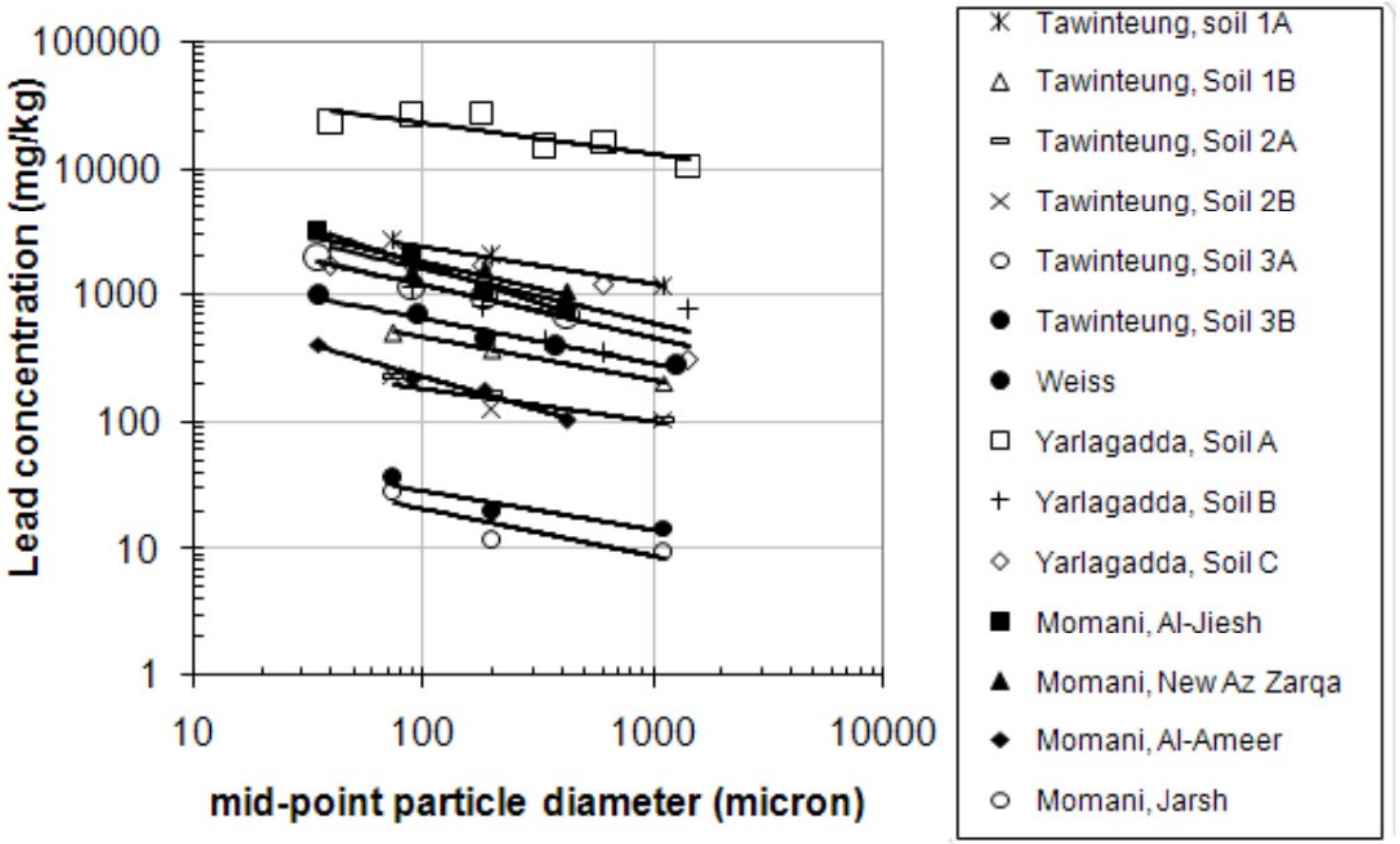


Figure 1. Lead concentration as a function of particle size or several soils reported in the literature.

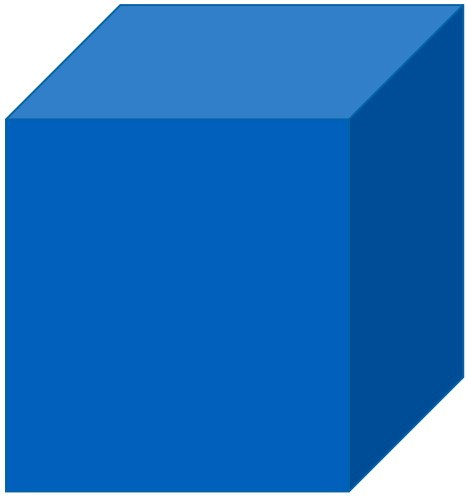
Metal concentration usually increases with decreasing particle size

→ Larger grains less contaminated

Example: harbor-sludge treatment METHA (Hamburg)

- **Contaminant sorption/interaction occurs at the particles surface (solid/water interface)**
- **Smaller particles have larger specific surface area (m^2/kg)**

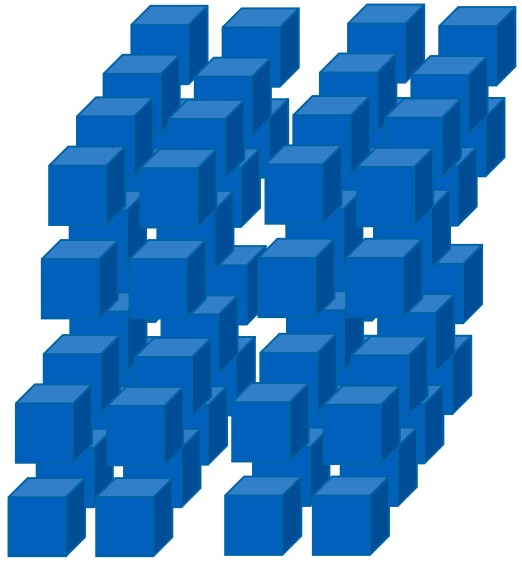
Length = 1µm



$SA_p = 6 * (1^2) = 6\ \mu m^2$

SSA = 2310 m^2 / kg

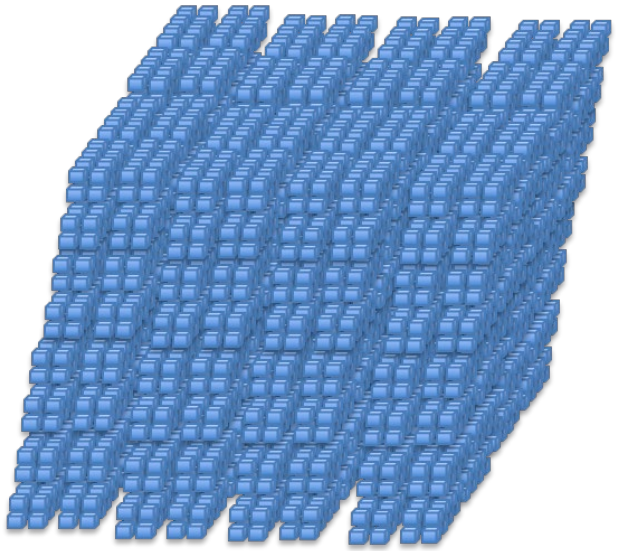
Length = 0.25µm



$SA_p = 6 * 64 * (0.25^2) = 24\ \mu m^2$

SSA = 9320 m^2 / kg

Length = 0.0625µm



$SA_p = 6* 4096 * (0.625^2) = 96\ \mu m^2$

SSA = 36,920 m^2 / kg

particle density: 2.6 g/cm^3

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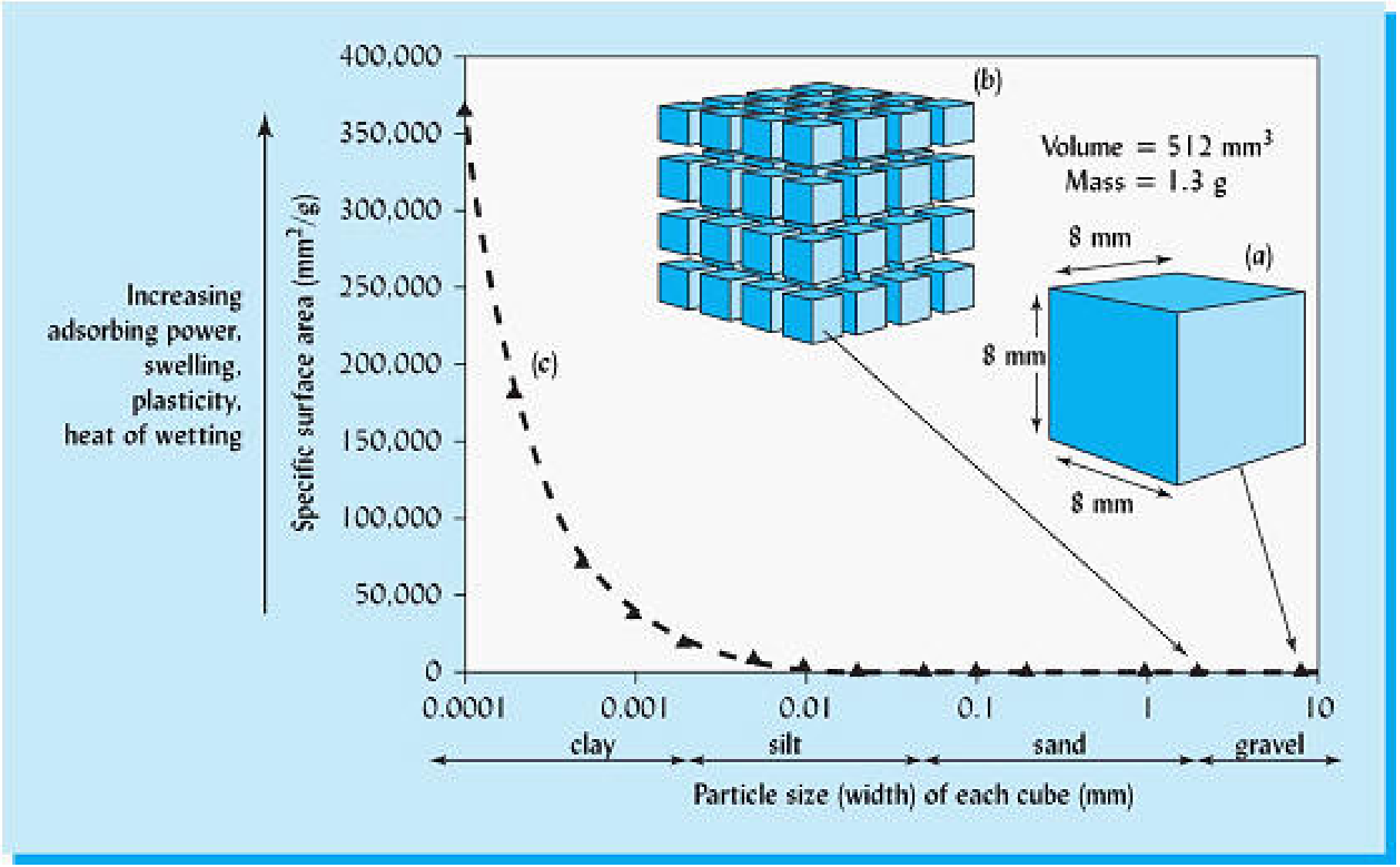
Relation of particle size with pollutant load and surface area



http://www.geo.hunter.cuny.edu/tbw/soils.veg.fall.2016/lecture.outlines/soils.chap.1.2/soils.chap.1.2.htm

Relation of particle size with pollutant load and surface area

Soil particle size (after sieving), total Hg concentration in soil fraction and leachable Hg

Table 2

Distribution of particle size fractions and total Hg (Hg_T) in solid soil samples leachates of the soil particle size fractions (±SD, $n = 3$).

Texture	Particle size (mm)	Hg_T (mg kg^{-1})	Hg_S (µg kg^{-1})
Clay/silt	<0.063	49 ± 2	16 ± 2
Sand	0.063–0.125	42 ± 2	27 ± 4
	0.125–0.25	30 ± 1	25 ± 1
	0.25–0.5	25 ± 6	37 ± 6
	0.5–1	20 ± 3	35 ± 3
	1–2	24 ± 5	16 ± 3
Gravel/stone	2–4	10 ± 1	4 ± 2
	4–6.3	8 ± 1	–
	6.3–12.5	6 ± 2	–
	12.5–25	3 ± 1	–
	>25	3 ± 3	–

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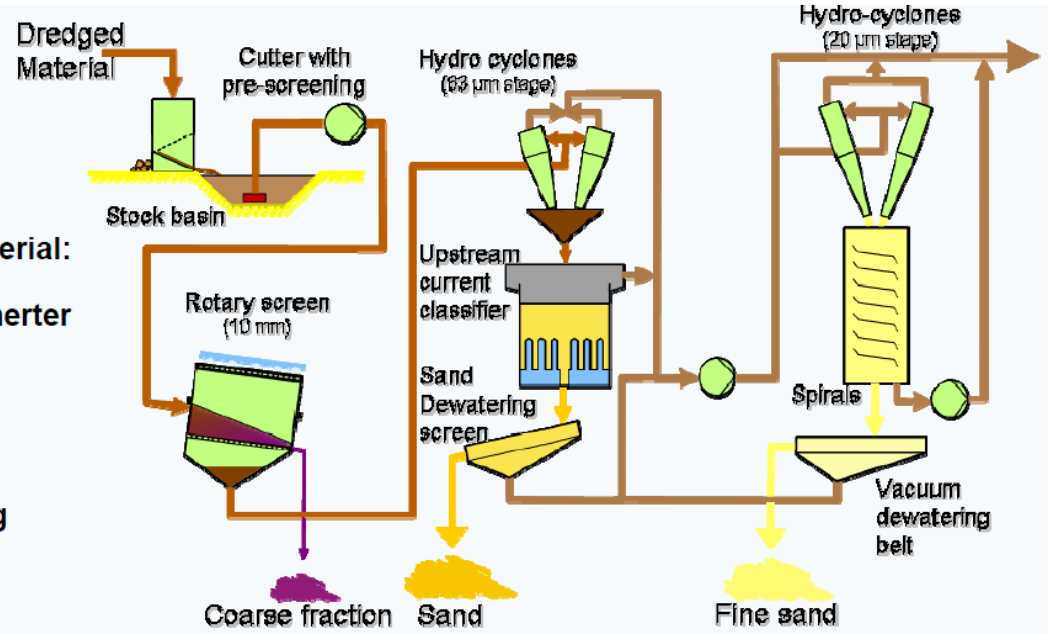
Example: harbor-sludge treatment METHA (Hamburg)

- Only physical separation
- Build 1992
- 1600 m³ /h
- 4500 t treated sludge per day
- 40 t silt dried per h
- 200 t coarse sand per h
- costs 13 M€ per year

- Trennung der Kornfraktionen
- Entwässerung
- => METHA-Material: qualitätsgesicherter Baustoff
- => Verwertung Beseitigung



Hamburg Harbor total:
~ 7.000.000 m³ per year

1.500.000 m³ treated by METHA

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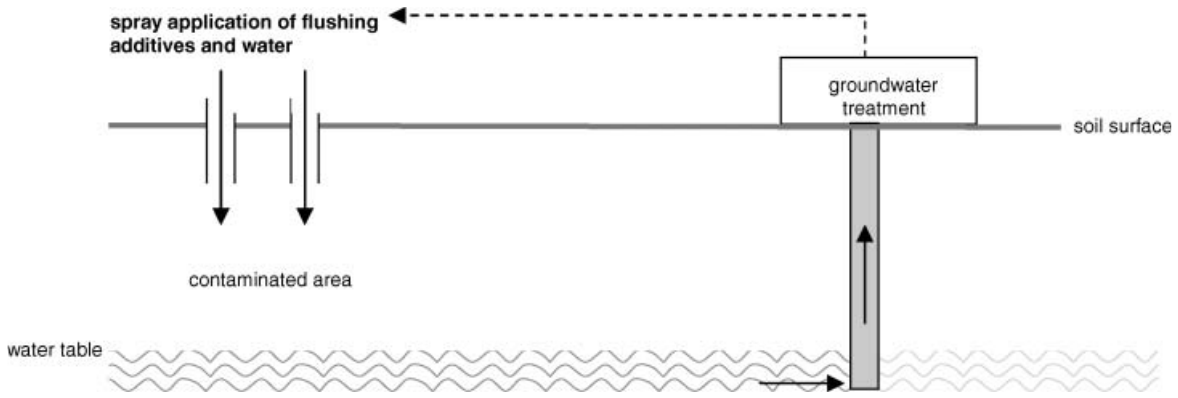
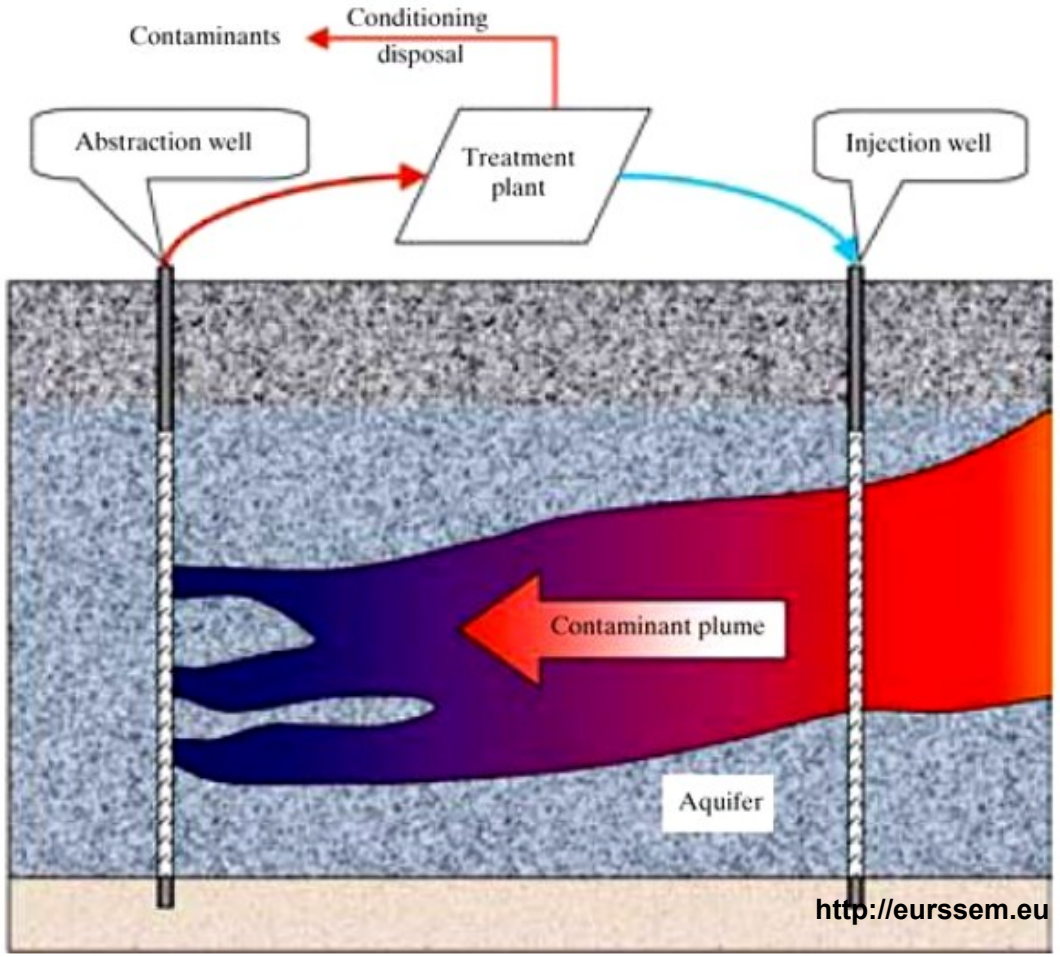
Soil Washing

Advantages	Problems
Reduction of volume (up to 90%)	Ex-situ (excavation)
Mobile units: on-site treatment possible	No immobilisation – residual soil has to be disposed
Organic & inorganic contaminants targeted	Washing water requires treatment
Enables metal recovery	Large and expensive equipment
Possible chemical recycling	High silt/clay/humus content interferes with extraction (metals strongly bound)
Closed ex-situ system enables controlled conditions (pH, redox...)	Soil properties destroyed (if chemical treatment as e.g. acidic addition)
	Toxic chemicals used for extraction

Soil Flushing

- **Pump & treat**
- **Plus injection of water or reactant / extractant**





- **In-situ technique**
- **Extraction fluid:**

  water + additives: chelating agents, acids, surfactants
- **Injection or infiltration**

  injection well, surface flooding or spraying,
  surface trenches, ↔↓drain systems
- **Capture via groundwater-extraction well**
- **Extracted groundwater has to be treated**
- **Cleaned groundwater might be reused for flushing**
- **Ex-situ alternative: heap leaching**

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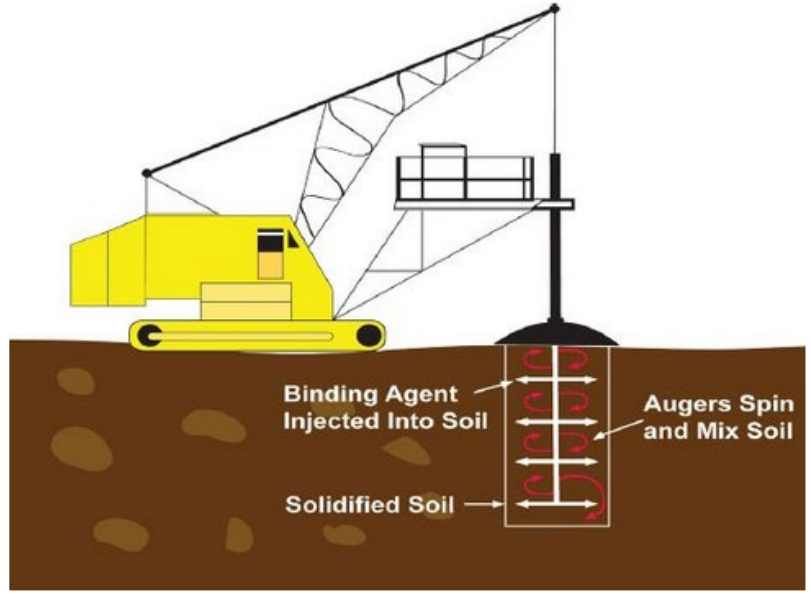
Soil flushing

Advantages	Disadvantages
In-situ	Water treatment (costs)
Cost-reasonable	Permeability dependent non-permeable hot-spots not treated well
Metal recovery possible (precipitation, ion-exchange, adsorption)	Detailed data on hydrogeology prevent that flushing solution escapes
Pumped solution can be reused as flushing fluids	Long remediation times source zone depletes slowly
	Energy consumption
	Slow desorption reactions lead to rise of concentrations after stopping the flushing

Stabilization & Solidification

Applicable to wide range of contaminants:

- **Metals (best)**
- **Radionuclides**
- **Non- or semi- volatile organics**
- **Not ideal for volatile contaminants**



http://www.geoengineer.org/

Stabilization & Solidification

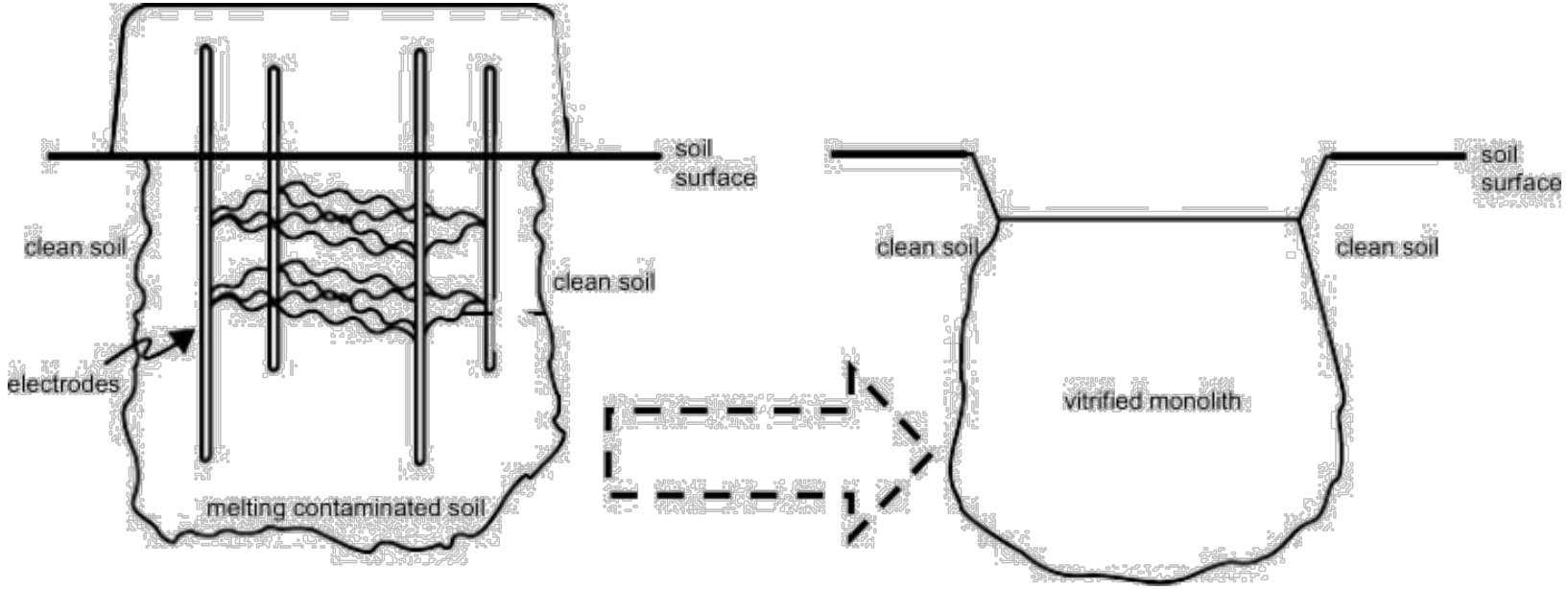
STABILISATION:

- Addition of (inexpensive) **amendments**
  - Minerals (apatite, zeolite, clay, lime)
  - Waste by-products (steel shot, iron-rich biosolids,...)
- Change chemical **speciation** →less soluble/mobile/toxic
- Consider **soil conditions** and history (geochemistry)

Stabilization & Solidification

<u>SOLIDIFICATION:</u> physical encapsulation in a **monolith**

- **Solidifiers**
  - Bitumen, cement
  - Portland cement, fly ash, kiln dust... (cementious matrix, raise pH)
- **Temperature: vitrification**
  - Melt soil at 1,600-2,000°C
  - Immobilisation in **inert glass**



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Stabilization & Solidification

Waste Component	Treatment Type			
	Cement-Based	Pozzolan-Based	Thermoplastic Microencapsulation	Surface Encapsulation
ORGANICS				
Organic solvents and oils	May impede setting, may escape as vapor	May impede setting, may escape as vapor	Organics may vaporize on heating	Must first be absorbed on solid matrix
Solid organics (e.g., plastics, resins, tars)	Good-often increases durability	Good-often increases durability	Possible use as binding agent in this system	Compatible-many encapsulation materials are plastic
INORGANICS				
Acid wastes	(trass-cement) Cement will neutralize acids	Compatible, will neutralize acids	Can be neutralized before incorporation	Can be neutralized before incorporation
Sulfates	May retard setting and cause spalling unless special cement is used	Compatible	May dehydrate and rehydrate causing splitting	Compatible
Halides	Easily leached from cement, may retard setting	May retard set, most are easily leached	May dehydrate and rehydrate	Compatible
Heavy metals	Compatible	Compatible	Compatible	Compatible
Radioactive materials	Compatible	Compatible	Compatible	Compatible

(Reproduced from: USEPA, 1986)

Stabilization & Solidification

Advantages	Disadvantages
In-situ (inexpensive)	In-situ: no removal Ex-situ: displacement
Quick and straight forward remedy	Efficiency decreases over time or when geochemistry changes
Prevents contaminant spreading (exposure)	Long-term monitoring necessary
	Depth-limited (costs)
	Stabilisation: mainly metals captured
Solidification: all non-volatile contaminants captured	**Solidification**: increases contaminant volume
Vitrification: inert glass	**Vitrification**: toxic gasses may form very high energy consumption


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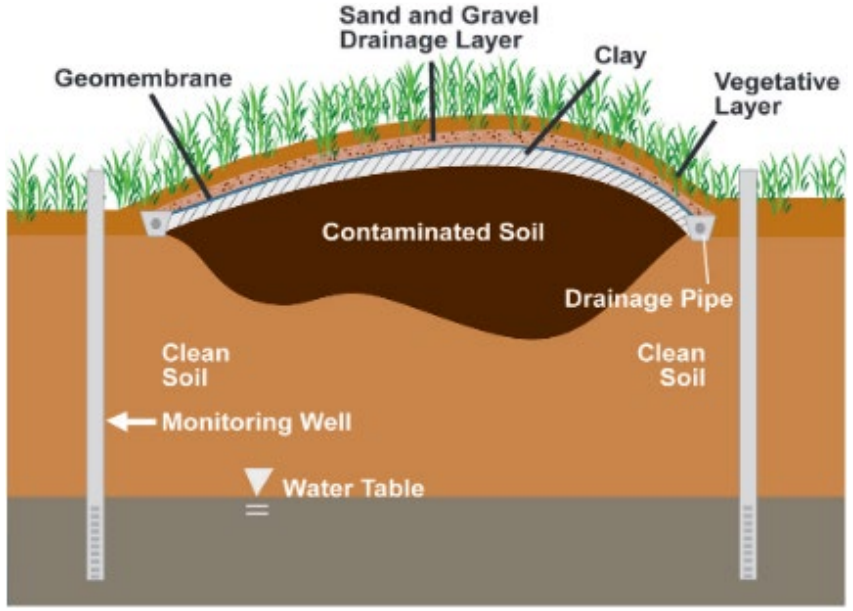
Encapsulation

- ***In situ*** physical isolation/containment
  - Horizontal caps, vertical walls
- Prevent **infiltration** or **groundwater-flow**

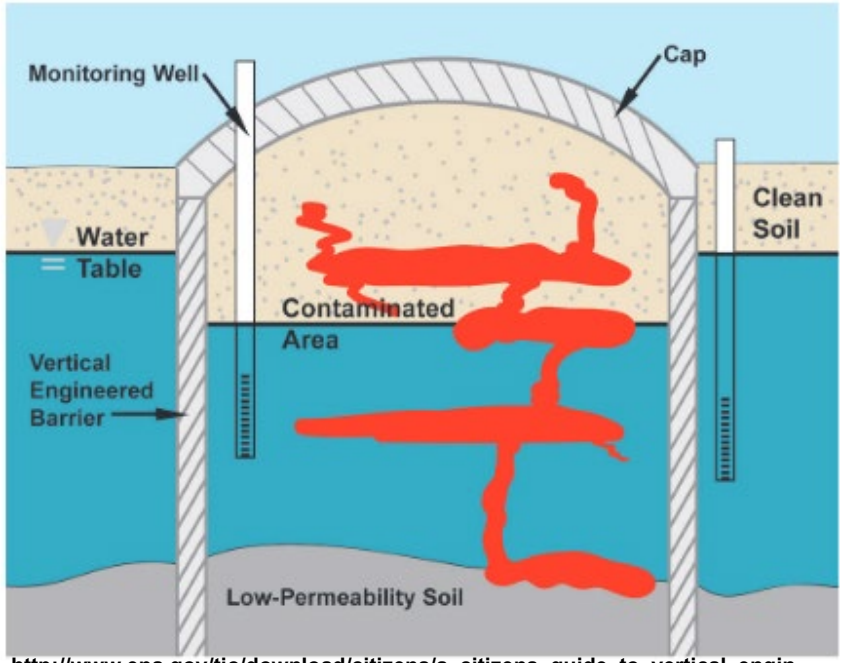
  →Reduce / prevent **leaching**
- Land re-use
- **Prevent** human & ecological **risks**
- Also **isolate & treat (reactive walls)**
- One or several layers: **barrier/drainage layer**

- Barrier materials

  - Geosynthetic liners (PE, PP, PVC,...)
  - Clay (bentonite)
  - Combination!



https://clu-in.org/download/Citizens/a_citizens_guide_to_capping.pdf



http://www.epa.gov/tio/download/citizens/a_citizens_guide_to_vertical_engineered_barriers.pdf

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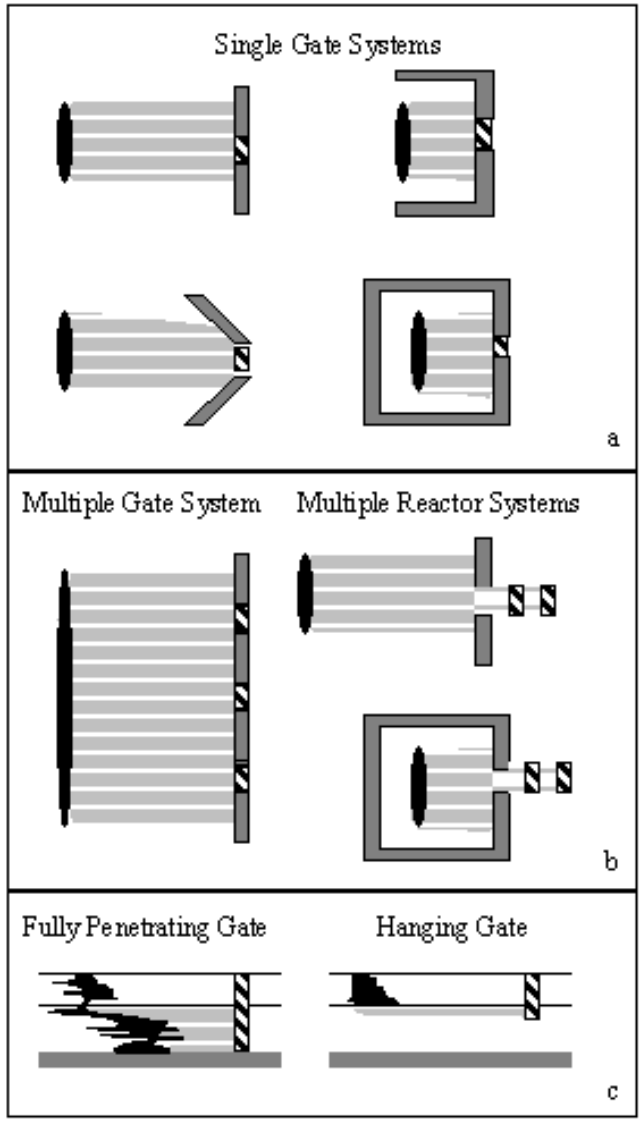
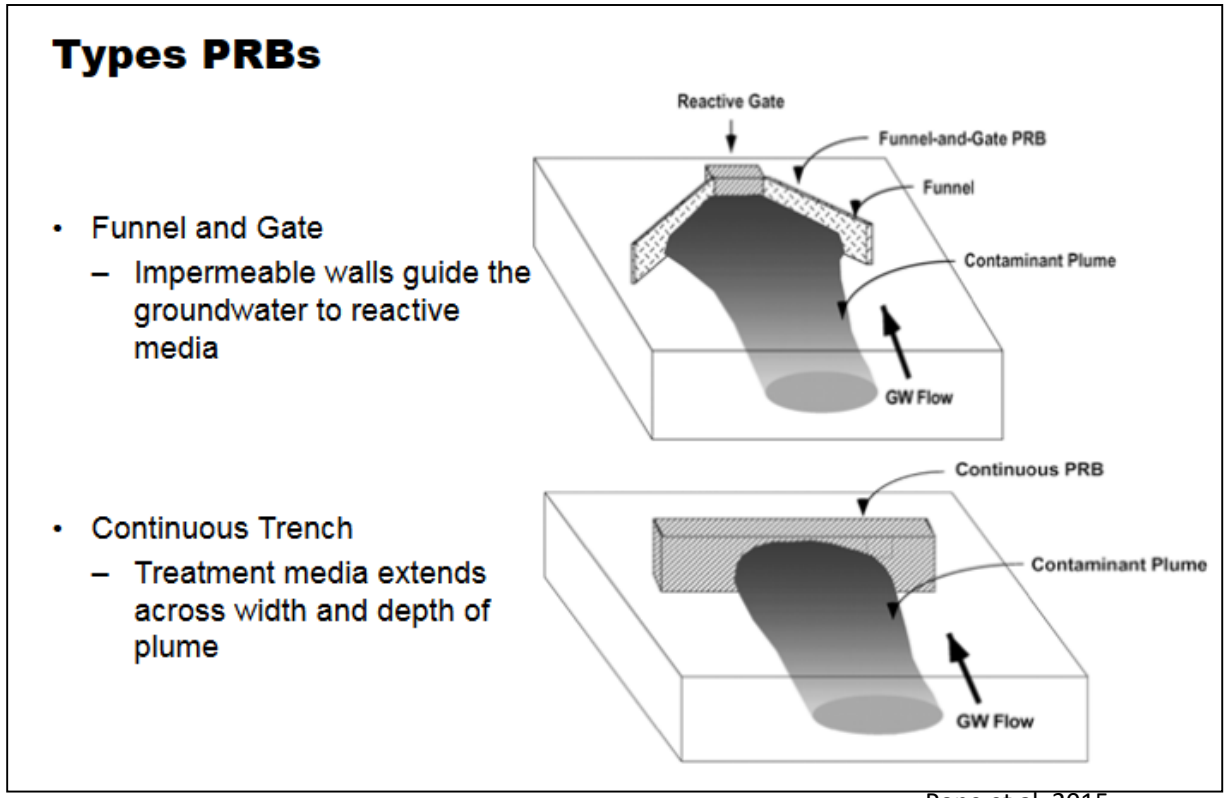
Encapsulation

Advantages	Disadvatages
In-situ	No removal
Inexpensive	Efficiency decreases over time
Quick remedy	Monitoring necessary
Prevents contaminant spreading (exposure)	If water penetrates, pump & treat required
	Depth-limited (→costs)

Encapsulation & permeable reactive walls



Starr & Cherry 1994

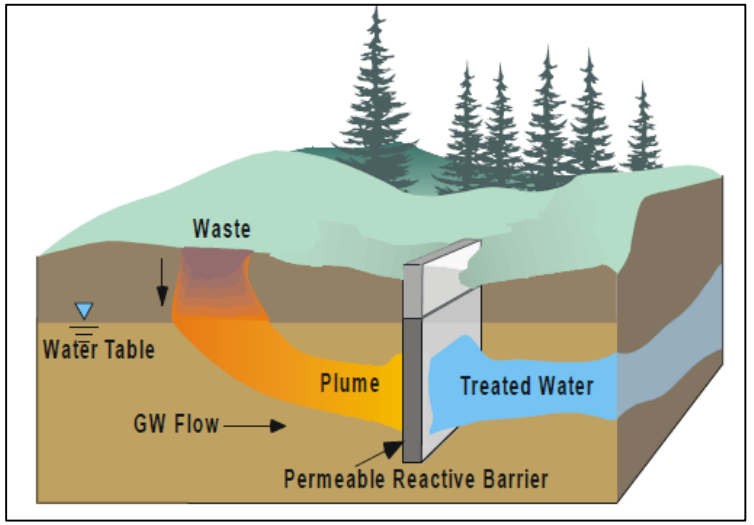


Pope et al. 2015

- Treatment of flowing contaminated ground water
- Predominantly used for organic contaminants
- Few examples for inorganic contaminants & mine effluents

Encapsulation & permeable reactive walls

- Transformation of contaminant
  - Redox change → Cr(VI) to Cr(III) with Fe°
- Adsorption of contaminant
  - Arsenic to FeOx and Fe° (oxidized surfaces)
  - Mercury to FeS
  - Several metals to organic rich material
- Precipitation
  - At increased pH (i.e. on limestone)
  - As sulfides (bioreactor, sulfate reduction)

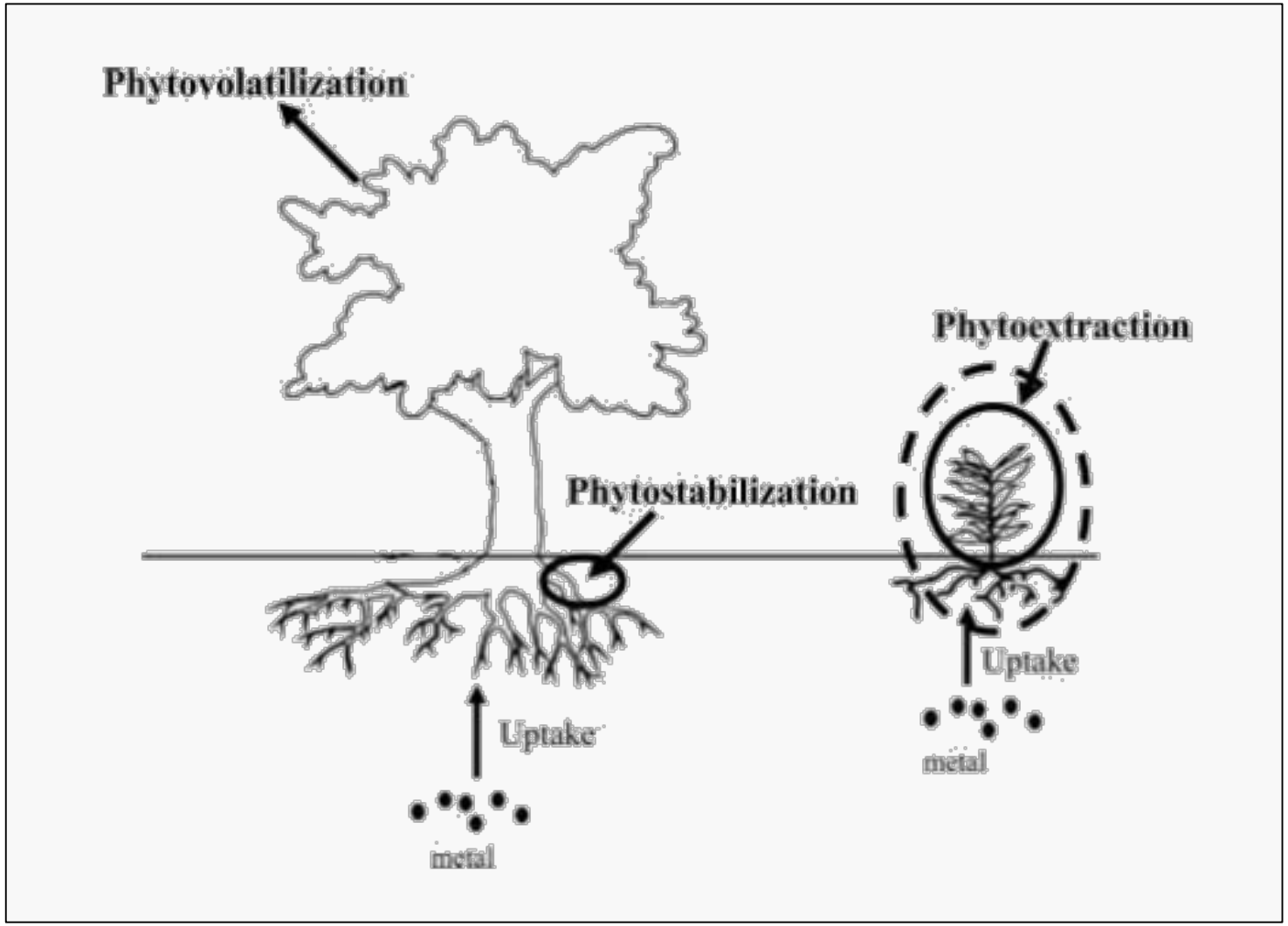


US EPA

Encapsulation & permeable reactive walls

Advantages	Disadvantages
In-situ	No removal
Comparably simple	efficiency decreases over time
Prevents contaminant spreading (exposure)	Monitoring necessary
	Depth-limited (→costs)
	Costs

Phytoremediation



Phytovolatilization

Volatized through stomata

Phytoextraction

Stored in harvestable tissue (metals can be recovered = phytomining)

Phytostabilization

Immobilized below ground

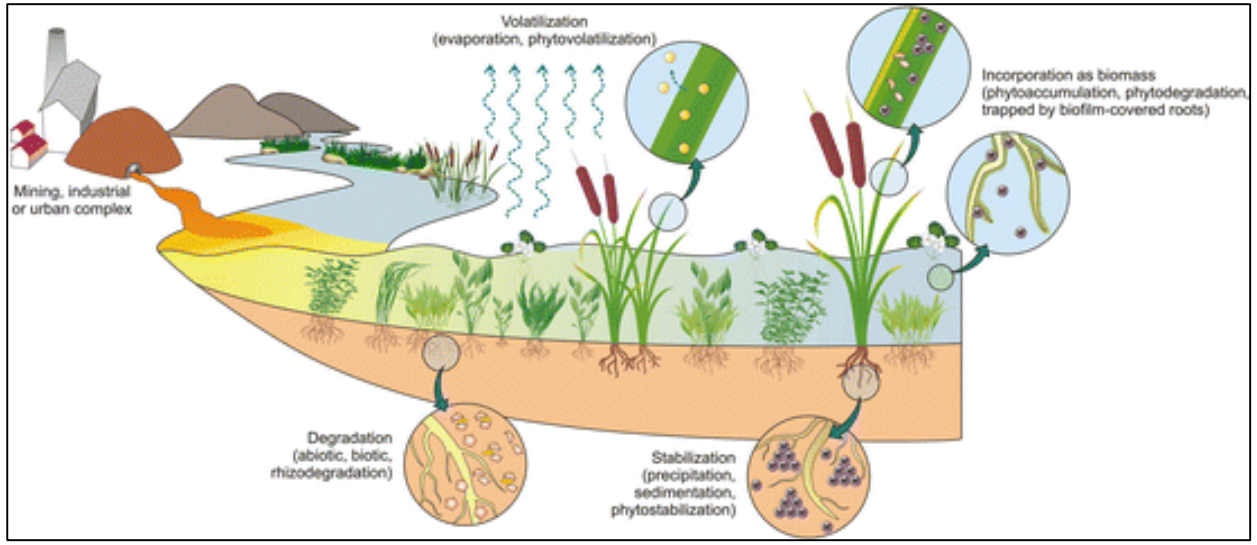
erosion control (interaction with rhizosphere)

Phytoremediation

Known Hyperaccumulators

- *Thlaspi caerulescens* (Cd/Zn)
- *Schoenoplectus lacustris* (Cr)
- *Typha latifolia* (Ni)

https://en.wikipedia.org/wiki/Schoenoplectus_lacustris



Favas, Pratas, Paul, Sarakar, Prased Ed. *Phytoremediation*, (**2016**)

http://www.pinelandsnursery.com/2015/02/typha-latifolia-broadleaf-cattail.html

http://www.luontoportti.com/suomi/en/kukkakasvit/alpine-pennycress

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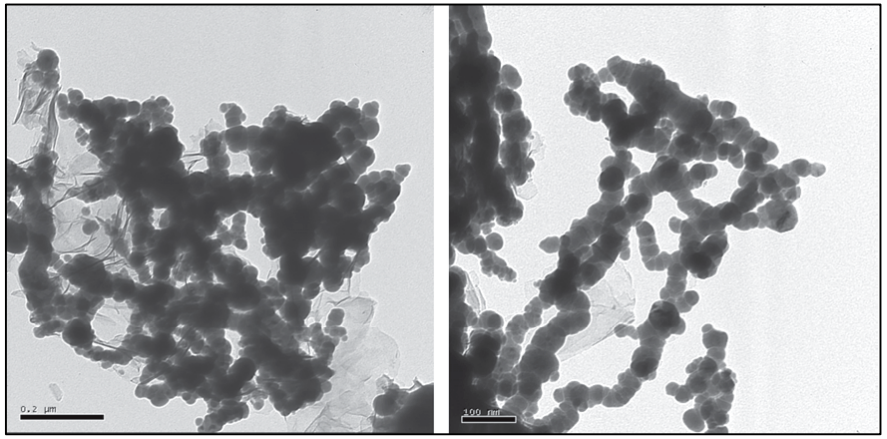
Phytoremediation

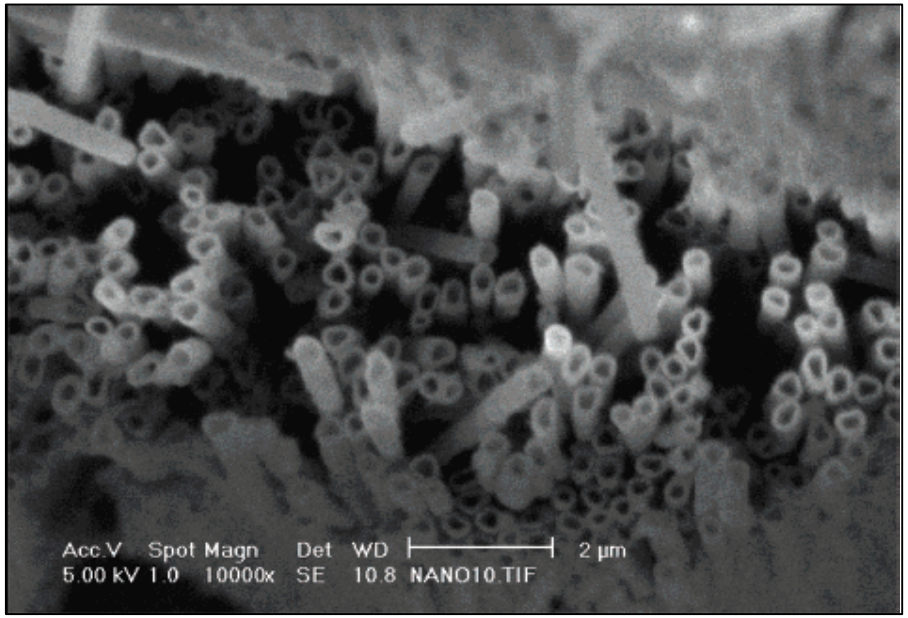
Advantages	Disadvantages
Eco-friendly	**Very slow process**
Highly **accepted** in public	Dependent on **environment**
Noninvasive	**Bioavailability** of contaminant Plants must tolerate the pollutant
Minimal maintenance But plant material needs to be harvested	**Shallow** contamination (root zone)
Preserve **soil function**	**Bioaccumulation** in animals possible

Nanotechnology – an option for remediation?

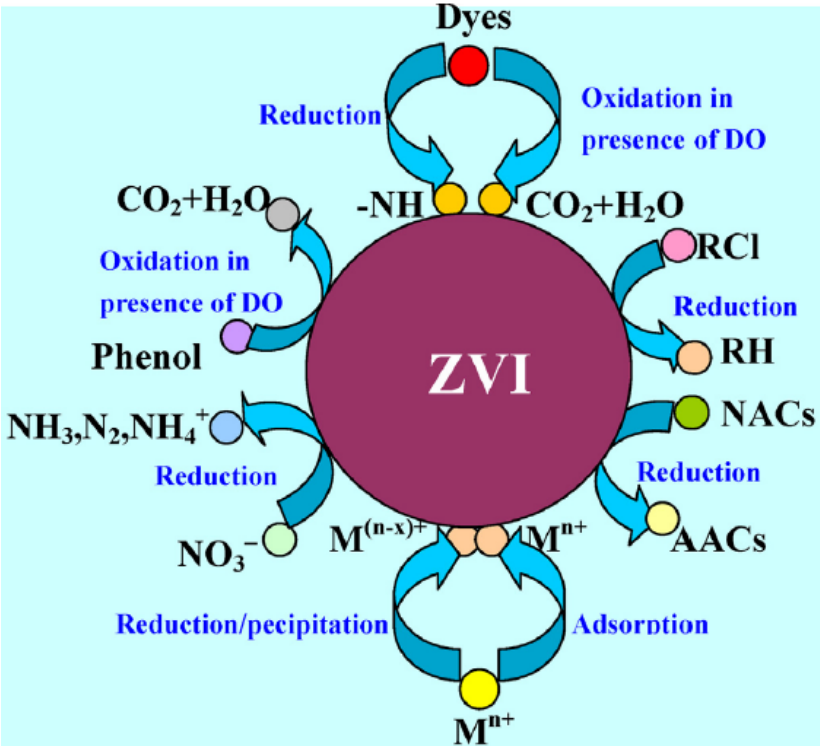
- Highly reactive (high SSA)
- Unique optical, electrical, thermal properties for remediation (quantum confinment)
- Used in direct injection/PRBs/soil additives
- Still underdeveloped, questions regarding efficacy



Nano Zero valent iron NPs (N-ZVI) (EPA)

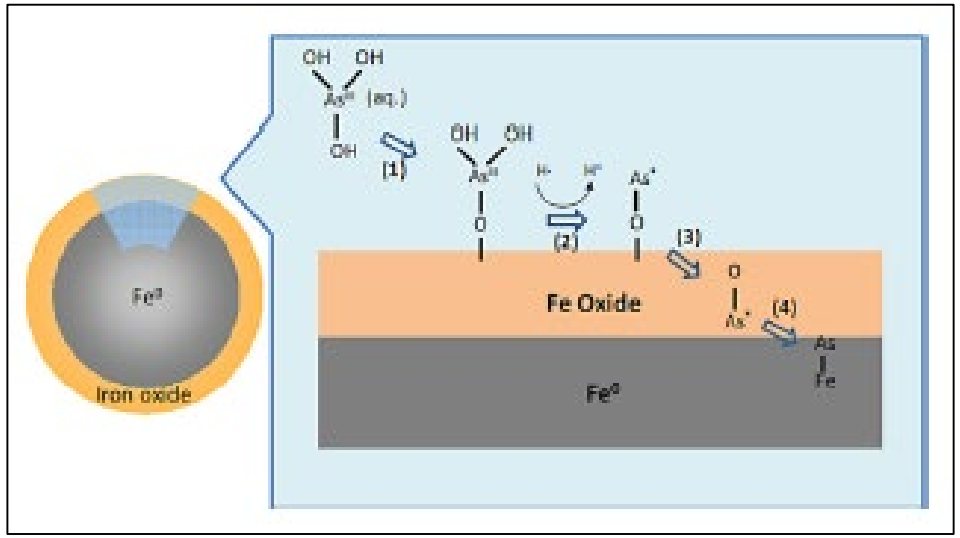


Titanium dioxide nanotubes(EPA)

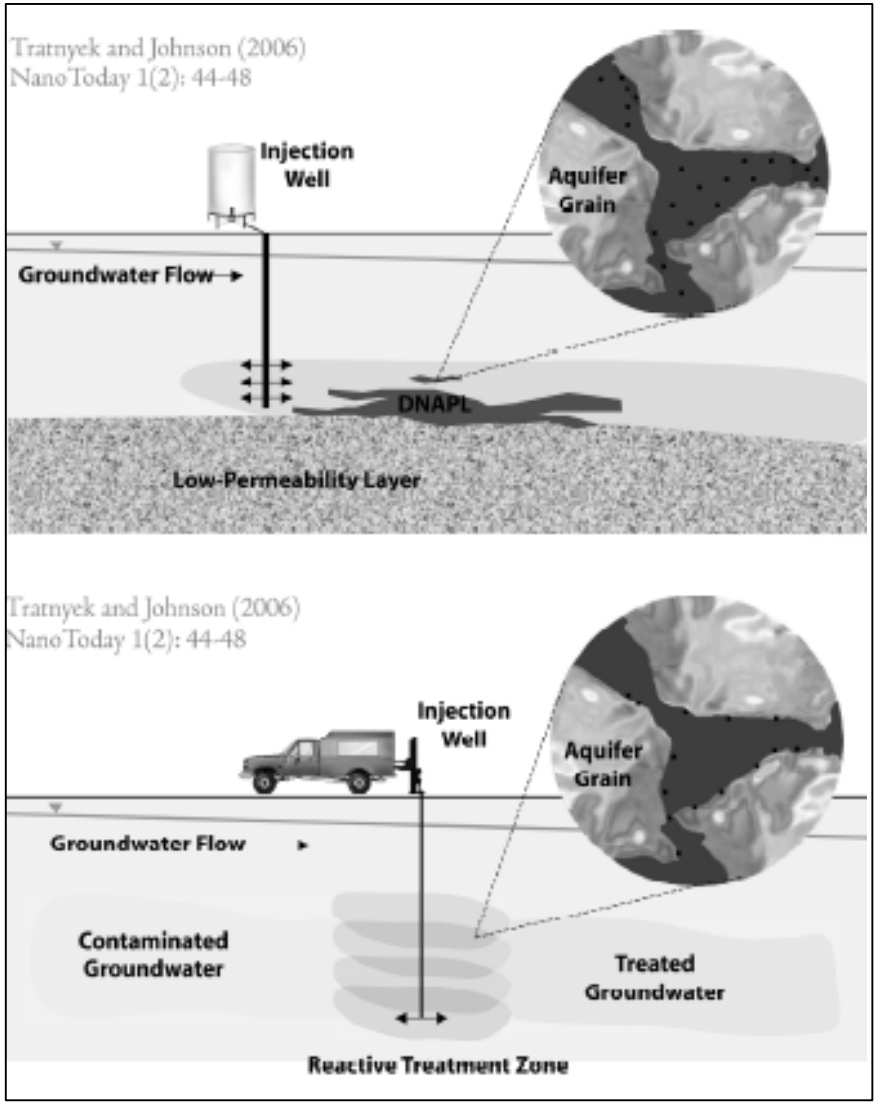


Nanotechnology – an option for remediation?

- Nanoscale zero-valent iron has many potential applications for the treatment of heavy metals (Pb, Cr), radionuclides (U, Pu), and other toxic elements (As)
- Exact mechanism is still under study (Fe is oxidized, reducing contaminant to less mobile form)
- Problems with nZVI mobility in environmental matrices, the longevity & reactivity

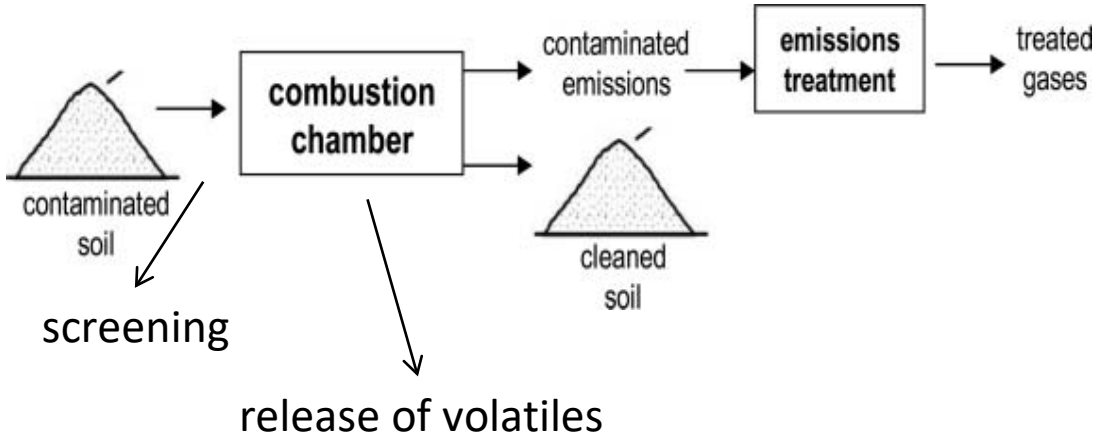


Proposed As reduction mechanism
Fu et al. *J. Haz. Mat* (**2014**)



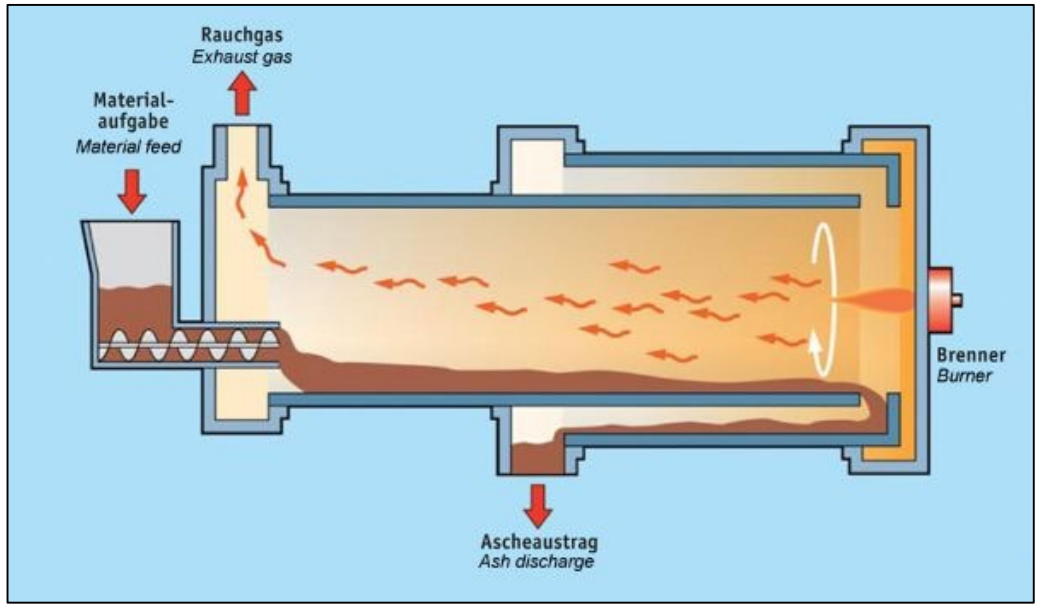
GW remediation using nZVI
Tatnyek et al. *Nanotoday* (**2006**)

Thermal desorption (TD) / combustion



http://www.beneficiationequipment.com/

- **Direct-fired** TD (**flame**)
- **Indirect-fired** TD (**combustion gas**)
- **Indirect-heated** TD (**inert carrier gas**)
- **High temperature** TD (320-560°C)
- **Low temperature** TD (90-320°C)
- Usually for organics (hydrocarbons)
- → **Volatile metals (Hg, As)**
  volatilise Hg^{2+} compounds (HgS, HgO, $HgCO_3$)
  at **600-800°C**
- Effective for metals at >500°C



- Combustion ~ 1200 °C

Thermal desorption (TD) / combustion

Advantages	Disadvantages
Metal recovery possible	Ex-situ technique → excavation (exposure)
High desorption efficiency (up to 99%)	Need to treat carrier gas
LTTD: soil physical properties retained if only desorption is applied (but metals unaffected)	High energy cost (metals only possible with HTTD)
	HTTD destroys organics
Hardware available off-shelf	Water content reduces efficiency (dewatering necessary)
Mobile on-site units available	Non-volatile metals stay in residue (stabilisation necessary) Combustion for glassification
Rather quick (weeks, months)	High clay/silt/humic content increases reaction time

Remediation (clean-up) options

Table 5: Indicative costs of remediation, UK experience (NATHANAIL, 2000)

Remediation technology	Indicative unit price
Engineering capping	£ 15-£30/ m²
Excavation and disposal to landfill	£ 50/m³
Encapsulation (shallow cut-off wall)	£ 40 - £ 60/ m²
Encapsulation (deep cut-off wall)	£ 70 - £ 120/ m²
'Typical' landfill gas control system	£ 200,000 per site
'Typical' grout curtain/ vent trench	£ 220,000 per site
Bioremediation	£ 35 - £ 45/ tonne
Vitrification	£ 40/ tonne
In-situ vitrification (5t/hr)	£ 150 - £ 215/ tonne
Incineration (special wastes)	£ 750 - £ 1,000+/ tonne
Dechlorination	£ 100 - £ 300/ tonne
Soil vapour extraction	£ 40-60/m³ vadose zone
Soil washing	£ 30 - £ 35/ tonne
Enhanced Thermal Conduction	£ 35 - £ 45/m³
Six phase heating	£ 20 - £ 30/m³
In situ chemical oxidation	£ 40 - £ 80/m³
Pump and treat	£ 20 - £ 30/m³
Free product recovery	£ 10 - £ 20/m³ vadose zone
Air sparging	£ 45 - £ 55/m³ groundwater
Oxidation of cyanide	£ 400/ tonne
Solvent extraction and incineration	£ 400/ tonne
Thermal desorption (including excavation and pre treatment)	£ 35 – £ 150/ tonne

- **Phyto-remediation**

  25 – 100 US$ / ton

  (Glass 2000)

Case study (of how not to do…)

- Uranium contamination at old mine site from left over tailings
- Wells were established with acetate stimulation of sulfate reducing bacteria
- Intended reduction/immobilization of uranium: U(VI) → U(IV)
- Unintended mobilization of arnseic with thioarsenate complexation
- Holistic view of geochemistry parameters important for remediation