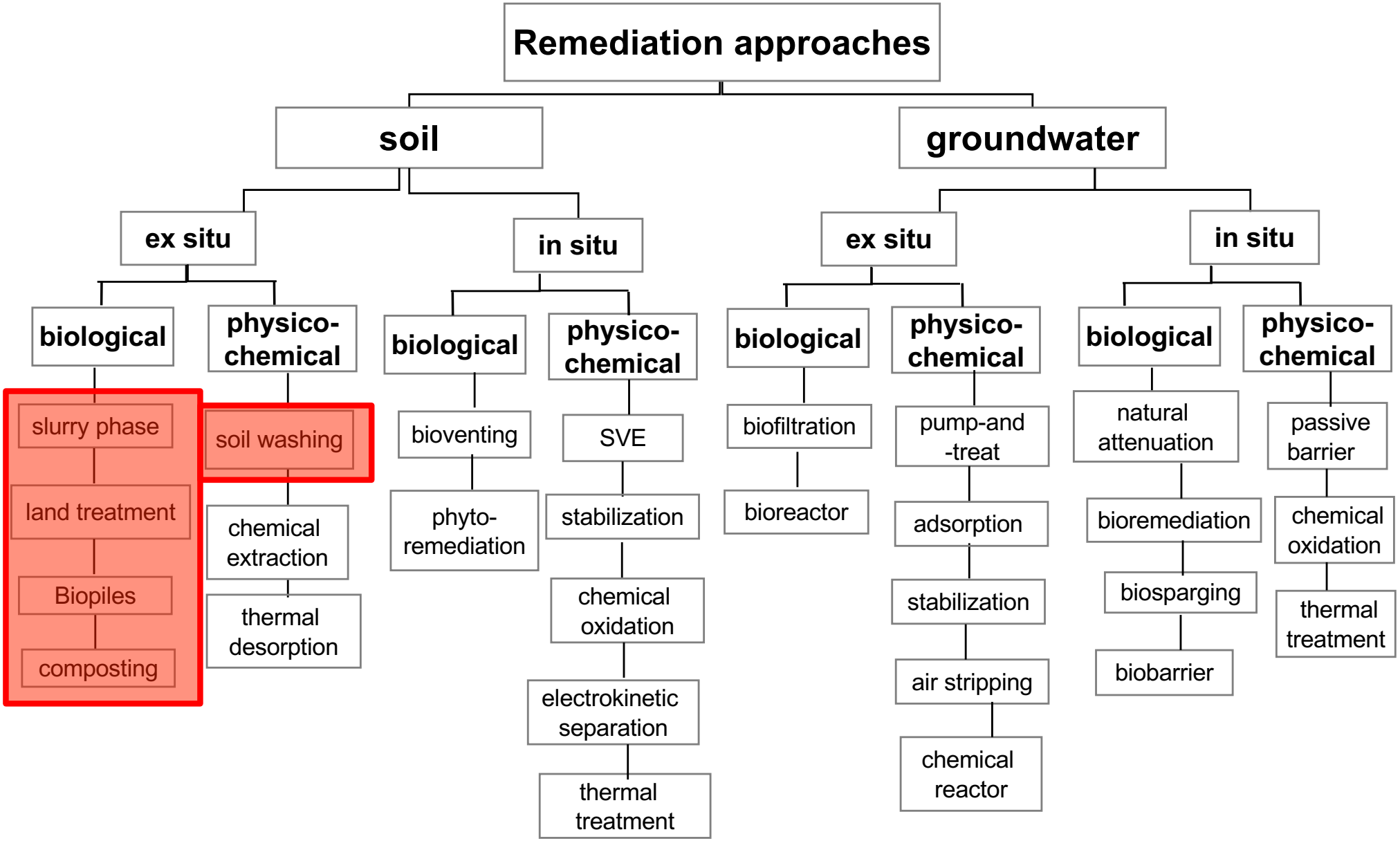
Land and soil treatment + soil washing

Lecture 7

Learning outcomes

- Land treatment
- Composting (windrows and biopiles)
- Soil washing (chemical)
- Slurry biodegradation

Today's lecture



Land Treatment



Windrows





Biopiles

Land treatment

Land treatment

- Material excavated, **transported** in fixed facility
- Application of contaminated soil to the land at a **controlled rate**
- Use cultivation tools (rototiller or disk harrow) for mixing/spreading
- Large surface areas are needed
- ZOI=zone of incorporation (10-30 cm) (zone in which the soil is mixed)
- Well suited to treat petroleum hydrocarbons
- Max. 1-5% hydrocarbon concentration in initial soil (to treat)
- **Perimeter dike**: prevent runoff based on 25-year flood
- **Leachate control**: high-integrity liner, slotted lateral pipes in gravel, slope 0.5-2%
- Access ramp for tilling equipment
- Cover if needed (for rainwater, T, and gas)

Land treatment

- Place contaminated material
- Mixing and aeration (soil is tilled)
- Watering (sprinkler system)
- Nutrient addition: slow-release fertilizer
- Removal when treated

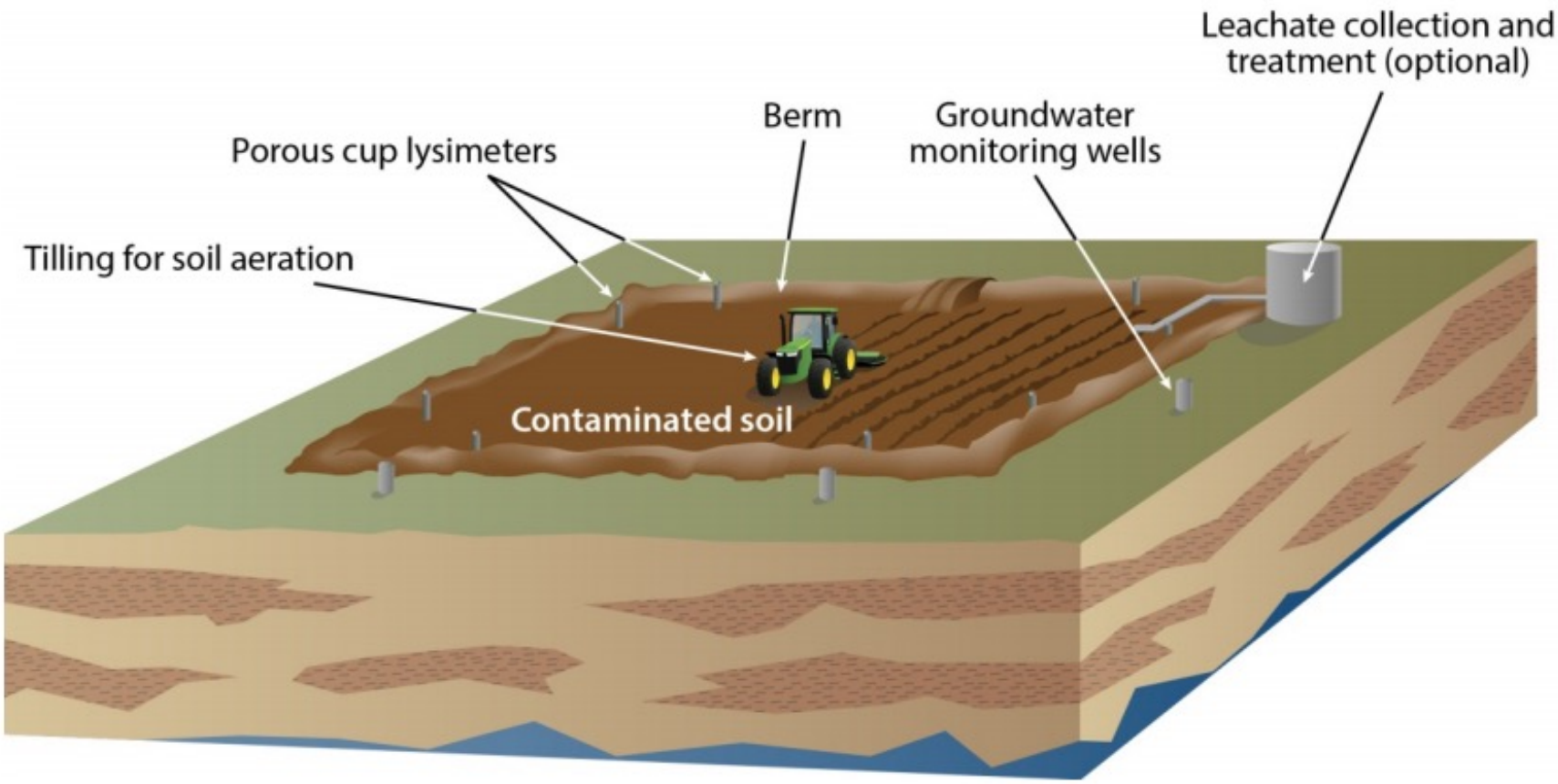
Issue with water management: Need proper drainage

- Migration from the incorporation zone and infiltration

Issue with air-mediated migration:

- Volatilization
- Windblown dust

Land treatment – basic principles of the design



Source: USEPA 1994

Land treatment – basic principles of the design



Moldboard Plow: Effective at breaking lumps and turning over soil from depths of 30 cm

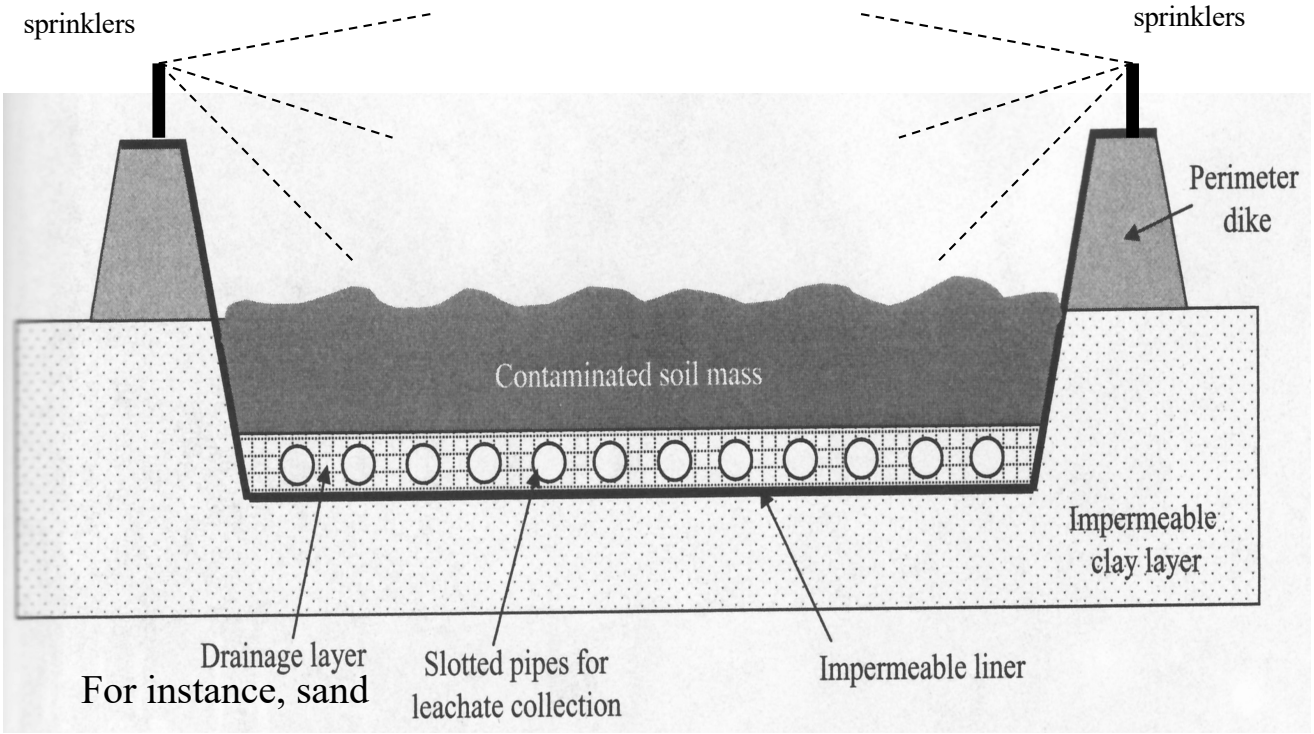


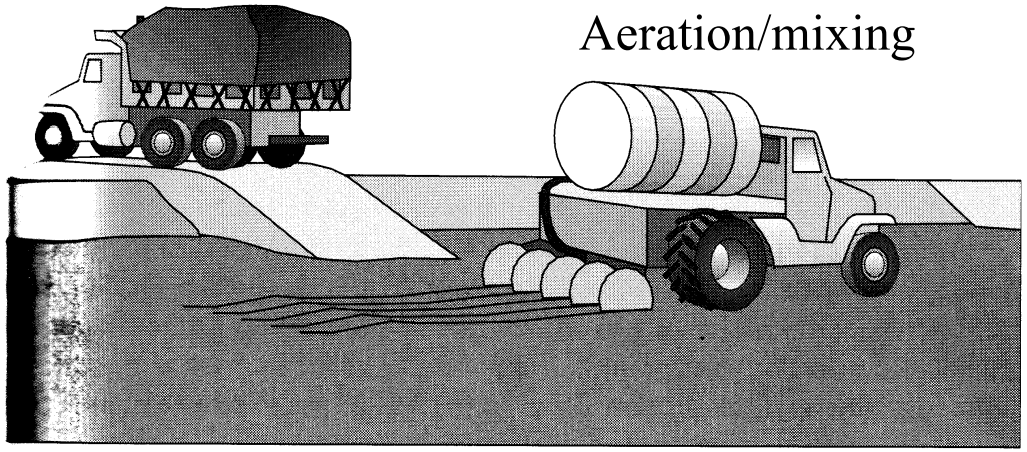
Disc Plow: Effective at loosening, turning over soil from depths of 30 cm



Rotavator: Effective at mixing soils and crumbling soils from depths of <15 cm

Land treatment



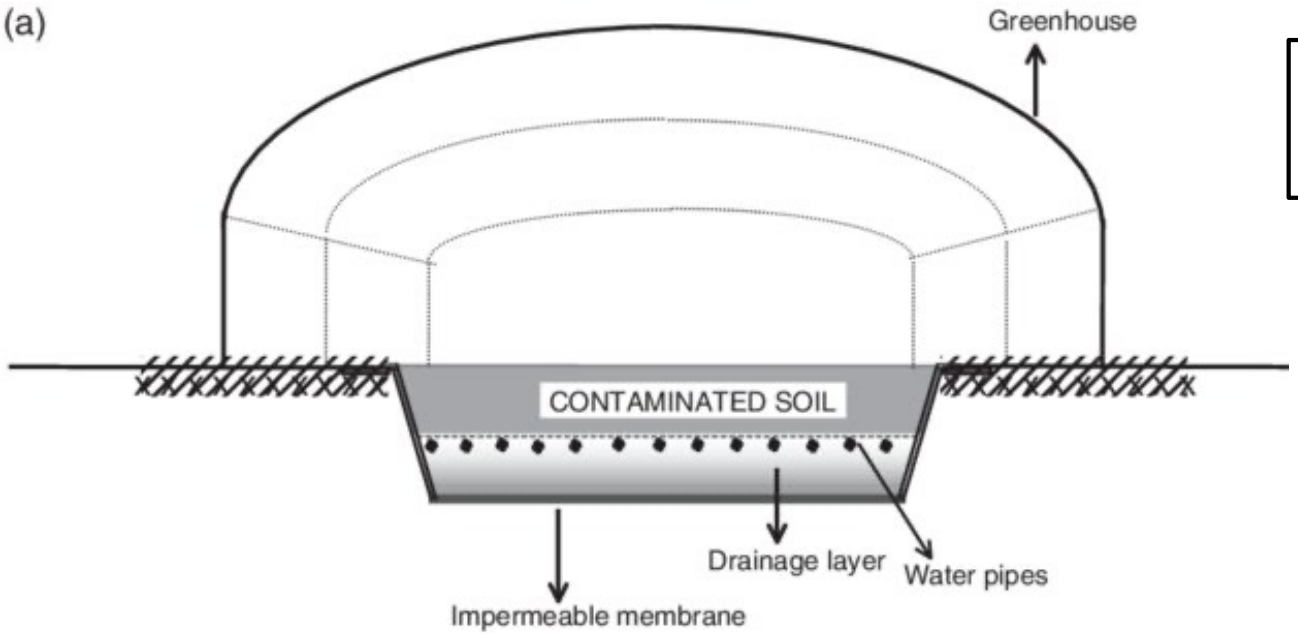


Aeration/mixing

75-100 CHF/m^3

Land treatment – cover to control rain, temperature or gas emissions

(a)



Can have an air treatment unit

(b)



Land treatment

Organic compounds are degraded by microorganisms

- Cumulative amount applied *must be* < cumulative amount degraded
- typical half-life for a petroleum-derived products is 200-500 days

Heavy metals adsorb to soil particles => no removal!!

- Immobilization of metals is pH dependent -> interest of lime/soil amendments
- Presence of cationic and anionic metals can challenge immobilization
- Concentrations will rise and become toxic to microorganisms

Feasibility testing

Soil characteristics:

- Assess important parameters in the soil to be tested
- And their **variability**

Microcosm stimulation test:

- Run by adding nutrients to soil
- C:N:P is 400:10:1- empirically determined
- Soil pH adjusted to 6.5-8.0 (for ex. with crushed limestone)
- Water added to 50-80% of field capacity
- After 1-4 weeks, soil tested for hydrocarbon content (determine a good **criterion of success**! Which parameter to follow?)

-> Ability of native microorganisms to degrade the contaminant?

-> Adjust the treatment for optimization (test several microcosm treatments)

Land treatment

Aeration and Zone of Incorporation (ZOI)

O_2 penetration by diffusion $$L = \sqrt{\frac{2\varepsilon D C_0}{r_0}}$$

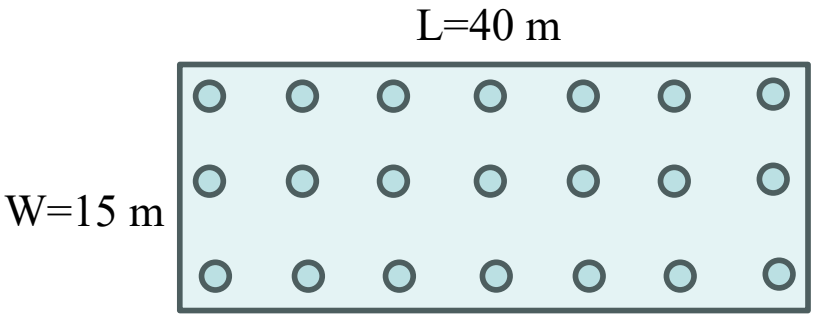
L= depth at which O_2 conc. reaches zero (m)
ε = porosity [-]
D= diffusion coefficient ($m^2 \cdot s^{-1}$)
C_0= oxygen concentration at surface ($g.m^{-3}$)
r_0= rate of oxygen consumption ($g.m^{-3}.s^{-1}$)

-> ZOI=zone of incorporation is typically 10-30 cm
Soil layer typically < 50 cm

Example 1: Land treatment case study

- BP Oil refinery in Louisiana conducted a pilot land treatment project to demonstrate the degradation of contaminants in soils polluted with refinery waste
- Used soil with high clay content. Area= 15m*40m; volumetric moisture content 0.1; wet bulk density=1,540 kg/m^3
- Added soil (1 m deep) and a dike (hydrology management)
- Contaminated soil added, and zone of incorporation (0.1 m) tilled weekly
  - The waste contained six volatile organics
- Moisture, nutrient balance and pH monitored
- First order degradation rate k=0.008 d^{-1}

Time (days)	**Average measured concentration in ZOI (g/kg)**
0	20
110	13
229	9
298	2



Calculate the total remaining contaminant mass after 298 days

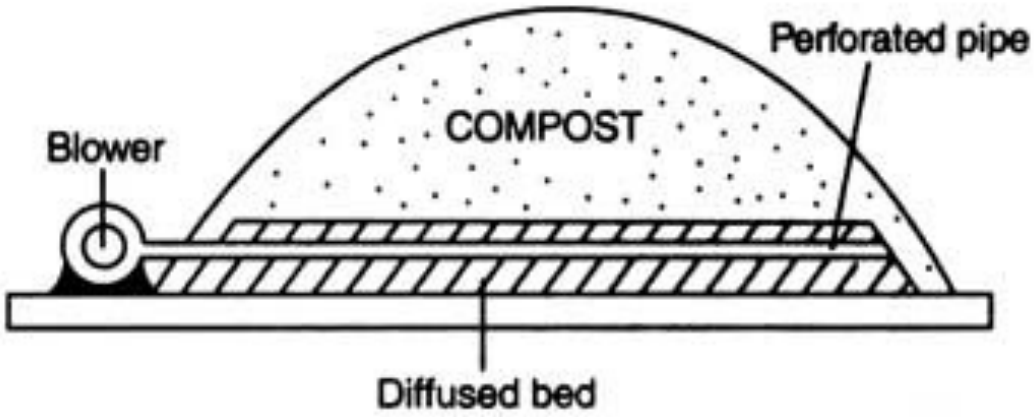
Composting (windrows and biopiles)

Composting

- Examples: biopiles, windrows, composting reactor
- Similar to land treatment in basic principle (but can be more efficient for complex organic solids – less appropriate for low-organic contents)
- Soil excavated and heaped for treatment
- Aerobic process
  - Aeration of piles by turnover (windrows)
  - Aeration by forcing air through the composting material placed in piles (biopiles)



Windrows



Biopiles

Composting

Typical parameters to control:

- T (degradation typically occurs in the thermophilic range (55-65 C)
- Too high temperature can kill the microorganisms
- Moisture
- Oxygen level
- Organic content

Composting

Windrows:

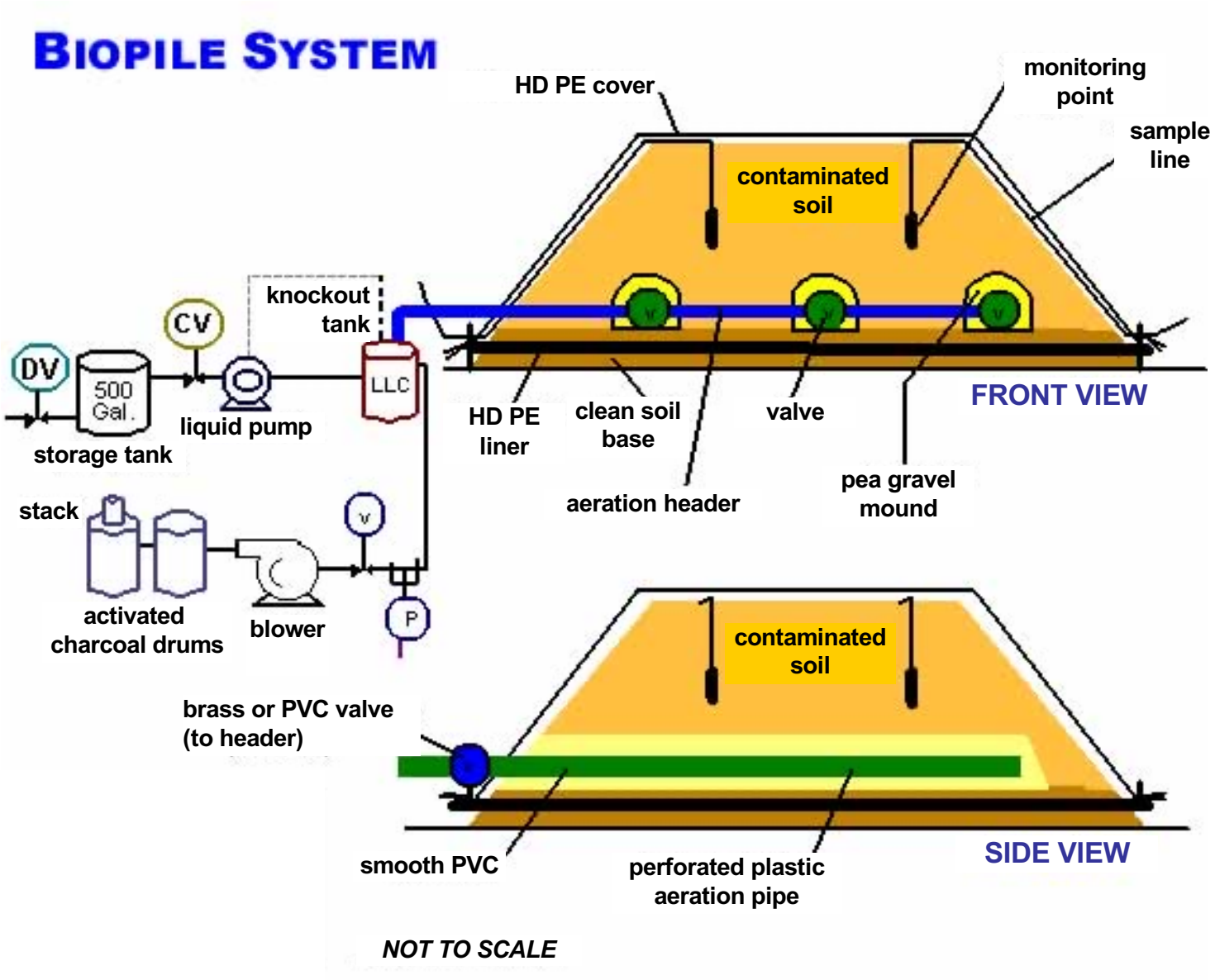
• bulking agent (ex. Wood chips) added to increase porosity and decrease moisture levels
•Piled in **long rows**
•maximum size: 1.5 m tall and 3.5 m wide
• mechanically **mixed** (1-2/week)
• front-end loader or **turner needed for aeration**
• turning to **aerate** pile and **release heat**

Biopiles

• **static**
• need aeration system
• can be bigger than windrows
• typically 3 m high
• air pushed through (most common)

(Dynamic biopiles requiring turnover exist but are not common)

Biopile

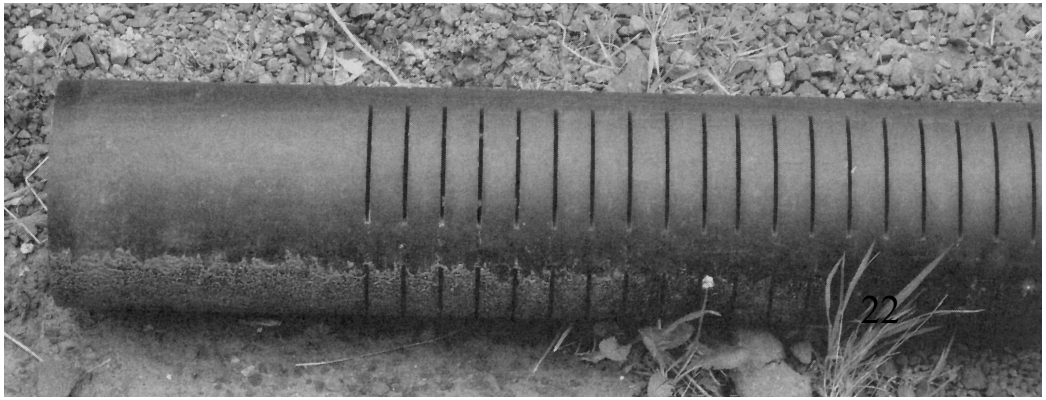

BIOPILE SYSTEM
HD PE cover
monitoring point
sample line
contaminated soil
knockout tank
CV
DV
500 Gal.
LLC
liquid pump
storage tank
HD PE liner
clean soil base
valve
FRONT VIEW
aeration header
pea gravel mound
stack
activated charcoal drums
blower
P
contaminated soil
brass or PVC valve (to header)
smooth PVC
perforated plastic aeration pipe
SIDE VIEW
NOT TO SCALE

Biopiles

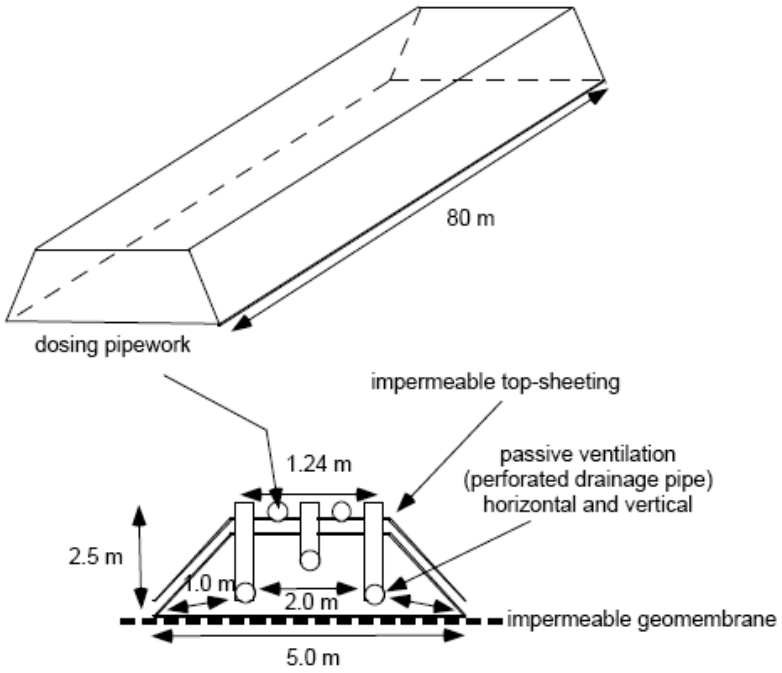
- Design critical for optimal performance
- Temporary and permanent (concrete base)
- Considerations:
  - Height limited by reach of front-end loader
  - Height also limited by aeration (passive vs. forced aeration)
  - Slope too steep: aeration of sides not center
  - Slope too shallow: waste space
- Biopile base
  - Solid surface, usually soil /clay foundation
  - impermeable liner (HDPE) 1-2 mm
  - trench for leachate
  - Clean soil on top of liner to protect it
  - Slope of 1 or 2%
- Graded, sieved soil (30-50 mm)
- Add bulking agents (wood chips, straw), water, P, N

Aeration systems

- Constructed on top of liner
- Slotted plastic pipes embedded within gravel or wood chips
- Low power blowers- too rapid airflow dries soils; too slow insufficient aeration
- Issue of VOC: can operate in vacuum mode
  - treat the gas (GAC)- 15 pore volumes per day
  - entrain condensate: need water knockout and collection
- Fixed rate aeration: can be turned on or off but not changed. Disadvantage is that pile can be over-aerated when low microbial activity (beginning) and then under-aerated when high microbial activity
- Variable rate: not used much- need day to day monitoring. Rate of aeration starts out high and decreases with time.
- Automated: computer controlled in response to temperature in pile.



Example 2: Design of biopile



Calculate:

1. Water volume
2. Air volume
3. Solid volume
4. Volume of water needed
5. Mass of nutrients needed
6. Volume of air needed
7. Expression for $C_{i,aq}$
8. How much time to reach 98% mass removal?

Height: 2.5 m
Upper width: 1.24 m
Lower width: 5 m
Length: 80 m
Bulk density: ρ_{wb}= 1200 kg/m^3
ε=0.55 [-]
Target water content: 45% (volume)
Initial water content: 20% (volume)
$TPH_{t=0}$: 80 g C/kg dry soil (assume C_7H_{16})
Rate of degradation (in water): 0.05 d^{-1}
Molar ratio C: N: P = 100:10:1
Assume use Ammonium sulfate ($(NH_4)_2SO_4$)
MW= 132 g/mol ; Trisodium phosphate (Na_3PO_4•$12H_2O$) MW=380 g/mol)
O_2 content in air: 0.3 g/L
Air flow rate: 0.2 m^3 air/m^3 soil/min
Density of C_7H_{16} $\rho_{heptane}$= 680 kg/m^3

Windrows

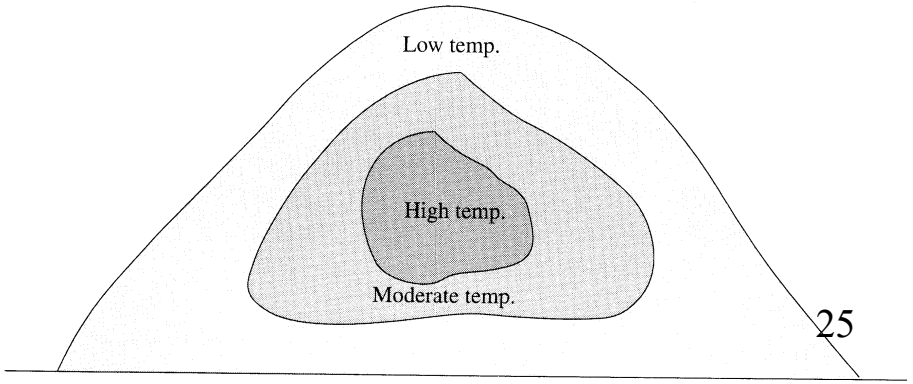




Piles are **turned** front-end loader or turner needed for aeration
Releases excess heat
And volatiles…

Windrow composting

- Organics added to the windrows
- Increase metabolic rate of indigenous hydrocarbon oxidizers
- Increase bioavailability of hydrophobic pollutants
- If moisture content too high, gas transfer rates decrease significantly
- Optimal moisture content about 50%
- Does not reach very high temperatures (<45ºC)
- **Turnover to dissipate heat**
- Add bulking agents to aid in heat dissipation
- Frequency of turning varies between once a day to once a month
- Piles that are not turned: passive aeration. Temperature gradient causes convective airflow. Such aeration is limited by porosity and pile depth



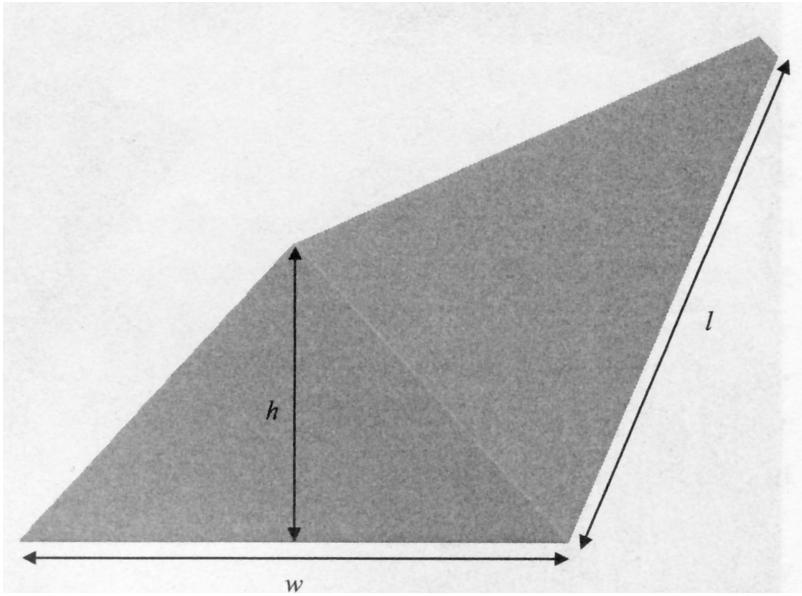
Covers

- Many projects without covers
- Waterproof plastic sheet
- Fleece liners (PP). Resist to rainfall, not impermeable, gas permeable. Equipment to remove/replace liner
- Offer advantages:
  - Prevent leachate formation
  - Lose little water so no need to irrigate
  - Still must monitor water content since forced aeration remove water



Considerations

- Apply manure, sewage sludge, garden waste
- Shaped as a triangular prism
- Windrow turner needed-saves space
- No need for pipes for aeration
- Issues: odors, VOC emissions, climate-dependance
- Slower than enclosed reactor



Comparison of composting systems

Control level	Windrow system	Static pile system
Operational skill level	Low	Moderate
Process flexibility	High	Medium
Material load flexibility	High	Medium
Process control	Low	Medium
Moisture control	Low	Medium
Air emission control	Low	Medium
Runoff control	Medium	Medium
Space requirement	High	Medium
Pathogen destruction	Medium	High
Climatic dependency	High	Medium
Capital cost	Low	Medium
Maintenance cost	Low	Medium

Conclusions

- Disruptive techniques
- Need a large amount of space
- Useful for certain applications (e.g., hydrocarbons)
- Limitation in terms of:
  - Capacity (amount that can be treated)
  - Rate (amount per given time < degradation rate)
  - Loss via volatilization and leaching
- Adaptable concept, many variations

Soil-washing (chemical)

Contaminants are associated with fines

- Finer particles have higher area to volume ratio and adsorb most of the contaminants

Example 1:

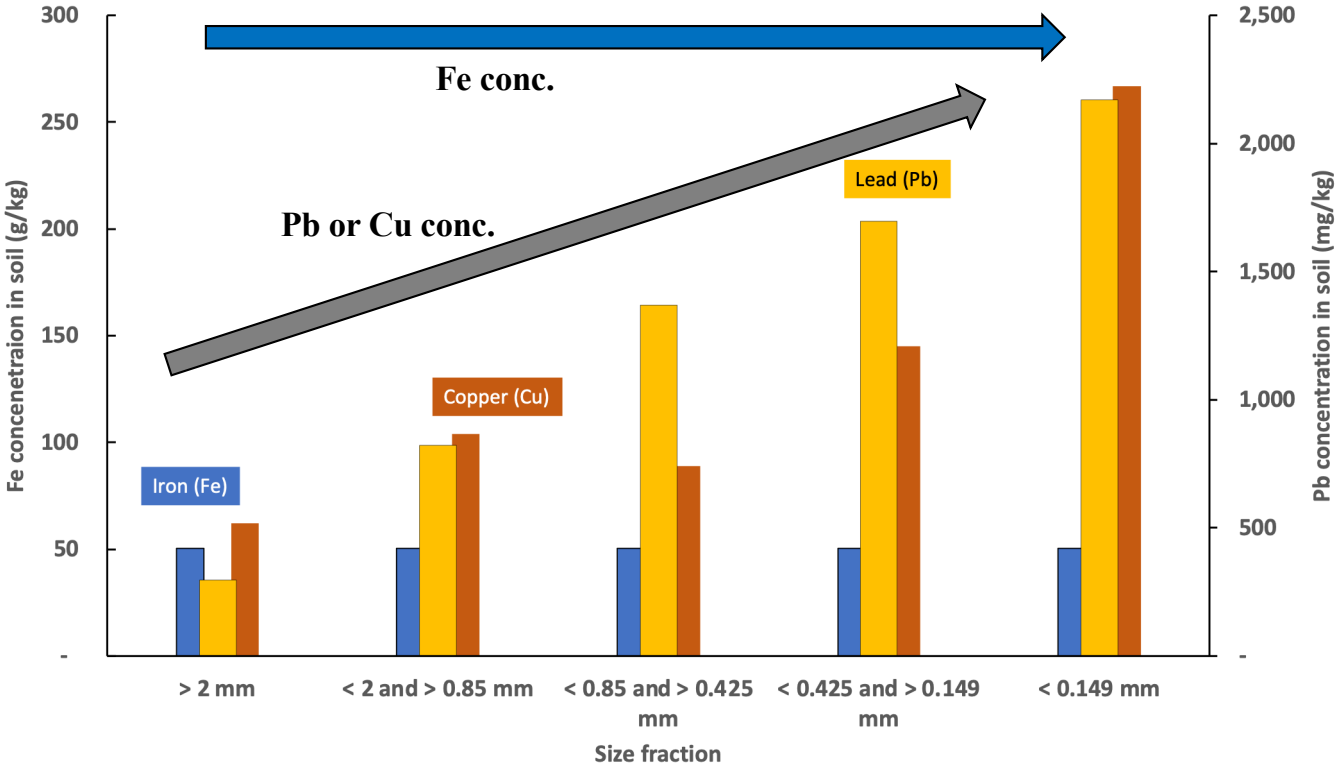
Distribution of COD by soil component

Component	%mass	%COD
Coarse	29	2.9
Fines	55	88.8
Tars	0.3	8.8
Water	15.7	0

Source: Black et al., 1991

COD=Chemical Oxygen Demand => equivalent of organic content

Example 2:

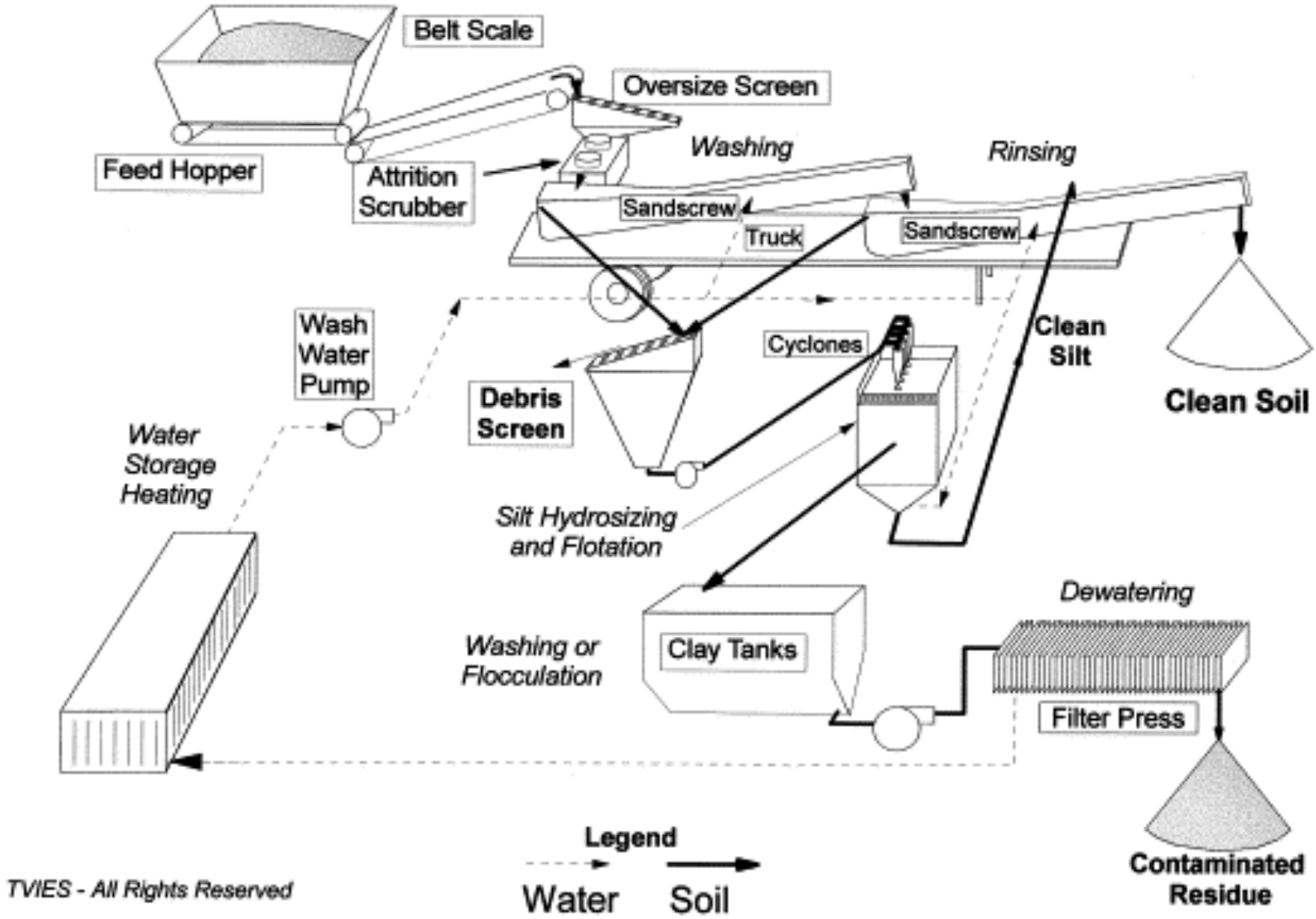


Source: McCabe et al., 1997

Soil-washing

- Soil washing is a volume reduction/waste minimization treatment process
- The soil fine fraction carrying the largest amount of contaminant is separated from the bulk soil
- The rest of the soil (depending on its contaminant content) can be used as backfill, or disposed of as non-hazardous material
- Physical soil-washing: separation based on particle grain size, settling velocity, specific gravity, surface chemical behavior. Some removal of contaminant is possible through particle attrition

Physical soil washing



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Soil-washing

- Soil washing is a volume reduction/waste minimization treatment process
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- Physical soil-washing: separation based on particle grain size, settling velocity, specific gravity, surface chemical behavior. Some removal of contaminant is possible through particle attrition
- **Chemical soil-washing: transferring the contaminants from the soil surface into solution (often using chemical compounds). The resulting suspension is separated from the aqueous solution (the latter is treated).**

Chemical soil-washing

- Contaminants adsorbed onto fine soil particles are separated from bulk soil in an aqueous-based system based on particle size (remove sand and gravel).
- Slurry: suspension of a solid phase in liquid
- The soil is suspended in aqueous medium (water) until reach target density
- The wash water may be amended to enhance the removal of the compound into water
- For heavy metals, pH adjustment of a chelating agent may be used:
  - Removal of metals from soil through soil washing
  - Decrease the pH to a value below the edge (e.g., Pb^{2+}, pH <3)
  - Amendment of chelator that outcompetes the soil for the binding of the metal
- For organic contaminants, a surfactant may be used
- Equilibrium calculation of the aqueous concentration for batch systems

Soil washing

$$N = \frac{ln\left[\left(C_{i,s,a} - C^{*}_{i,s,a}\right)/\left(C_{i,s,b} - C^{*}_{i,s,b}\right)\right]}{ln[1/K * Q_L/Q_{soil}]}$$

$$C_{i,aq,n+1} = \frac{Q_{soil}}{Q_L} * C_{i,s,n} + \frac{Q_L * C_{i,aq,a} - Q_{soil} * C_{i,s,a}}{Q_L}$$

Where N= number of stages needed

$C_{i,s,n}$= solid phase inlet contaminant mass fraction (kg contaminant/kg soil)

$C_{i,s,n}{}^{*}$= solid phase equilibrium contaminant mass fraction (kg contaminant/kg soil) with respect to $C_{i,aq,n}$

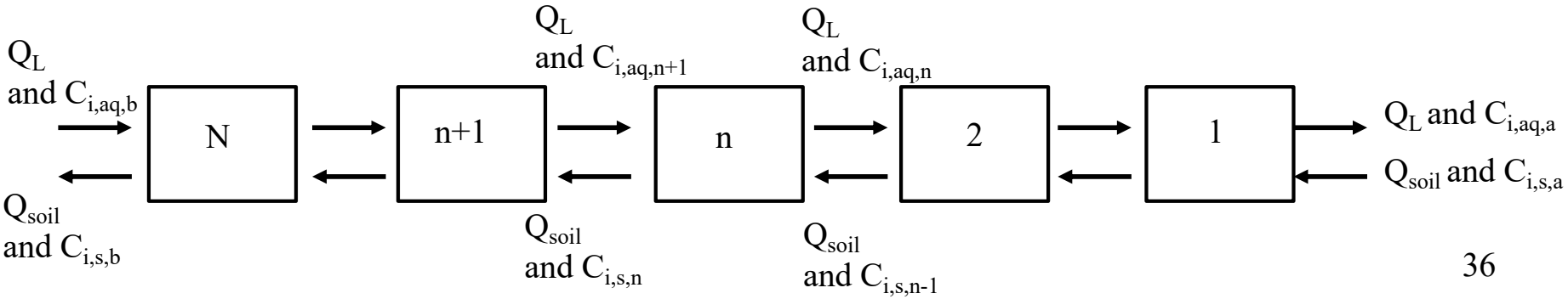
K=equilibrium line slope (assuming linear relationship)

Q_L=extractant mass flow rate (kg/h)- constant at all stages

Q_{soil}= soil mass flow rate (kg/h)- constant at all stages

n= stage number

$C_{i,aq,n}$=effluent extracting fluid mass fraction (kg contaminant /kg extractant)



Countercurrent leaching cascade

Example 3- Soil washing example

A soil contaminated with lead (Pb^{2+}) is being treated by soil washing under acidic conditions using a countercurrent leaching procedure. The <75 µm fraction contains the majority of Pb^{2+} (354 mg/kg) and will be treated. The ideal ratio of solid to liquid flow rate was found to be 0.025 kg soil/L water.

Due to the pH dependency of the sorption, the equilibrium isotherm is pH dependent with K=2 (L/kg) at pH 2. $C_{i,s} = KC_{i,aq}$

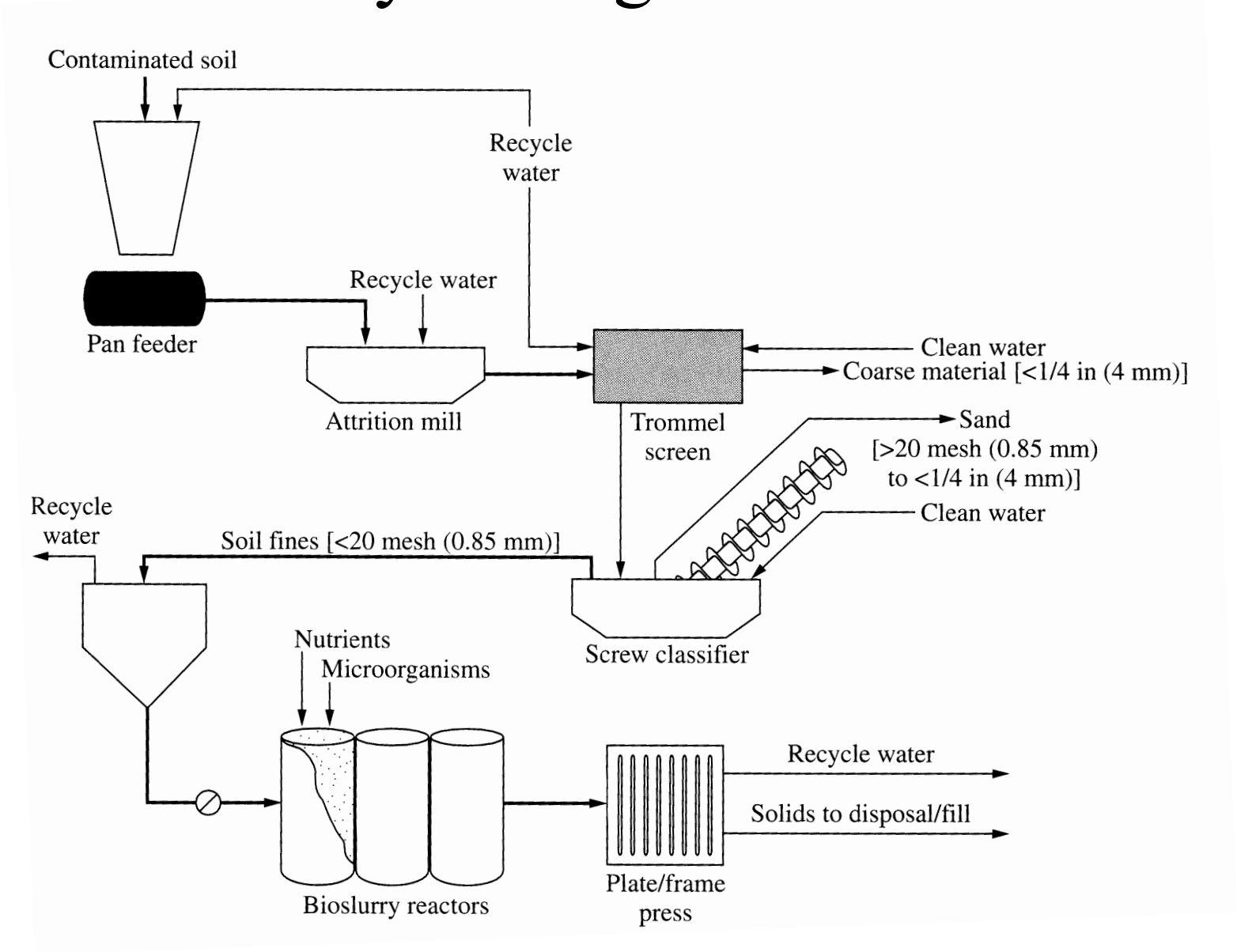
How many stages are needed for the treatment to the soil fraction at pH 2 to reach a concentration of 0.12 mg/kg given that the aqueous concentration of lead is 10 mg/L and 0.05 mg/L at the effluent and influent, respectively ?

Slurry phase biodegradation

Slurry biodegradation

- Slurry biodegradation is used to treat soil that is excavated
- Biological degradation of the contaminant instead of desorption
- Amended with nutrients, pH adjusted
- Mixing energy needs increase with density
- For high contaminant concentration: require higher O_2 transfer so more dilute slurry
- Keep solids in suspension to increase contact with microorganisms
- Mixing and aeration to break up clumps and increase mass transfer rate
- Treatment with most contact btw contaminant and microorganisms
- Desorption of contaminant from solid particles
- Microorganisms degrade aqueous contaminant but **there are microorganisms in the water and on the solid surface**

Slurry biodegradation



Can be done in a single reactor or in multiple stages

Slurry biodegradation

Degradation from biomass in liquid phase

Degradation from biomass in solid phase

$$\int \frac{dC_{i,aq}}{dt} = -\frac{X_w}{Y(V_L + M_s K_D)}\left[\frac{V_L \mu_{aq,max} C_{i,aq}}{K_w + C_{i,aq}} + \frac{M_s K_b \mu_{s,max} K_D C_{i,aq}}{K_s + K_D C_{i,aq}}\right]$$

Where:

V_L= volume of solution in reactor (L)

M_s= mass of dry soil in reactor (g)

$\mu_{s,max}$= maximum specific growth rate in cells on solid phase (h^{-1})

$\mu_{aq,max}$= maximum specific growth rate in cells in aqueous phase (h^{-1})

K_s= half-velocity constant for solid phase associated cells ($mg.g^{-1}$)

K_w= half-velocity constant for liquid-phase associated cells ($mg.L^{-1}$)

X_w= concentration of cells in liquid phase ($mg.L^{-1}$)

Y= growth yield coefficient for the cells vs. substrate (mg cells/mg substrate)

K_b= partition coefficients for cells onto the solid phase ($L.g^{-1}$)

K_D is given by

$C_{i,s} = K_D C_{i,aq}$ with Ci,aq in $mg.L^{-1}$ and Ci,s in $mg.g^{-1}$ and K_D in $L.g^{-1}$

Can only be solved numerically

Simplified relationship

Assume that degradation is mainly driven by solid-associated biomass

$$\int \frac{dC_{i,aq}}{dt} = -\frac{X_w}{Y(V_L + M_s K_D)}\left[\frac{M_s K_b \mu_{s,max} K_D C_{i,aq}}{K_s + K_D C_{i,aq}}\right]$$

Where:

V_L= volume of solution in reactor (L)

M_s= mass of dry soil in reactor (g)

$\mu_{s,max}$= maximum specific growth rate in cells on solid phase (h^{-1})

K_s= half-velocity constant for solid phase associated cells ($mg.g^{-1}$)

X_w= concentration of cells in liquid phase ($mg.L^{-1}$)

Y= growth yield coefficient for the cells vs. substrate (mg cells/mg substrate)

K_b= partition coefficients for cells onto the solid phase ($L.g^{-1}$)

K_D is given by

$C_{i,s} = K_D C_{i,aq}$ with Ci,aq in $mg.L^{-1}$ and Ci,s in $mg.g^{-1}$ and K_D in $L.g^{-1}$

$$K_S \ln\left(\frac{C_{i,aq}}{C_{i,aq,0}}\right) + K_D\left(C_{i,aq} - C_{i,aq,0}\right) = -\frac{X_w M_s K_b \mu_{s,max} K_D}{Y(V_L + M_s K_D)} * \mathrm{t}$$

Example 4: slurry biodegradation

Phenol-contaminated soil is being remediated with a slurry phase bioreactor with no gas phase.
This process is first tested in the lab in a reactor containing 0.25 L of water and 20 g of dry soil.
The initial solid phase concentration of phenol is 0.5 $mg.g^{-1}$.
The sorption behavior is given by $C_{i,s}=K_D\ C_{i,aq}$ with K_D =5 $L.g^{-1}$

How much time needed for the aqueous concentration to diminish by 95%?

$\mu_{s,max}$= 0.29 h^{-1} K_s= 2.12 $mg.g^{-1}$ X_w= 2 $mg.L^{-1}$
$\mu_{aq,max}$= 0.23 h^{-1} K_w= 1.99 $mg.L^{-1}$ Y= 0.34 mg cells/mg substrate
K_b= 0.167 $L.g^{-1}$

Microbial inoculum

- Develop adequate microbial community
  - Mixed cultures often most stable to carry out process
  - A single bacterium often cannot break up pollutant to CO_2
  - Product sometimes toxic to microorganism so downstream degradation mitigates toxicity
  - Variation in community with time or spatial heterogeneity
- Insure suitable concentration of microorganisms
- Control toxicity