

ES473 Environmental Geology Spring 2019

(Updated with Corrections June 3, 2019)

Student Presentations – Soil and Groundwater Remediation (20 points)

Instructions: Each student will be assigned a journal article / reading assignment related to topics in groundwater and soil remediation technology. The goal will be to read the paper, summarize the main points, and compile a 1-page handout and a 10-minute power point summary for presentation to the group.

Week 10 Tuesday June 4

2:00-2:10	Taylor Introduction
2:10-2:20	Wegner: Groundwater Remediation Overview
2:20-2:30	Hagan: Permeable Reactive Barriers
2:30-2:40	Pardini-Adams: Arsenic Remediation
2:40-2:50	Garcia-Lopez: Pump and Treat Overview
2:50-3:00	Manju: Phytoremediation of PCB contaminated soil
3:00-3:10	Willingham: Cost-Benefits of Groundwater Remediation
3:10-3:20	Singleton: Sustainable Groundwater Remediation
3:20-3:30	Knott: Physical and Chemical Remediation Technologies
3:20-3:40	Freilinger: Iron-Based Remediation Technologies
3:40-3:50	Taylor Conclusion

Week 10 Tuesday June 6

2:00-2:10	Taylor Introduction
2:10-2:20	Hojnowski: Life Cycle Assessment of Active/Passive Remediation
2:20-2:30	Moshinsky: Chromium Remediation
2:30-2:40	Griffith: Remediation of Metals Contaminated Soil and Groundwater
2:40-2:50	Hernandez: Transformer Repair Facility / Case Study
2:50-3:00	Hall: Sustainability Appraisal of Remediation Techniques
3:00-3:10	Micek: PCB Remediation Techniques
3:10-3:20	Baldwin: Nanoparticles and Remediation Strategies
3:20-3:50	Taylor Conclusion

Materials for Summary Presentation:

- 1-page printed handout / outline with key summary bullet points + figures on topic
- Optional creative problem solving or a video-clip (youtube, etc.) illustrating the topics
- 10 to 15-minute powerpoint presentation with images and text on topic, list key take-home message (target: 6-8 slides)

Assigned Readings

1. Acid Sulphate Soil Interaction with Groundwater: A Remediation Case Study in East Trinity **[OPEN]**
2. An application of permeable reactive barrier technology to petroleum hydrocarbon contaminated groundwater **[HAGEN]**
3. Remediation Technologies for Arsenic Contaminated Drinking Waters **[PARDINI-ADAMS]**
4. Sustainable groundwater remediation and reuse case study **[SINGLETON]**
5. The Benefits and Costs of Policies Related to Groundwater Contamination **[WILLINGHAM]**
6. Processes Affecting the Remediation of Chromium-Contaminated Sites **[MOSHINSKY]**
7. Groundwater Remediation: The Next 30 Years **[WEGNER]**
8. Physical and Chemical Groundwater Remediation Technologies **[KNOTT]**
9. Groundwater Contamination: Pump and Treat Remediation **[GARCIA LOPEZ]**

MORE ON BACK.....

10. Use of iron-based technologies in contaminated land and groundwater remediation: A Review **[FREILINGER]**
11. Life cycle assessment of active and passive groundwater remediation technologies **[HOJNOWSKI]**
12. Remediation of Metals-Contaminated Soils and Groundwater **[GRIFFITH]**
13. Nanoparticles for Remediation: Solving Big Problems with Little Particles **[BALDWIN]**
14. A case study for demonstrating the application of U.S. EPA's monitored natural attenuation screening protocol at a hazardous waste site **[OPEN]**
15. Case Studies of Phytoremediation of Petrochemicals and Chlorinated Solvents in Soil and Groundwater **[OPEN]**
16. Supercritical Fluid Technology For Remediation Of PCB/PAH-Contaminated Soils/Sediments **[OPEN]**
17. Overview of in situ and ex situ remediation technologies for PCB-contaminated soils and sediments and obstacles for full-scale application **[MICEK]**
18. Remediation with surfactant foam of PCP-contaminated soil **[OPEN]**
19. Phytoremediation of a PCB-contaminated soil by alfalfa and tall fescue single and mixed plants cultivation **[MANJU]**
20. Sustainability appraisal tools for soil and groundwater remediation: How is the choice of remediation alternative influenced by different sets of sustainability indicators and tool structures? **[HALL]**
21. Case Study of a Transformer Repair Facility, Soil and Groundwater Remediation, Richmond, BC **[HERNANDEZ]**

Groundwater Remediation: The Next 30 Years

Terminology

MCL-- Maximum Contaminant Levels

OoMs-- Orders of Magnitude

VOCs-- Volatile Organic Compounds

SDWA-- Safe Water Drinking Act

NAPL-- Non-Aqueous Phase Liquid

TMDL-- Total Maximum Daily Load

Box 1

Getting to MCLs

The MCL was originally developed as a criterion for evaluating public drinking water supplies, both from surface water and groundwater sources. However, soon after the Love Canal Superfund Site was discovered, MCLs were being widely applied as cleanup criteria for plumes of contaminated groundwater, regardless of whether or not such plumes would ever enter drinking water supply wells. Since then, the term "getting to MCLs" has become the catch-phrase typifying the life of those working in the remediation community.

Box 3

Order of Magnitude

An **order of magnitude** is the class of scale or magnitude of any amount, where each class contains values of a fixed ratio to the class preceding it. In its most common usage, the amount being scaled is 10 and the scale is the (base 10) exponent being applied to this amount. Such differences in order of magnitude can be measured on the logarithmic scale in "decades" (i.e., factors of 10). This is useful for getting an intuitive sense of the comparative scale of familiar objects (Wikipedia 2011a).

Box 4

Plume Magnitude Classification System (Newell et al. 2011)

Mag 1 Plume: <0.001 g/d
Mag 2 Plume: 0.001 to <0.01 g/d
Mag 3 Plume: 0.01 to <0.1 g/d
Mag 4 Plume: 0.1 to <1 g/d
Mag 5 Plume: 1 to <10 g/d
Mag 6 Plume: 10 to <100 g/d
Mag 7 Plume: 100 to <1000 g/d
Mag 8 Plume: 1000 to <10,000 g/d
Mag 9 Plume: 10,000 to <100,000 g/d
Mag 10 Plume: ≥100,000 g/d

Table 1
OoMs vs. MCLs Everywhere

OoMs	MCLs Everywhere
SMART (specific, measurable, attainable, relevant, time-bound)	Generally not utilized with SMART attributes
Scalable	Not scalable
Fits description of a "model"	Not a "model"
Mass discharge is a vector	MCL is a point measurement
Allows inclusion of other factors	Does not consider other factors
Offers hope for a different future	Identified with shortcomings of the status quo
Dynamic	Static
(Relatively) new	Old
Developed specifically for groundwater remediation	Developed for water systems
Mass transport	Regulatory/enforcement based
Risk-based	Regulatory/enforcement based

MCL Approach

Before Remediation



NOTE: Actual presence and location of receptors NOT important.

After Remediation



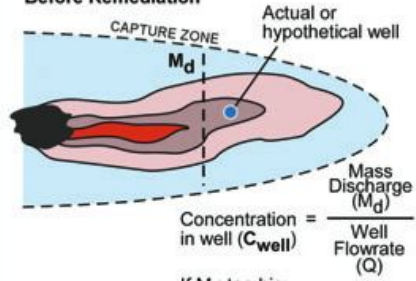
Analysis

MCLs not achieved. Future concentration reductions progressively more difficult and expensive.

OoMs / Mass Discharge Approach

Water Supply Well

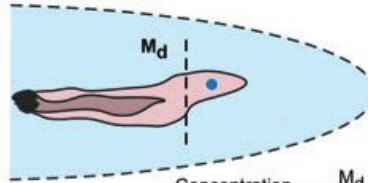
Before Remediation



$$\text{Concentration in well (C}_{\text{well}}) = \frac{\text{Mass Discharge (M}_d)}{\text{Well Flowrate (Q)}}$$

If M_d too big:
C_{well} > MCL

After Remediation



$$\text{Concentration in well} = \frac{M_d}{Q}$$

C_{well} < MCL

Analysis

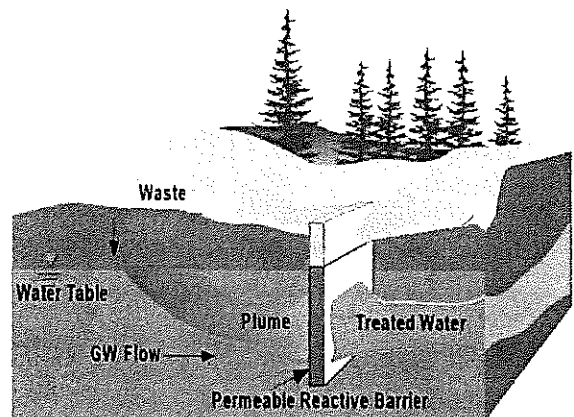
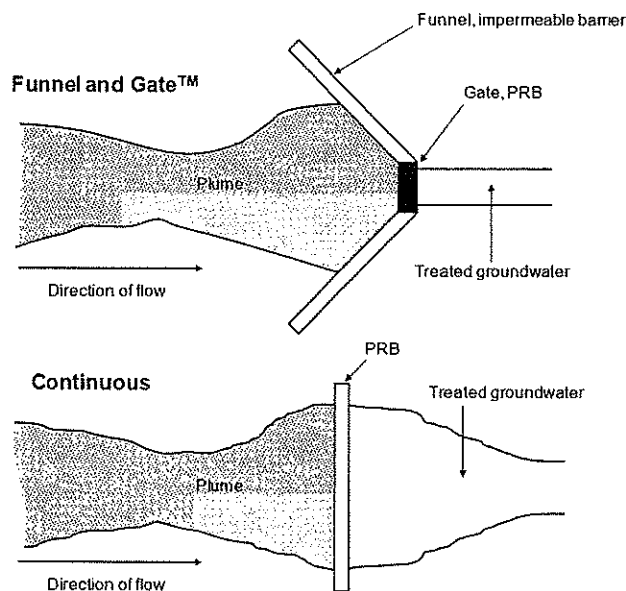
Actual risk reduction is at well location.
Remediation achieves Risk Reduction Goal.

Permeable reactive barriers

By: Timothy Hagen

Main points:

- The funnel and gate system is comprised of the funnel that helps guide in contaminants and the gate, that filters the contaminants.
- Multiple sources of hydrocarbons that leaked from the factory towards the river.
- Models of the plumes of the contaminated soil and groundwater were made.
- 14 wells were put on site to monitor the ground water.
- Peat and scoria were the two main sources of the filter material
- The funnel and gates system was overall 75% productive in the removal of hydrocarbons
- This system best fits for shallow river channels



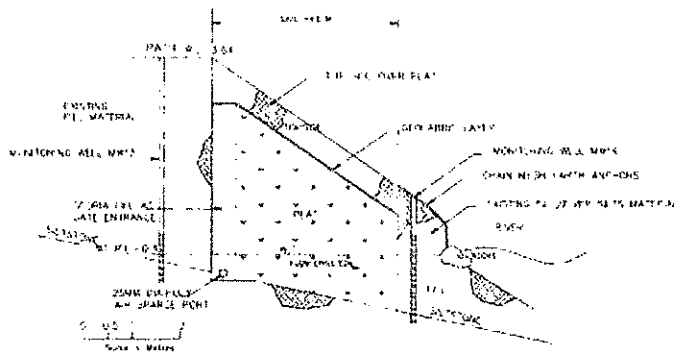


Fig. 2. Transect through the funnel and gate system.



ARSENIC REMEDIATION

Arsenic is a toxic metalloid recognized to be a contaminant of drinking water, affecting localities worldwide, but having the strongest effect in the impoverished regions of South Asia. Long term exposure to arsenic contaminated drinking water is associated with an increased risk of certain cancers, cardiovascular disease, diabetes, and neurological damage. Arsenic is usually found in combination with sulphur, oxygen, and iron.

Water is considered contaminated with arsenic if the levels exceed 10 µg/L, according to the EPA and WHO.

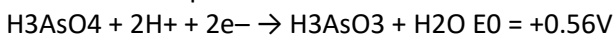
Sources of arsenic can be:

- Natural (most common in groundwater)
 - 200+ mineral forms (60% are arsenates, 20% sulfides and sulfosalts, 20% includes arsenides, arsenites, oxides, silicates and elemental arsenic)
 - Recoverable in metalliferous deposits: iron pyrite, galena and chalcopyrite
- Anthropogenic (less common, mostly affects surface water)
 - industrial
 - wastes; phosphate ores; fertilizers; burning fossil fuels (mainly coal); oil; cement production; mine tailings; smelting; ore
 - processing; metal extraction; metal purification; chemical
 - production; glass; leather; textiles; alkali production; petroleum refineries; alloys; pigments; desiccants and wood preservatives, insecticides; herbicides and catalysts

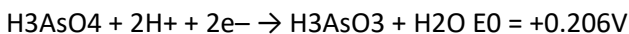
Things that affect the physical state of arsenic (aq vs. s) in the water:

- mineral precipitation / dissolution, **adsorption / desorption**, oxidation / reduction and biological transformations
- arsenic can be mobilized under a wide range of oxidizing and reducing conditions at the pH values typically found in groundwaters (unlike other heavy metalloids and oxyanion forming elements) and is typically found as the species As(III) or As(V) (trivalent arsenic is 60% more toxic than pentavalent arsenic)
- Concentrations of As(III) and As(V) vary depending on redox conditions in the geological environment.

The redox of both species is as follows:



- for 50% oxidation



- for 99% oxidation

More trivalent arsenic than pentavalent arsenic is found in reducing groundwater conditions, whereas the converse is true in oxidizing groundwater conditions.

Current technologies for remediating arsenic rely on basic chemical processes:

- **Oxidation / Reduction reactions:** does not remove arsenic from solution but often required for process optimization for all technologies that require arsenic to be present in its higher oxidation state (V rather than III) in order to achieve effective removal.
- **Precipitation / Co-precipitation reactions:** dissolved arsenic can form low solubility metal arsenates (e.g. calcium arsenate) upon the addition of appropriate chemicals (remaining floc can be removed).
- **Adsorption and Ion exchange reactions.** Some solids, including iron and aluminum hydroxide flocs, have a strong affinity for dissolved arsenic. Arsenic is strongly attracted to sorption sites on the surfaces of these solids and is effectively removed from solution. Ion exchange involves the reversible displacement of an ion adsorbed onto a solid surface by a dissolved ion.
- **Solid / Liquid separation processes:** If the solids are formed in situ (through precipitation or coagulation) they must be separated from the water via filtration or gravity settling.
- **Physical exclusion (membrane) processes:** membranes can act as a molecular filter to remove dissolved arsenic – along with many other dissolved and particulate compounds
- **Biological removal processes:** Phyto-filtration and the fact that bacteria can play an important role in catalyzing many of the above processes.

Treatment Options:

- **Coagulation / Precipitation:** aluminum sulphate – $\text{Al}_2(\text{SO}_4)_3$ or ferric chloride, FeCl_3 . The precise pH range and efficiency of arsenic removal is different for both coagulants, but arsenic can be removed by both, in the pH range 5–7. In general, these processes remove As(V) more effectively than As(III) and most researchers suggest that FeCl_3 is more efficient than $\text{Al}_2(\text{SO}_4)_3$.
- **Lime softening:** softening is a successful technology for achieving greater than 90 percent As(V) removal, but a redox reaction must take place first in order to have the arsenic in the pentavalent form.
- **Adsorption:** The criteria for selection of a suitable adsorbent include the cost of the medium; ease of operation and handling; adsorption capacity (break through point); potential for reuse – possibility of regeneration. Iron fillings, ferric salts, granular ferric hydroxide, alumina-manganese oxide, Aqua-bind™ and kimberlite tailings are all listed as potentially low-cost adsorbents and can remove arsenic after simple mixing and in a relatively short time and all the adsorbents can then be removed from the water by filtration. To avoid filtration, arsenic is removed simply by passing groundwater through a column. Natural alternatives include Kimberlite tailing, water hyacinth, wood charcoal, banana pith, coal fly ash, spent tea leaf, mushroom, saw dust, rice husk ash, sand, activated carbon, bauxite, hematite, laterite, iron oxide coated sand and hydrous granular ferric hydroxide. These materials can remove 5-92% of As(III) and 12-99% of As(V).
- **Activated alumina:** Activated alumina (Al_2O_3) works to remove arsenic from water by a physical / chemical process by which ions in the feed water are sorbed to the oxidized alumina surface. Activated alumina is used in packed beds and water is continuously passed through the bed to remove such contaminants. When adsorption sites on the alumina surface become filled, the bed must be regenerated. pH, arsenic oxidation state, competing ions, empty bed contact time and regeneration have significant effects on the arsenic removal efficiencies achieved with alumina. The optimum pH for arsenic removal to be in the range of 5.5 to 6.0. Thus, to treat many groundwaters it is necessary to first lower their pH to below pH 6 for optimal arsenic removal and adjust the pH after removal.
- **Bioremediation:** The following plants that are currently used in phytoremediation to remove arsenic: poplar; cottonwood; sunflower; Indian mustard; maize; grasses such as ryegrass and prairie grasses and hyper-accumulating ferns. Technology can use microbes to promote the precipitation / co-precipitation of arsenic from water. The microbes used may be either suspended in the water or attached to a submerged solid substrate. Iron or hydrogen sulphide may also be added to increase the efficiency of removal.
- **Ion-exchange membrane:** Reverse osmosis and nanofiltration are possible and very effective at removing arsenic but are extremely expensive and not fit for domestic use.

Overall, it would seem that considerations of local geography, geology, climate, water characteristics and population density suggest that for many of the areas currently effected by arsenic water contamination mitigation is not practical. Based on the data, the most appropriate remediation treatments in developing countries are precipitation / co-precipitation and sorption onto activated alumina.

Table 2: Comparison of the efficiencies of some coagulation-precipitation, lime softening and adsorption methods for the removal of arsenic from water (adapted from Jiang 2001)

Treatment Technology	Influent arsenic, $\mu\text{g L}^{-1}$	Effluent arsenic, $\mu\text{g L}^{-1}$	Percentage removal
Coagulation-precipitation			
Oxidation / Iron coagulation	110	10–85	23–91
	200	80	60
	1100	5	99
Lime softening			
	220	30	86
	75	5	95
	100	5	95
Adsorption			
Activated alumina	88	<50	>43
	103	<50	>51
Activated carbon	300	10	96
Iron oxide coated materials	250	10	96

Table 1: Worldwide occurrences of arsenic in groundwater (adapted from: Smedley 2003 and Moinuddin 2004)

Country	Source term	Range of contamination, $\mu\text{g L}^{-1}$ (ppb)	Estimated population exposed
Argentina	Natural	100–2000	200,000
Chile	Natural – associated with quaternary volcanism	Not available	400,000 over an area of 125,000 km ²
Bangladesh	Natural – deriving from geological strata	<1–2300	57 millions exposed to As >10 $\mu\text{g L}^{-1}$ and 35 millions exposed to As > 50 $\mu\text{g L}^{-1}$
China	Natural, in reducing environment	40–4400	5.6 million
Ghana	Mining activities	Not available	100,000
Hungary and Romania	Natural	2–176	400,000
West Bengal, India	Natural – deriving from geological strata	<10–3200	Over 5 millions exposed to As >50 $\mu\text{g L}^{-1}$; 300,000 suffering from arsenicosis
Mexico	Natural	1–500 (average 100)	400,000
Nepal	Natural (?)	<10–340	550,000 exposed to As >50 $\mu\text{g L}^{-1}$ and 3.19 million exposed to As >10 $\mu\text{g L}^{-1}$
Taiwan	Natural	10–1800	10,000 (?)
Thailand	Mining activities	1–5000	15,000
USA	Natural, geothermal and mining related sources	Varied	13 million exposed to As = 10 $\mu\text{g L}^{-1}$
Vietnam	Natural	1–3100	> 1 million

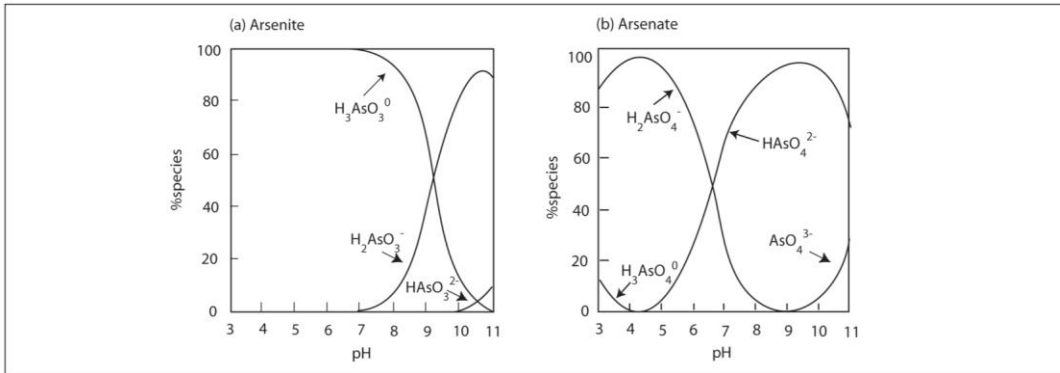


Fig. 2: Arsenite (As(III)) and arsenate (As(V)) species predominance in water as function of pH (ionic strength of approximately 0.01M) (adapted from Smedley and Kinniburgh 2002)

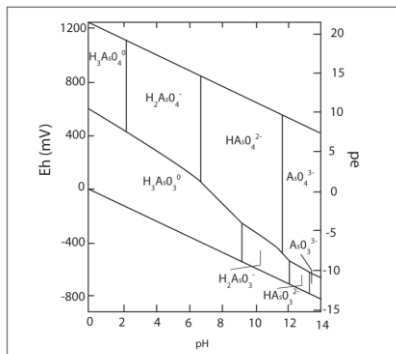


Fig. 1: Eh-pH diagram of aqueous As species in the system As–O₂–H₂O at 25°C and 1 bar total pressure. (adapted from Smedley and Kinniburgh 2002)

Groundwater contamination: Pump-and-treat remediation

Salvador Garcia Lopez

Focused on organic contaminants because they are the most common.

- **CERCLA:** Comprehensive Environmental Response, Compensation, and Liability Act
- **RCRA:** Resource Conservation and Recovery Act
- **NAPL:** Non-aqueous phase liquid
- **Sorption:** Physical and chemical process by which one substance becomes attached to another.
- **Desorption:** The release of an adsorbed substance from a surface.
- **Pump-and-treat approach:** Method for cleaning up groundwater contaminated with dissolved chemicals, including industrial solvents, metals, and fuel oil. Groundwater is pumped from wells to an above-ground treatment system that removes the contaminants.
- **Injections of steam:** Common method of extracting heavy crude oil.
- **Surfactants:** A substance which tends to reduce the surface tension of a liquid in which it is dissolved.
- **Retardation factor:** Defined as the ratio of the distance traveled by the center of a spot to the distance traveled by the solvent front

Before CERCLA, monitoring of groundwater at industrial and waste disposal sites was rare

What is Pump and Treat:

- Common method for cleaning up contaminated groundwater that has bad juices in it
- The groundwater is pumped up above ground to a treatment plant that separates the water from the contaminants
- After this, water gets pumped back into the ground and the contaminants are kept locked away 5ever

Pros vs. Cons:

Pros:

- It does the job and keeps harmful chemical away from humans and the environment

Cons:

- This type of clean up is expensive, requires a lot of money, research, work, and time
- Accuracy of the plume is important because if we drill lower than where the plume is, the plume will flow towards the deeper part of the aquifer or even into a different aquifer

Safe?

- Yes, when done right
- Contaminants leak or are released into the ground
- It moves downhill
- Come in contact with extraction well
- Contaminants sucked up like a straw
- The contaminated water goes through either air stripping or carbon adsorption
- Clean water is released into the wild, contaminants are treated and stored

How does it work?



Phytoremediation of Polychlorinated biphenyls (PCBs) Contaminated Soil

Polychlorinated biphenyls (PCBs):

- Were widely used for industrial applications until banned in 1970's
- Are semi-volatile and undergo long-range transport
- Are hydrophobic and contaminate sediments and soil

PCB Biodegradation

- Highly/Moderately chlorinated PCBs are degraded by reductive dechlorination in anaerobic environments.
- Lower/Moderately chlorinated PCBs are degraded by cometabolic aerobic oxidation initiated by biphenyl dioxygenases
- Plants promote PCB biodegradation by releasing root exudates and stimulating the microbial activity.

Plants

- Alfalfa supports symbiotic nitrogen fixing bacteria and PCB-degrading bacteria
- Tall fescue has the ability to grow in PCB contaminated soil

Objectives

- 1. Evaluate alfalfa and tall fescue in single and combined plant cultivation on PCB dissipation in a historically PCB-Polluted soil**
- 2. Investigate the impact of different plant species and cropping patterns on soil total bacteria, enzyme activities, and relative abundance of the biphenyl dioxygenase genes**

Greenhouse Experiment

- Soil samples were collected from PCB-containing transformer and capacitor storage sites
- Soil was fertilized to promote plant growth
- There were 3 separate pots for each treatment:
 - ❖ Alfalfa alone
 - ❖ Tall Fescue alone
 - ❖ Combined cultivation
 - ❖ Unplanted fertilized
 - ❖ Unplanted unfertilized
- Soils and plants were sampled after 150 days of plant growth

Results

- Removal of PCB's:
 - ❖ Greatest in tall fescue planted soil (39.6%)
 - ❖ Followed by combined planted soil (32.7%)
 - ❖ Alfalfa single planted soil (30.6%)
 - ❖ Non-planted fertilized soil (27.1%)
 - ❖ Non-planted unfertilized soil (20.0%)
- Total bacteria counts were highest in combined planted soil

Conclusions

- Tall fescue had highest plant biomass, resulting in the highest proportion of PCBs extracted by tall fescue
- Alfalfa was unable to survive in highly PCB-contaminated soil
- Inoculation with arbuscular mycorrhiza increased alfalfa yield and enhanced phytoextraction of PCBs
- Tall fescue extracted more PCB from weathered soil with high PCB contamination

The Benefits and Costs of Policies Related to Ground Water Contamination

Robert L. Raucher

The Costs and Benefits

- Table 1 provides remedial response options for the three sites. As you can see, the 58th street site is by far the most expensive in terms of remediation.

Site and Remedial Response Option:	Discount Rate		
	0%	2%	10%
58TH STREET^b			
Isolate (counterpump) and deep well inject	\$ 65.4	\$ 26.8	\$ 8.1
Close (final cover), isolate (counterpump), and deep well inject	43.2	24.0	9.8
Close (final cover), isolate (counterpump), treat, and dispose (surface water)	99.8	55.4	20.5
Open new drinking water wellfield	50.0	48.1	41.3
Treat affected municipal water	465.0	182.0	46.5
DAVIE^c			
Provide bottled water (private wells no longer used for drinking water or cooking)	1.2	0.4	0.02
Isolate (counterpump) and deep well inject	15.4	6.5	2.2
Connect to municipal water system (close private wells)	27.4	13.7	6.8
Close (sludge removal), isolate (counterpump), treat, and reinject	16.5	14.2	9.3
GILSON ROAD^d			
Partially isolate (7.5-acre slurry wall), partially treat (arsenic removal only), and recirculate (inject within wall)	6.1	5.7	4.5
Partially isolate (7.5-acre slurry wall), treat (organics and inorganics), and recirculate	7.6	7.1	5.5
Isolate (20-acre slurry wall), treat (organics and inorganics), and recirculate ^e	12.1	11.3	8.7
Same as directly above, plus treat plume beyond slurry wall, and recirculate	34.5	27.8	14.5

TABLE 2
COSTS OF PREVENTIVE AND CORRECTIVE MEASURES
AT BISCAYNE SITES
(\$1982 × 10⁶)

Rate Discount	Costs (X _j) ^a	"Benefits" (C _j) ^b	
	PV Cost of "Prevention"	PV Cost of Most Economical Remedial Response	
		Time Horizon of 30 Years	Time Horizon of 120 Years
58TH STREET:^c			
0%	50.8	18.7	43.2
2%	67.5	14.7	24.0
10%	267.5	7.8	8.1
DAVIE:^d			
0%	0.91	0.10	1.24
2%	0.93	0.07	0.36
10%	2.68	0.02	0.02

Raucher: Groundwater Contamination

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TABLE 3
COSTS OF PREVENTIVE AND CORRECTIVE MEASURES
AT GILSON ROAD SITE
(\$1982 × 10⁶)

Scenario	Discount Rate		
	0%	2%	10%
Preventive Options ("Costs" X _j): ^a			
Send Waste Elsewhere	\$ 1.6	\$ 1.7	\$ 2.4
On-site: Single Liner	8.8	5.5	4.7
On-site: High Standard	4.3	4.4	5.3
Response Options ("Benefits" C _j): ^b			
Small Slurry Wall, Partial Treatment	\$ 6.1	\$ 5.7	\$ 4.5
Small Slurry Wall, Full Treatment	7.6	7.1	5.5

Juneau Singleton

ES 473

Spring Term 2019

Sustainable Groundwater Remediation and Reuse Case Study

Authors: Marc Carver and Mitchell Gertz

Environmental Resources Management

Introduction:

To start off, because of technological advancements, there are many remediation options to choose from when it comes to contaminated groundwater. There is a lot to consider when figuring out which method is best (Read slide).

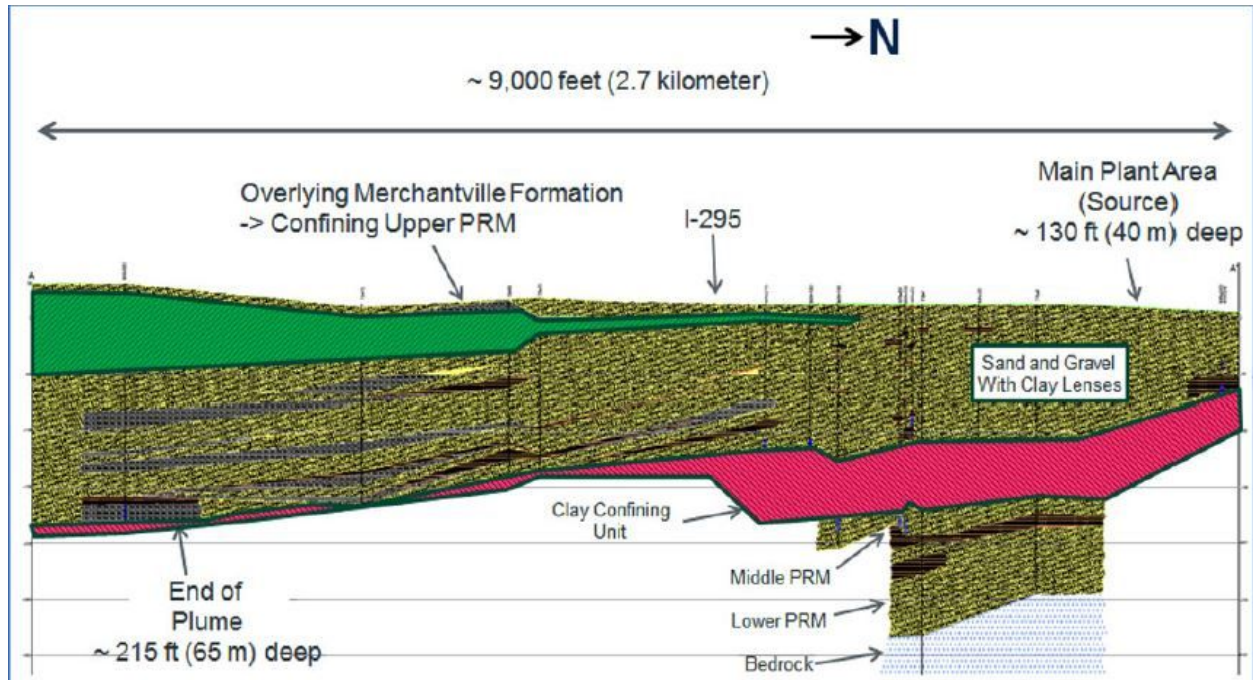
Decisions about which remediation technique to use are usually driven by:

- Government regulatory requirements
- Business decisions
- Cost
- Land use development plans
- Management of risks and liabilities
- Sustainability: relatively new approach
 - Minimizes unnecessary allocation of natural resources
 - Saves money
 - Reduces environmental footprint of cleanup

Sustainability is a relatively approach that is gaining traction due to its benefits such as saving money as well as resources. This case study emphasized sustainability during selection and implementation of groundwater remediation.

Site Background:

The property as a whole is 243 acres in West Deptford Township, New Jersey. The industrial portion of the property takes up about 34 acres. This is referred to in the article as “the main plant area,” which was a refrigerant gas plant in the 70’s, then converted to a fluoropolymer plant in 1985. There is a shallow aquifer, called the “Upper Potomac-Raritan-Magothy aquifer,” the name is abbreviated as PRM. There is a confining clay layer between the Upper PRM aquifer and the middle and lower PRM aquifers. Due to regional pumping, groundwater flows away from the Delaware river. Downgradient of the site, the shallow aquifer changes from unconfined to confined because of the overlying presence of the Merchantville formation, which has a notable clay component.



Here is a cross-section of the area from the north (source area) to the south end of the plume. General lithology consists of surficial deposits underlain by sands and interbedded silts and clays. At a depth of approximately 120-130 ft below ground, distinctive dark gray clay overlying a very stiff red and gray mottled clay layer is present. The clay layer dips down toward the south and acts as a confining unit between the upper and lower aquifers.

Primary Volatile Organic Compounds:

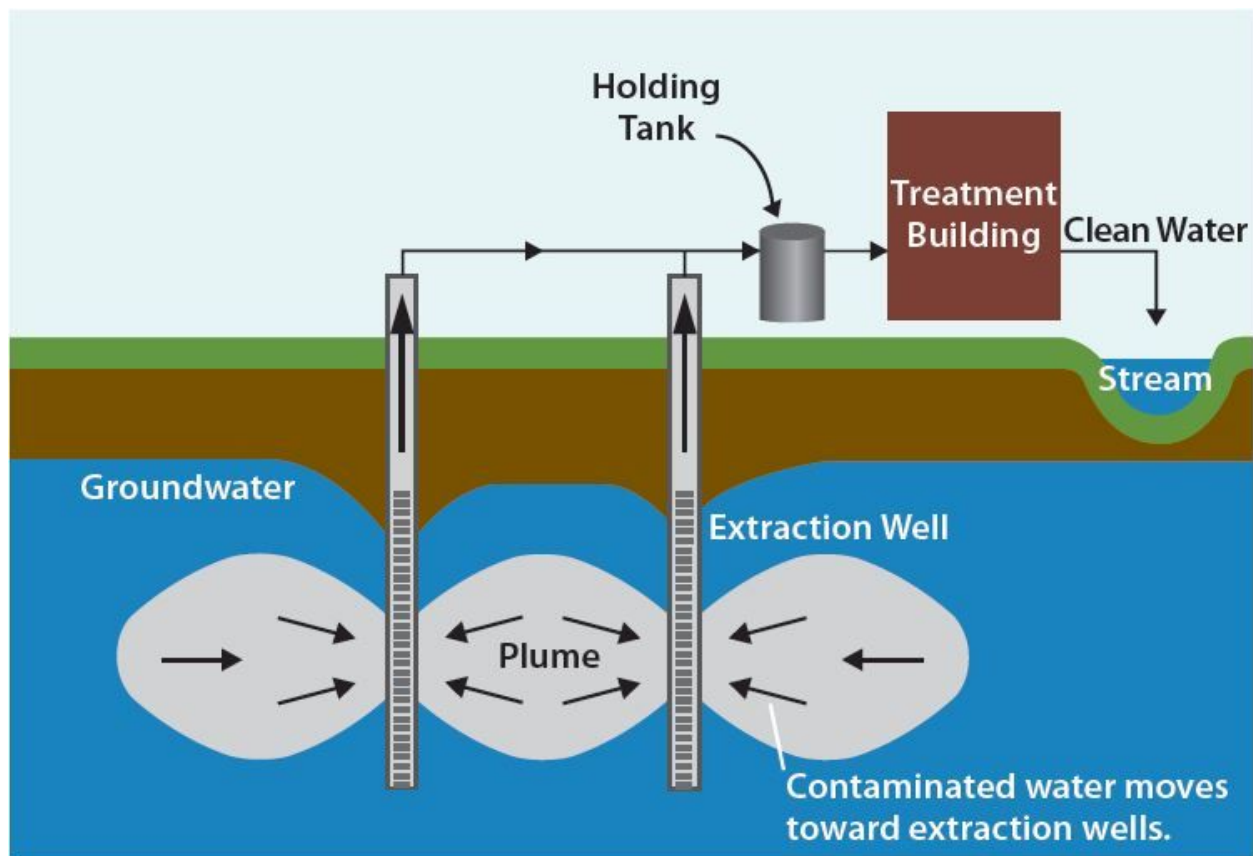
- 1, 1, 1-trichloroethane
- 1, 2-dichloroethane
- Carbon tetrachloride
- Site specific compounds:
 - 1-chloro-1, 1-difluoroethane
 - 1,1,1-trifluoroethane
 - 1,1-dichloro-1-fluoroethane
- **1,1-dichloroethane and 1,1-dichloro-1-fluoroethane were observed at concentrations exceeding the New Jersey Department of Environmental Protection Ground Water Quality Standards 8,000 ft south of the source area**

These are some examples of the main volatile organic compounds of concern. However, dichloroethane and dichloro-fluoroethane were the compounds observed as exceeding the New Jersey Department of Environmental protection groundwater quality standards, 8,000 ft south of the source area. The New Jersey Department of Environmental Protection considers any groundwater concentrations exceeding one percent of the effective solubility as indicative of free and/or residual product. Additionally, if free or residual product is present, it must be treated or removed “to the extent practicable” in accordance with NJDEP regulations.

Remedy Selection:

An air sparge and soil vapor extraction pilot study was performed at the suspected source area. Air sparging from what I understand, is the process of injecting air directly into groundwater which volatilises the contaminants and enhances biodegradation. The air pushes contaminants up to the unsaturated zone, and as contaminants move in to the soil, the soil vapor extraction is used. This method was discovered to be ineffective due to the depth of the water column and presence of low permeability layers.

The Pump and Treat method was selected as the most favorable option due to technical feasibility and cost effectiveness. The PRM aquifer is well suited for hydraulic control given its high flow rates and high conductivity. P & T is considered a passive remediation approach, which was selected seeing as actively removing the contamination would be too costly, disrupt off-site property owners, and not provide any significant protection to human health and environment.



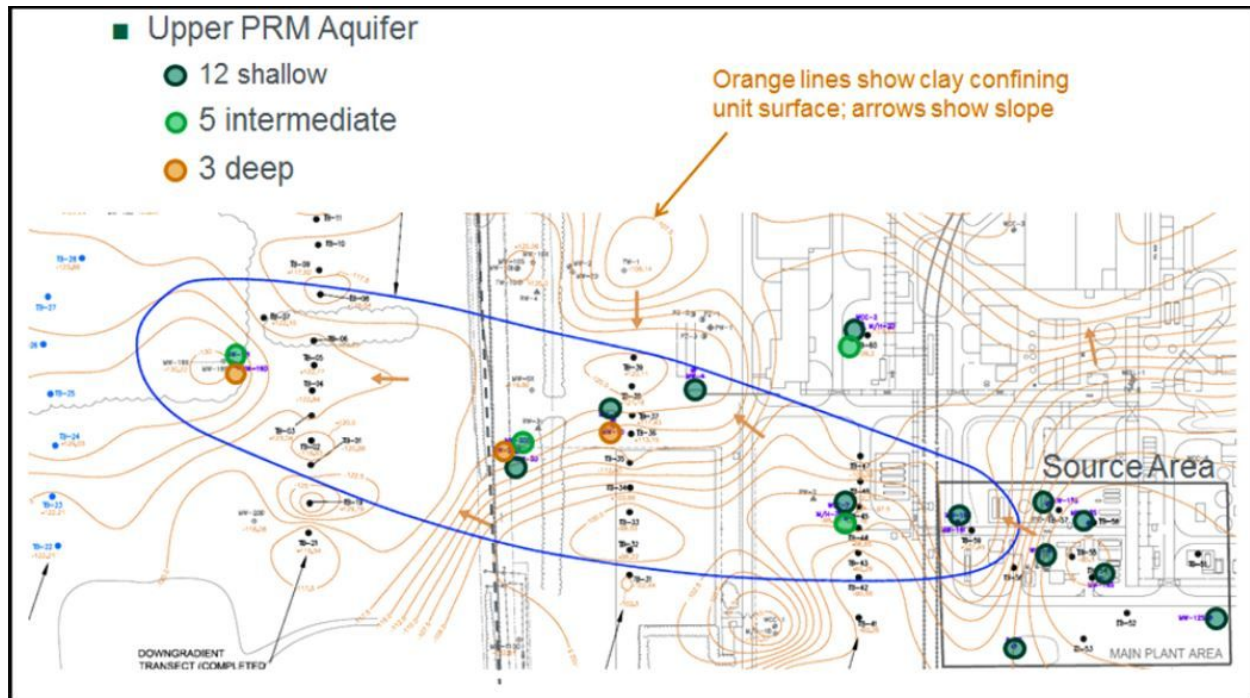
Here is an example of what a pump and treat system might look like, this graphic is from the EPA. I did a little additional research just so I could have a better understanding of how it works. P & T methods involve installing extraction wells that pump water out of the aquifer and into a treatment system that can use a variety of treatment methods. The more contaminants in the water, the more treatment methods will be required to remove the different chemicals. After the water has been properly treated it can be returned under ground, discharged to streams or rivers, repurposed for agriculture, or put into the sewer system for further treatment. Pump and treat can take a few years to a few decades to get all the contaminants out, which is why it is considered a passive remediation method.

Delineation methods:

There were several methods that the team who conducted the study utilized to characterize and delineate the extent of contamination including:

- Visual observation
- Hydrophobic dye testing
- Membrane Interface Probe
- Geophysical techniques for confining unit mapping
- Data interpretation techniques
 - Accurately assess the absence/presence of free/residual product using phase partitioning equations
 - Soil and groundwater samples were used in these equations
 - Investigation area
 - 19 acres, 9 borings, downgradient water plume
 - Observed low points in the topography of clay confining layer

More specifically, for data interpretation, they collected numerous soil and groundwater samples and used those in phase partitioning equations to accurately assess the absence or presence of free/residual product. The investigation area comprised of 19 acres, 9 borings in the suspected source area, and the downgradient water plume as well as observations of the low points of the clay confining layer. They also used monitoring wells, as well as photoionization detector and flame ionization detection field measurements to determine the extent of contamination. The results of the investigation found that most of the contamination was in the dissolved phase and some of the highest measurements were located in the intermediate sand and gravel zones above the clay. Because contamination was only observed within a one-acre area of the plume, active remediation was deemed unnecessary and far too costly.



Here is a map from the report showing the contour of the clay confining layer of the upper PRM aquifer. The blue circle is indicative of the investigation area, which was the 19 acres, and the box on the lower right is the main plant area. The wells located in the investigation area had reported concentrations exceeding 1% of effective solubility, which is grounds for an investigation in accordance with the NJDEP regulations.

Pump and Treat Implementation:

As I previously mentioned, pump and treat was selected as the best remediation method for this case based on its technological feasibility and cost. It is a highly conductive aquifer, so only four recovery wells were necessary to contain the contaminated plume. After evaluating multiple options for where to put the recovered groundwater, it was decided that the industrial facility would reuse it in their operations to offset the amount that the facility was recovering from the middle and lower PRM aquifers. This method is lower in cost than other alternatives, and has several sustainability benefits, for example, lowering the annual load on the drinking water aquifer by up to 138 million gallons per year. An added bonus is that the recovered groundwater actually works better for the facility because it requires less pretreatment to remove hardness and iron, therefore saving the company money in treatment costs among other things.

One of the major challenges that arose with the pump and treat system was iron sequestration. The PRM aquifer is rich in iron, mostly due to bacterial activity and a strong presence of iron reactive bacteria. They would periodically clean the wells with high pressure water or acid wash, but each time they did maintenance, the time between needed cleaning would reduce, so eventually a permanent chemical recirculation system was installed at three of the recovery wells.

Conclusions:

- The scientific approach to the investigation demonstrated that P & T was appropriate for protecting health/environment, as well as abiding by state regulations
- Both P & T and groundwater reuse yielded positive results related to overall cost savings
- The value of an approach emphasizing sustainability can be demonstrated to all stakeholders

Iron-based remediation methods

Kyler Freilinger

Summary

- Iron (Fe) is used as a deterrent in the movement of contaminations
- EPA estimates
 - 250,000 sites soil contamination
 - 3 million sites pollution
- A need to do away with tradition methods of contaminated land and groundwater treatment

Environmental Chemistry of Iron

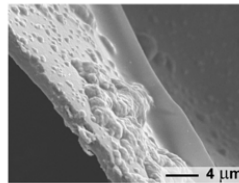
- 4th most abundant element in the Earth's crust
- Involved in many environmental processes
- Common iron bearing materials
 - Native
 - Carbonates
 - Phosphates
 - Sulphates
 - Sulphides
 - Silicates
- Can be broken down by...
 - Acidity (pH)
 - Microbes
 - Metabolized by oxidizing iron

Table 1 - Some common iron-bearing minerals present in surficial and near-surface environments

Mineral class	Name	Formula	
Native or metal ions (Fe)	Zero-valent iron (ZVI)	Fe	
	Oxides/hydroxides	Hematite	α -Fe ₂ O ₃
		Magnetite	Fe ₃ O ₄
	Oxides	Goethite	FeO · OH
		Lepidocrocite	Fe ₃ O ₄ · 2H ₂ O
		Ferrihydrite	Fe ₂ O ₃ · 5/2H ₂ O
		Green rust	Fe ₇ (OH) ₉ · 2H ₂ O · xH ₂ O
	Carbonates	Siderite	FeCO ₃
		Ankerite	CaFe ₂ (CO ₃) ₂
	Phosphates	Vivianite	Fe ₃ (PO ₄) ₂ · 8H ₂ O
Stromeyerite		FePO ₄ · 3H ₂ O	
Sulphates	Hydrated ferrous sulphate	FeSO ₄ · 7H ₂ O	
	Iron(III) sulphate	Fe ₂ (SO ₄) ₃ · xH ₂ O (where x = 0 to 0.11)	
Sulphides	Pyrite	FeS ₂	
	Marcasite	FeS ₂	
Silicates	Pyrrhotite	Fe _{1-x} S	
	Mackinawite	Fe _{1-x} S ₂	
	Greigite	Fe ₃ S ₄	
	Schreibersite	Fe ₃ P ₂	
	Chromite	Fe ₂ Cr ₂ O ₄ · 2H ₂ O	
Greenites	Greenite	Fe ₂ Si ₂ O ₇ · 2H ₂ O	
	Glaucophane	KMg ₂ (FeAl) ₂ (SiO ₃) ₂ · 3H ₂ O	

Sorbitivity/Stability of Iron

- Can be used to immobilize contaminants and improve vegetation
1. Iron oxides deposit of the surface of contaminants
 2. The Iron oxide creates a mesh that hold the contaminants in place



Nanoparticles increase the surface area that contaminants can interact with.

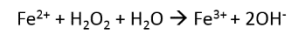
Sorbptivity

- The ability to hold on to or take contaminants chemically

Stability

- The ability to keep contaminants contained within an area

Fenton Reaction



Life Cycle Assessment of Active and Passive Groundwater Remediation Technologies

Taylor Hoj

Introduction:

- Groundwater is one of the most valuable natural resources
- Stored volumes over fifty times greater than the amount of surface water
- Most contaminate sites in industrial countries are hazardous organic chemicals

Pump-and-Treat Systems:

- Common and conventional
- Restoration not achievable through reasonable timeframes
- Most favorable because of hydraulic design, flexibility, and simplicity

Funnel-and-Gate Systems:

- Widely accepted alternative
- No “active work” needed after installation

Location:

- Karlsruhe, Germany
- Former manufactured gas plant
- Slightly confined, 12-meter-thick aquifer underlain by 16 meters of clay
- FGS installed in 2000

Methodology:

- Compared the implanted FGS to a hypothetical PTS
- Purpose is the comparison of the environmental performance of two different long-term technologies
- Energy consumptions and emissions were calculated

Results:

- FGS treated 40 tons of water vs PTS treating 72 tons
- Operation period was for 30 years
- PTS is less ecological damaging due to the installation costs of a FGS
- FGS would even out in another 15-30 years
- FGS requires more stability
- PTS is more flexible, accessible, and less demanding in terms of technological elements

1.

Table 1

Technical specifications of Karlsruhe site and key elements of FGS and PTS subject to LCA

Site parameter—former gas plant Karlsruhe	
Width of contamination	210 m
Hydraulic conductivity log mean	3.9E-03 m/s
Hydraulic conductivity log variance	1.31
Regional gradient	0.07–0.135% gradient direction (25% seasonal variation) NW/WNW
Contaminant concentrations Acenaphthene	400–600 ug/l
Averaged total flow rate through FGS	10 l/s

2.

Table 2

Variations between scenarios developed during the LCA

Scenario	Time (years)	FGS	PTS
Reference scenario		sheet piles	GAC 72t/yr
Scenarios with different wall technologies	30	diaphragm wall, slurry wall	
Scenarios with different wall technologies and variable operation time	10–50	sheet piles, diaphragm wall, slurry wall	
Scenarios with diff. wall technologies, variable operation time and variable GAC consumption for PTS	10–70	sheet piles, diaphragm wall, slurry wall	GAC var.

3.

Table 3
Characterisation factors for selected inventory data

Impact category ^{†,††}	Unit of indicator	Unit char. factor	Characterisation factors C_i for inventory data
Depletion of energy resources (DER)	crude oil eq. (COE)	kg COE/kg	brown coal 0.0409, hard coal 0.1836, natural gas 0.5212
Global warming potential (GWP)	CO ₂ eq.	kg CO ₂ /kg	CH ₄ 23, N ₂ O 296, CF ₄ 5700
Acidification potential (AP)	SO ₂ eq.	kg SO ₂ /kg	NO _x 0.70, HCl 0.88, HF 1.60, H ₂ S 1.88, NH ₃ 1.88
Terrestrial eutrophication potential (TEP)	PO ₄ ³⁻ eq.	kg PO ₄ ³⁻ /kg	NH ₃ 0.35, NO _x as NO ₂ 0.13
Aquatic eutrophication potential (AEP)	PO ₄ ³⁻ eq.	kg PO ₄ ³⁻ /kg	Nh ₄ ⁺ 0.327, NO ₃ ⁻ 0.095, N-comp 0.42, P-comp. 3.06, COD 0.022
Photochemical ozone creation potential (POCP) ††	C ₂ H ₄ eq.	kg C ₂ H ₄ /kg	C ₂ H ₆ 0.189, formaldehyde 0.421, CH ₄ 0.007, NMVOC 0.416, VOC 0.377
Human toxicity potential (HTP)	As eq.	kg As/kg	benzopyrene 20.9, C ₂ H ₆ 0.0019, dioxine 10500, PCB 0.28, Cd 0.42, Cr(VI) 0.28, Ni 0.06

[†]Indicators are calculated as $Indicator = \sum_i M_i C_i$, where M_i (kg) is the inventory data and C_i is the characterisation factor.

^{††}Indicator of POCP is expressed nitrogen corrected as $Indicator = \sqrt{M_{NO_x} \sum_i M_i C_i}$, where M_{NO_x} compounds (UBA 2000).

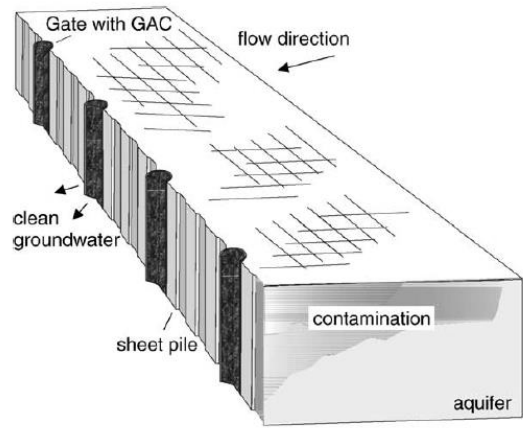
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FGS

Funnel depth	17 m
Funnel length	240 m
Gates depth	17 m
Gate borings diameter	2.50 m
Gate casings diameter	1.80 m
Steel/gate	8 × 12 t
Gravel/gate (50 m ³ /gate; 1.6 t/m ³)	8 × 80 t
Clay/gate (8 m ³ /gate; here 2 t/m ³)	8 × 16 t
GAC/gate (25 m ³ /gate; 0.6 t/m ³)	8 × 15 t
Lifetime (regeneration interval)	5 years

PTS

Number of wells	10
Installation depth	17 m
Pumping rate	18 l/s
PVC conduits	100 m
HDPE container (5 cm wall)	max. 20 m ³ each
GAC refill interval	1 year
GAC volume per fill	24–43.2 t/fill
Lifetime of conduits, pumps, vessels	10 years



5.

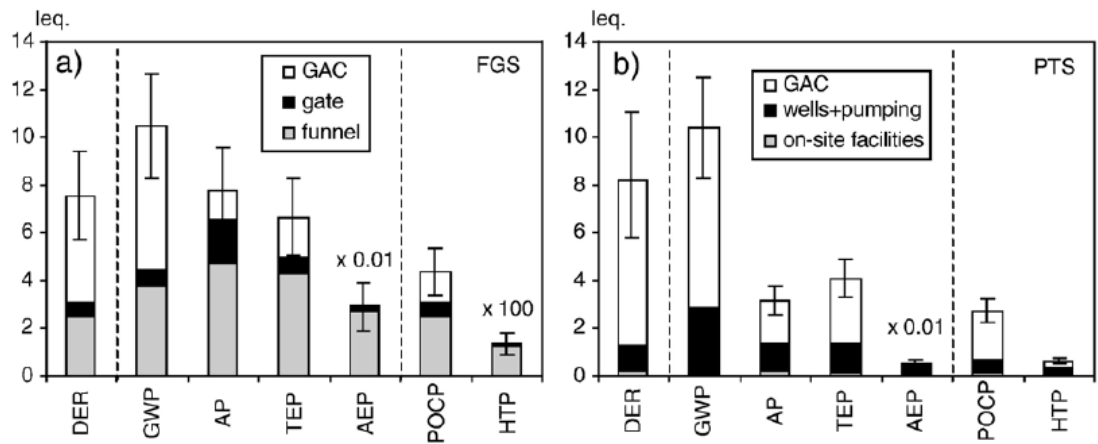


Fig. 5. Reference scenario with category-specific indicators: depletion of energy resources (DER), global warming potential (GWP), acidification potential (AP), terrestrial as well as aquatic eutrophication potential (TEP, AEP), photochemical ozone creation potential (POCP) and human toxicity potential (HTP). Indicators have been normalized against inhabitant emissions or consumptions and are expressed as inhabitant equivalents (leq.).

6.

Table 4
Impact assessment for key elements of FGS and PTS

Inhabitant value/year	Units	DER	GWP	POCP	AP	TEP	AEP	HTP
		(kg COE)	(kg CO ₂)	(kg C ₂ H ₄)	(kg SO ₂)	(kg PO ₄ ³⁻)	(kg PO ₄ ³⁻)	(kg As)
		2447	13167	56	5.7	7.8	14	0.006
GAC	ton	904.8	10975.1	1.21	5.83	0.52	1.1E-03	4.2E-05
GAC rec.	ton	328.3	1166.6	0.54	1.76	0.30	0	3.1E-05
GAC transport	ton	34.8	110.8	0.24	0.65	0.13	0	1.4E-05
Facilities	-	97.9	305.5	2.52	0.25	0.55	1.4E-07	4.2E-05
<i>FGS WALL</i>								
Sheet pile	m ²	44.5	363.3	1.02	0.20	0.24	2.8E-03	5.7E-03
Sheet pile + rec.	m ²	19.5	164.9	0.59	0.10	0.14	7.4E-04	1.4E-03
Facilities	-	562.8	1799.5	14.4	1.43	3.07	0	4E-05
Diaphragm wall	m ²	7.25	28.3	0.25	2.7E-02	6.0E-02	1.1E-10	1.7E-06
Facilities	-	765.3	2336.7	26.5	2.13	4.80	0	2.9E-04
Slurry wall	m ²	18.6	139.9	0.51	6.8E-02	0.12	1.4E-10	7.4E-06
Facilities	-	1757.7	5320.4	68.7	5.70	13.0	0	5.0E-04
<i>FGS GATE</i>								
Excavation	m ³	23.0	156.8	0.42	0.33	0.05	0	0
Facilities	-	470.3	1400.6	20.6	0.84	1.92	0	0
Rebuild	m ³	4.14	12.7	0.14	1.4E-02	3.2E-02	5.9E-09	1.2E-06
Facilities	-	89.5	281.6	2.18	0.22	0.49	1.3E-07	3.7E-05
Steel	ton	284.8	2596.5	5.13	1.22	1.23	2.1E-02	4.2E-02
Steel + rec.	ton	124.6	1178.3	2.99	0.62	0.70	5.6E-03	1.1E-02
Gravel	ton	6.56	20.3	0.17	1.4E-02	3.0E-02	0	3.1E-06
Clay	ton	27.9	77.9	0.39	0.06	9.4E-02	0	1.1E-05
<i>PTS</i>								
Installation	well (17 m)	146.3	351.1	3.71	0.37	0.58	1.3E-03	2.2E-05
Facility	-	12.56	42.46	0.23	3.2E-02	3.8E-02	0	4.6E-06
Pumping	10E+6 L	6.68	96.7	7.3E-02	1.7E-02	2.4E-02	1.5E-04	2.4E-06
Pump		2.35	23.1	4.9E-02	1.2E-02	1.1E-02	2.1E-04	1.2E-04
Conduits	100 m	2.52	7.95	4.0E-02	6.4E-03	6.9E-03	2.2E-04	1.6E-08
GAC container	vessel (20 m ³)	1340.0	2243.2	20.6	2.52	2.19	2.2E-02	4.8E-06

Average inhabitant emissions and consumptions for Germany are taken from IFU (2001).

7.

Processes Affecting the Remediation of Chromium-Contaminated Sites

Paper by Carl Palmer and Paul Wittbrodt

Summary by Hannah Moshinsky

Main Idea:

Understanding how chromium species move in groundwater and how they interact with groundwater in various compounds is crucial in understanding ways to strategize remediation techniques for sites contaminated with chromium waste.

Introduction to Chromium:

1. Popular in US industries for metallurgy, chemical industries, and refractory manufacturing
2. Waste is produced from processing ore, spills, poor storage, improper disposal, and leaks
3. Has 7 oxidation state (0 to 6)
4. Most stable species depends on the pH of the solution
5. Reactive with many other elements found in soils

Contamination Site Examples:

1. New York – Cr-IV moved at the same rate as the groundwater
2. Colorado – chromium contaminate moved at $1/10^{\text{th}}$ the rate of the groundwater
3. Oregon – leaking tanks, hexavalent chromium was an issue, pump and treat system in place

Physical Processes Affecting Migration of Chromium:

1. Groundwater flow
2. Diffusion-controlled transfer
3. Dispersion

Chemical Processes Affecting Migration of Chromium:

1. Oxidation-reduction reactions
2. Precipitation/dissolution reactions
3. Adsorption/desorption reactions

Remediation Techniques:

1. No action
2. Excavation
3. Pump and treat
4. Soil solidification/stabilization
5. Pump and treat with chemical enhancements
6. Geochemical barriers

Conclusions:

1. Many physical and chemical factors contribute to deciding the best clean-up method for chromium contaminated sites
2. Mathematical models can be helpful in estimating the movements of chromium in an aqueous environment, but these can be limiting and need to be further refined
3. Presence of co-contaminants in the soil and groundwater can react with the chromium making it either easier or more difficult to remove, and understanding of these potential reactions is important

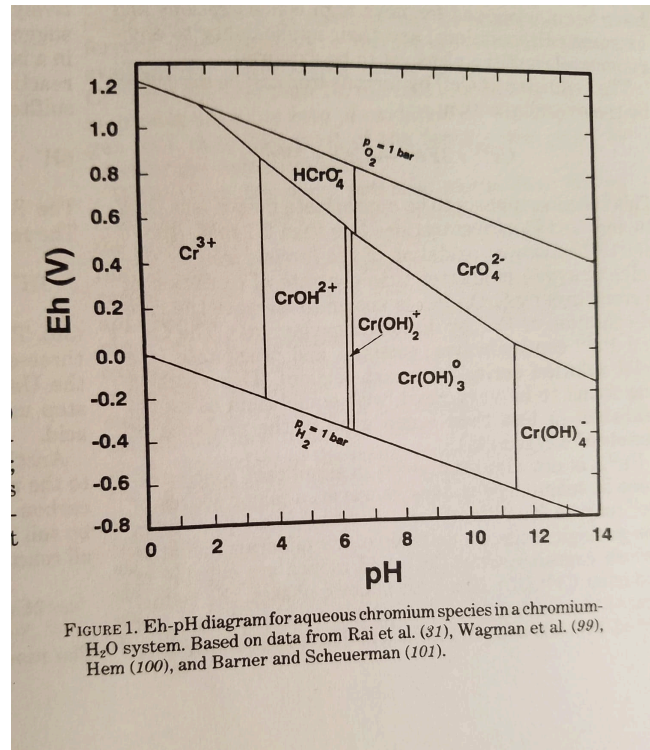


FIGURE 1. Eh-pH diagram for aqueous chromium species in a chromium-H₂O system. Based on data from Rai et al. (31), Wagman et al. (99), Hem (100), and Barner and Scheuerman (101).

Remediation of Metals-Contaminated Soils and Groundwater

Presented by Nick Griffith

Main Points:

- Problem with contaminants
- Sources of contaminants
- Chemical fate & mobility of contaminants
- Generalized remediation approaches & effectiveness
- Available commercial technologies
- Technology directions

Important terms:

- **Superfund site:** EPA funded U.S. federal government program which funds cleanup of sites contaminated w/ hazardous materials.
- **Leachate:** Any liquid that, in the course of passing through matter, extracts soluble or suspended solids, or any other component of the material through which it has passed.
- **Ionic Bond:** a type of chemical bond that involves the complete transfer (sharing) of valence electrons between atoms.
- **Electrokinetic Treatment:** a developing technology for treating contaminated land. An electric current is passed through the soil causing migration of charged species towards collection wells (electrodes).

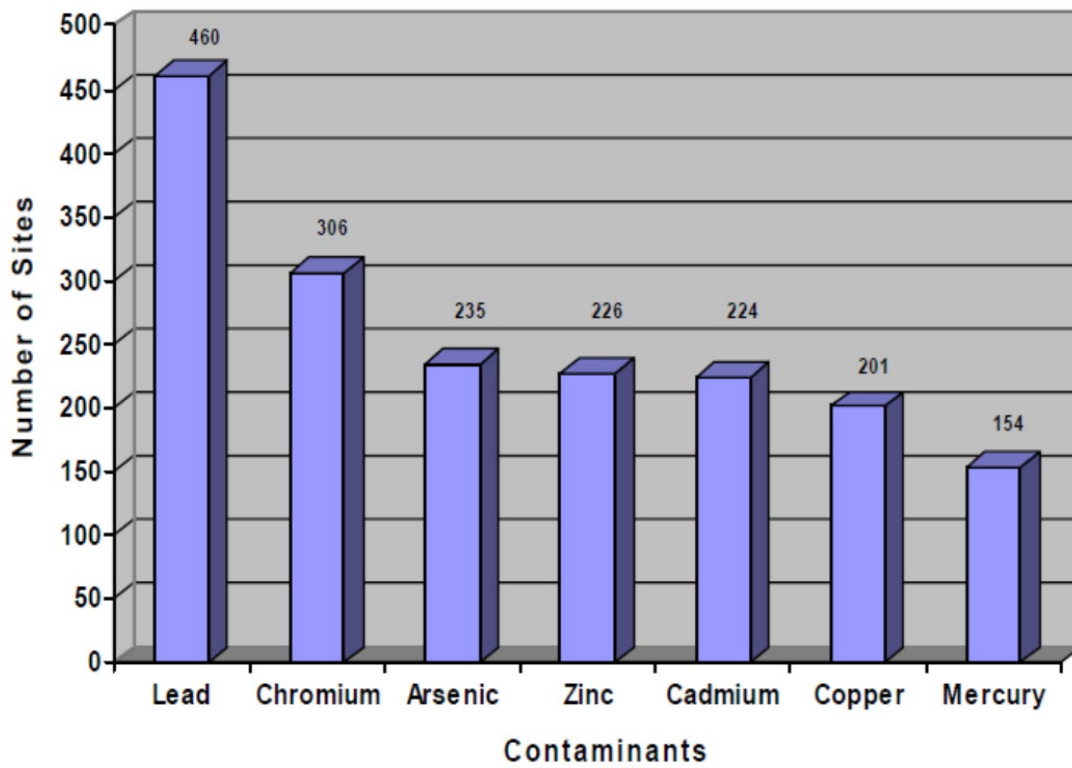


Figure 1: distribution of metal contaminants at superfund sites

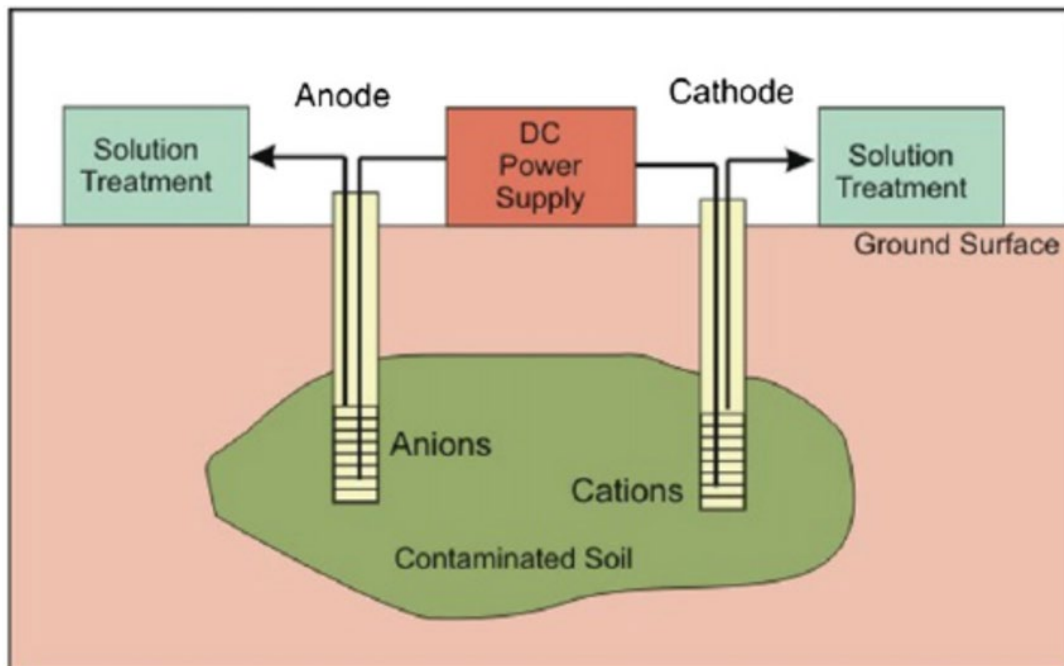


Figure 2: simplified diagram of the electrokinetic treatment process

Table 1. Remediation Technologies Matrix for Metals in Soils and Ground-Water

Remediation Technology	Metals Treated	Cost	Long-term Effectiveness/ Permanence	Commercial Availability	General Acceptance	Applicability to High Metals Concentrations	Applicability to Mixed Waste (metals & organics)	Toxicity Reduction	Mobility Reduction	Volume Reduction
Capping	1-3	+	«	+	+	«	+	«	+	«
Subsurface Barriers	1-3,5	+	«	+	+	«	+	«	+	«
Solidification/ Stabilization Ex situ	1-3,5	•	•	+	+	+	+	«	+	«
Solidification/ Stabilization In situ	1,2,4,6	+	•	+	+	+	+	«	+	«
Vitrification Ex situ	1-3,5	«	+	•	•	+	+	«	+	«
Vitrification In situ	1-3,7	«	+	•	•	+	+	«	+	«
Chemical Treatment	2	-	•	•	•	-	-	+	+	«
Permeable Treatment Walls	2	-	•	•	•	-	-	+	+	«
Biological Treatment	1-5	+	«	•	•	«	-	+	+	«
Physical Separation	1-6	•	+	+	+	+	«	«	«	+
Soil Washing	1-3,5-7	•	+	+	+	+	•	«	«	+
Pyrometallurgical Extraction	1-5,7	«	+	+	+	+	«	«	«	+
In situ Soil Flushing	1,2,7	+	«	+	+	+	+	«	«	+
Electrokinetic Treatment	1-6	•	+	+	+	+	-	«	«	+

1-Lead, 2-Chromium, 3-Arsenic, 4-Zinc, 5-Cadmium, 6-Copper, 7-Mercury

+ Good, • Average, « Marginal, - Inadequate Information

Figure 3: effectiveness statistics of each remediation technology for metal-contaminated groundwater & soils

PCB Remediation Techniques

PCB - Polychlorinated Biphenyls

- Persistent Organic Pollutants
- Used from the 30's to the 80's
- USA - 350 out of 1290 sites contaminated
- Canada - 148 contaminated site
- Europe - 242,000 contaminat

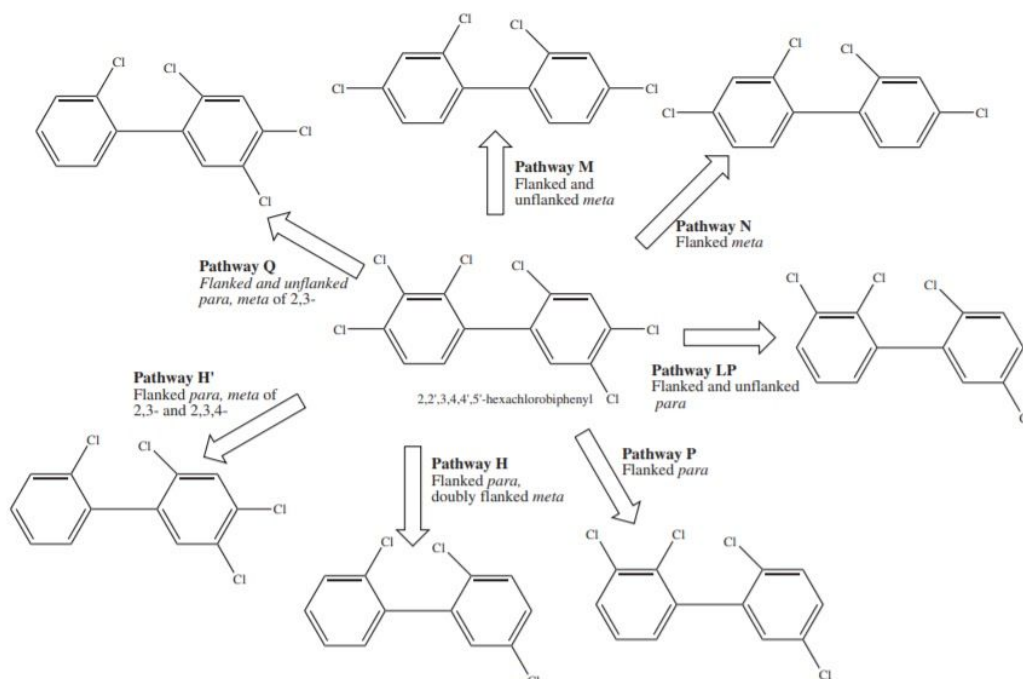
Aerobic and Anaerobic degradation

- The Breakdown of organic contaminants by micro-organisms when oxygen is present

Remediation Techniques

- Biological Remediation
- Chemical Remediation
- Physical Remediation
- Thermal Remediation

Biphenyl Degradation Pathway





ENVIRONMENTAL REMEDIATION WITH NANOPARTICLES

By Palmer Baldwin
ES 473
Spring 2019

TABLE 1

CLASSIFICATION OF REMEDIATION METHODS INVOLVING NANOPARTICLES

	In situ	Ex situ
Adsorptive	In situ sequestration of contaminants by adding binding agents, e.g. iron oxides	Extraction of contaminated solution, which is then treated with adsorbents, as in nanofiltration
Reactive	In situ reaction of nanomaterial, e.g. nZVI, with target contaminant	Extraction of contaminated solution, which is then treated with reactants, as in TiO ₂ photo-oxidation

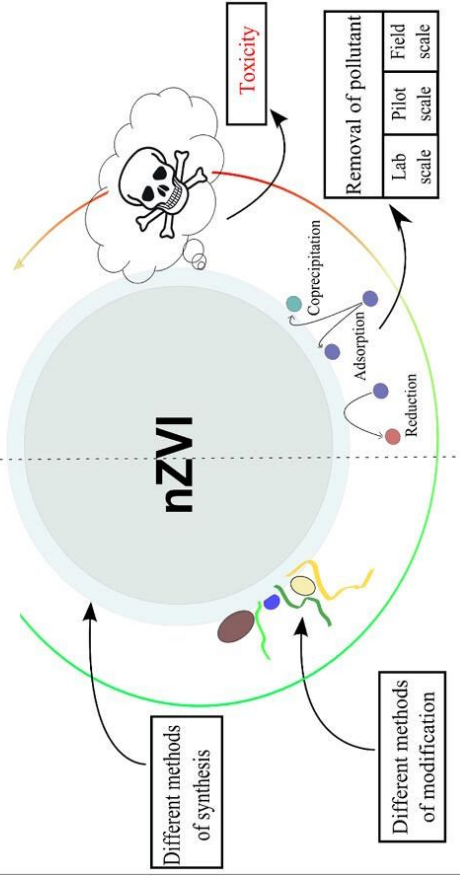
TABLE 2

EXAMPLES OF THE USE OF NANOPARTICLES IN REMEDIATION

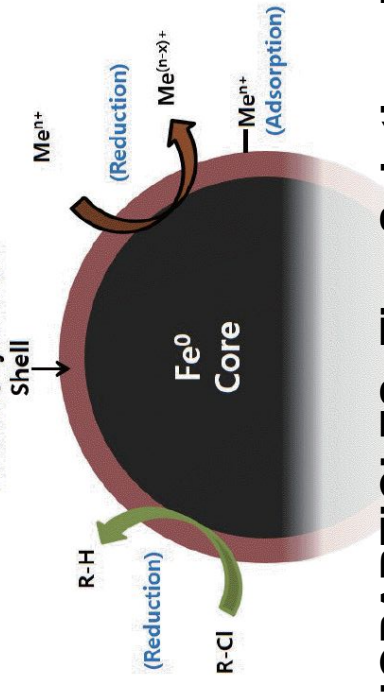
Process exploited	Nanomaterials used	Target compounds
Photocatalysis	TiO ₂	Organic pollutants
Adsorption	Iron oxides, dendrimers	Metals, organic compounds, arsenic
Redox reactions	Nanoscale zero-valent iron (nZVI), nanoscale calcium peroxide	Halogenated organic compounds, metals, nitrate, arsenate, oil

PRODUCTION OF NANOPARTICLES

ENVIRONMENTAL APPLICATIONS



Fe oxide/hydroxides



NANOPARTICLES: Tiny Solutions To Big Problems