Vapor phase processes

Lecture 5

Learning outcomes

- Soil vapor extraction
- Bioventing
- Biosparging
- Air stripping
- Biofiltration

Soil vapor processes

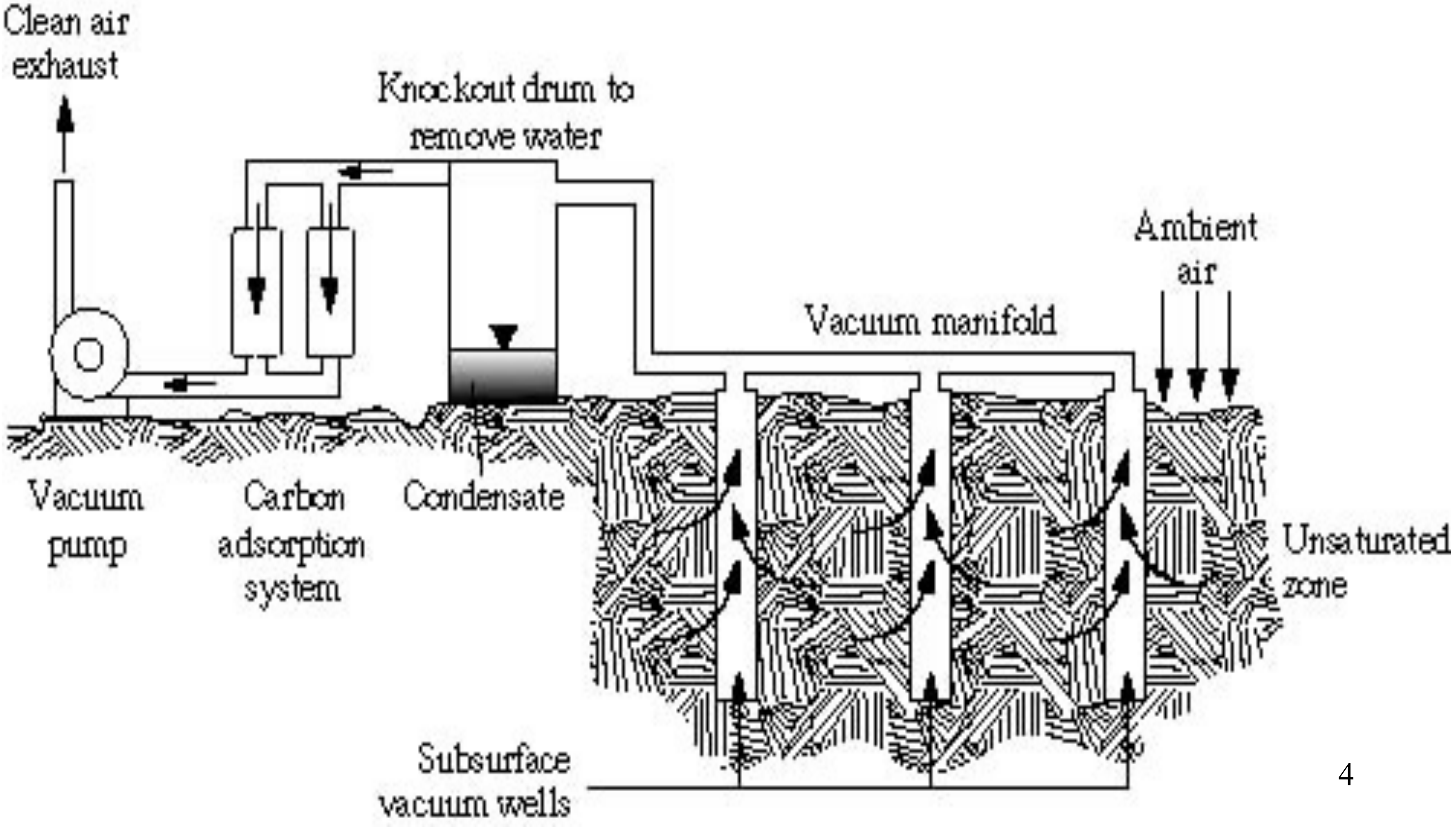
In situ

- Soil vapor extraction (soil): physicochemical means of removing VOCs from soil
- Bioventing (soil): biological means of removing VOCs from soils
- Biosparging (groundwater): biological means of removing VOCs from groundwater

Above ground

- Air stripping: above-ground treatment of groundwater via physicochemical means
- Biofiltration: above-ground treatment of vapor phase via biological means

Soil vapor extraction (SVE)



Soil vapor extraction (SVE)

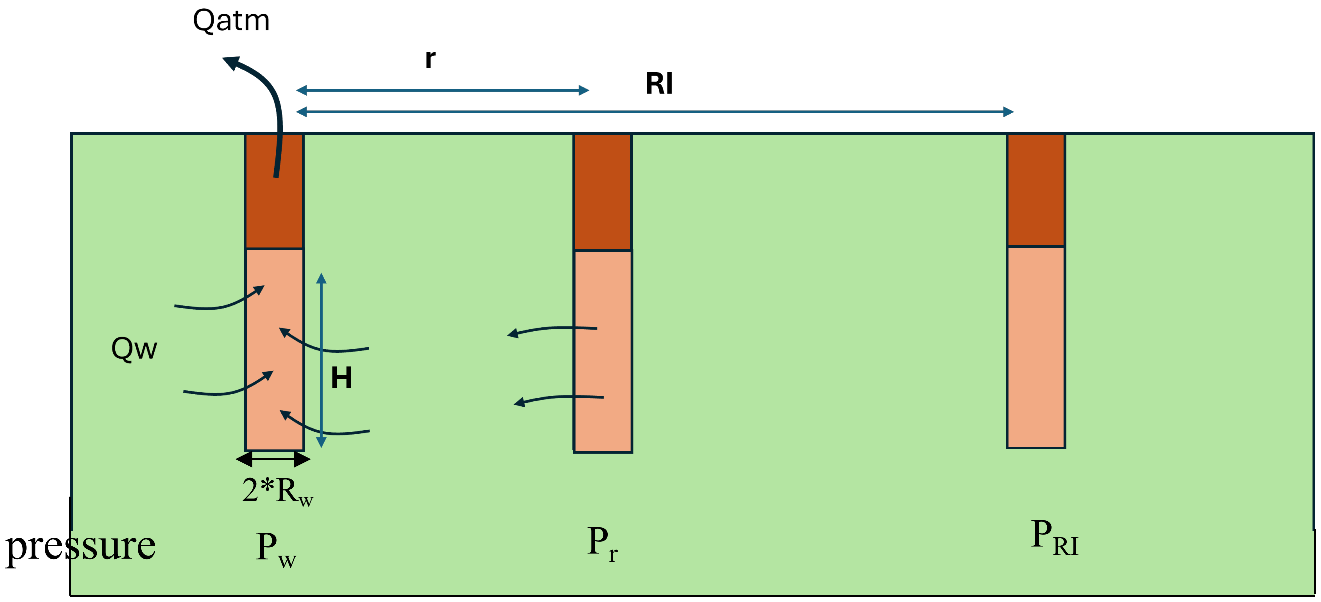
- SVE consists of passing an air stream through soil, transferring the contaminant to vapor phase
- Many alternatives:
  - Impermeable barrier over the surface (minimize short-circuiting)
  - Air recharge well around the zone

- Estimate extracted vapor concentration
- Calculate radius of influence from pressure profile
- Calculate vapor flow rates
- Calculate the rate of extraction

Soil vapor extraction (SVE)

Design considerations

- Radius of influence: defined as the distance from extraction well where the pressure drawdown is very small
- Should be determined from pilot testing



Where
P_r= pressure at radial distance r
P_w= pressure at extraction well
P_{RI}= pressure at radius of influence (=atm. pressure)
r= radial distance from extraction well
R_I= radius of influence where pressure=atm. pressure
R_w= well radius of extraction well

Soil vapor extraction (SVE)

Design considerations

- Radius of influence: defined as the distance from extraction well where the pressure drawdown is very small
- Should be determined from pilot testing

$$P_r^2 - P_w^2 = (P_{RI}^2 - P_w^2)\,\frac{ln\left(r/_{R_w}\right)}{ln\left(R_I/_{R_w}\right)}$$

Where:
P_r= pressure at radial distance r
P_w= pressure at extraction well
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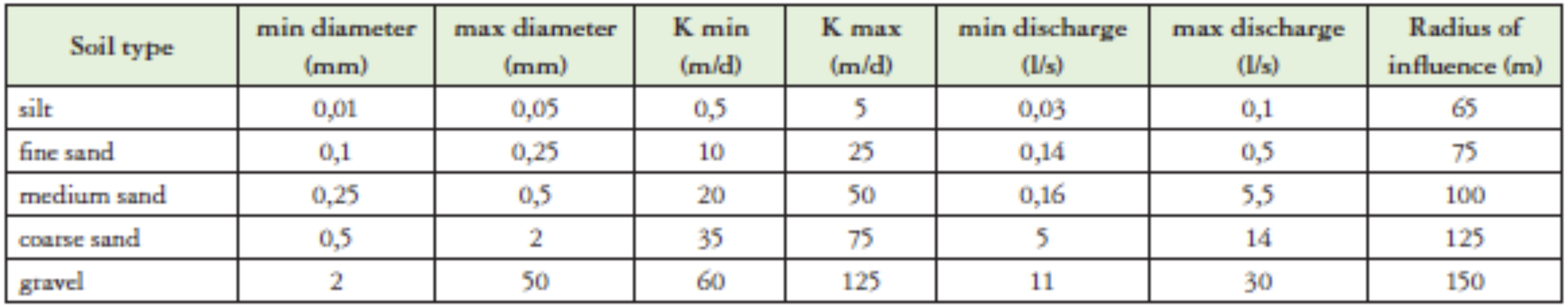


Soil type	min diameter (mm)	max diameter (mm)	K min (m/d)	K max (m/d)	min discharge (l/s)	max discharge (l/s)	Radius of influence (m)
silt	0,01	0,05	0,5	5	0,03	0,1	65
fine sand	0,1	0,25	10	25	0,14	0,5	75
medium sand	0,25	0,5	20	50	0,16	5,5	100
coarse sand	0,5	2	35	75	5	14	125
gravel	2	50	60	125	11	30	150

Radius of influence example

Pressure at extraction well =0.9 atm

Pressure at monitoring well 5m away=0.98 atm

Diameter of venting well= 10cm

$$P_r^2 - P_w^2 = (P_{RI}^2 - P_w^2)\frac{ln\left(r/R_w\right)}{ln\left(R_I/R_w\right)}$$

Where:

P_r= pressure at radial distance r

P_w= pressure at extraction well

P_{RI}= pressure at radius of influence (=atm. pressure)

r= radial distance from extraction well

R_I= radius of influence where pressure=atm. pressure

R_w= well radius of extraction well

$$0.98^2 - 0.9^2 = (1^2 - 0.9^2)\frac{\ln(\frac{5}{0.1})}{\ln(\frac{R_I}{0.1})}$$

$R_I \sim 14$ m

Soil vapor extraction (SVE)

Design considerations

- Vapor flow rate

$$Q_w = H\left[\frac{\pi k}{\mu}\right]\left[\frac{P_w}{ln\left({}^{R_w}/_{R_I}\right)}\right]\left[1-\left(\frac{P_{RI}}{P_w}\right)^2\right]$$

$$Q_{atm} = \left(\frac{P_w}{P_{atm}}\right) Q_w$$

Where:
Q_w= volumetric flow rate entering extraction well (m^3/sec)
P_w= pressure at extraction well (g/(cm.sec^2))
P_{RI}= pressure at radius of influence (g/(cm.sec^2))
H= length of screen in extraction well (m)
R_I= radius of influence (m)
R_w= well radius of extraction well (m)
k= permeability of formation (m^2)
μ= air viscosity = $1.8*10^{-4}$ g/cm.sec
Q_{atm}= volumetric flow rate to atmosphere (m^3/sec)

Atmospheric pressure= $1.013 * 10^6$ g/(cm.sec^2)

Vapor flow rate example

Pressure at extraction well = $0.912*10^6$ g/(cm.sec^2)

Radius of extraction = 14m

Radius of venting well= 10cm

Permeability of formation = 10^{-12} m^2; air viscosity= $1.8*10^{-4}$ g/cm.sec

Well screen length= 6m

$$Q_w = \mathrm{H}\left[\frac{\pi k}{\mu}\right]\left[\frac{P_w}{ln\left({}^{R_w}/_{R_I}\right)}\right]\left[1-\left(\frac{P_{RI}}{P_w}\right)^2\right] \qquad Q_{atm}=\left(\frac{P_w}{P_{atm}}\right)Q_w$$

*

Soil vapor extraction (SVE)

Design considerations

- Number of wells

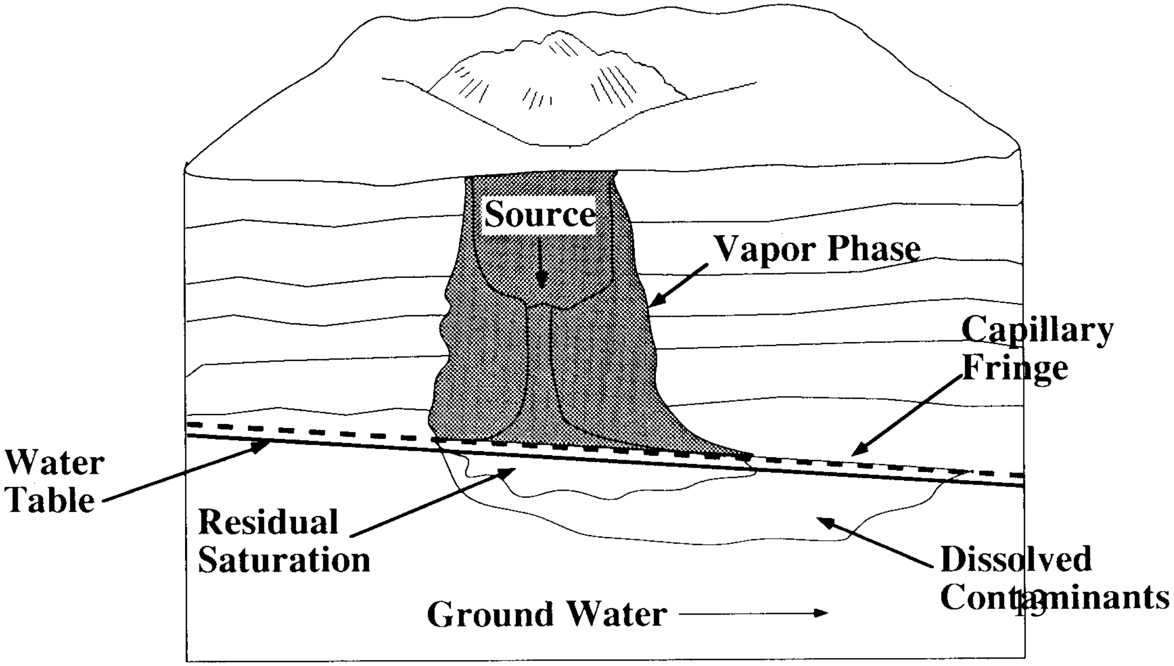
$$N = \frac{1.2A}{\pi R_I^2}$$

Where:
N= number of SVE wells
A= area of contamination (m^2)
R_I= radius of influence of extraction well (m)

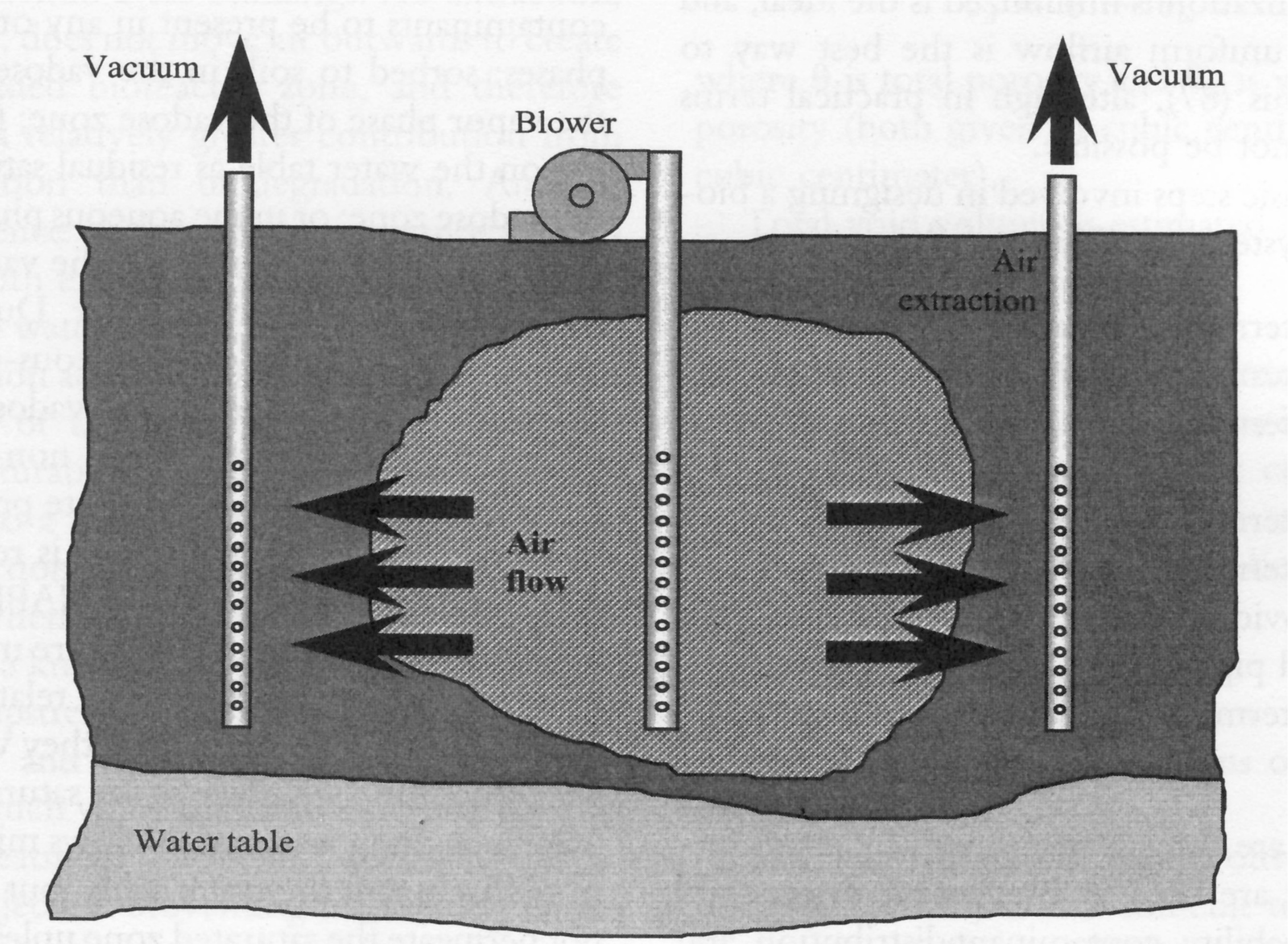
Bioventing

In situ soil bioremediation

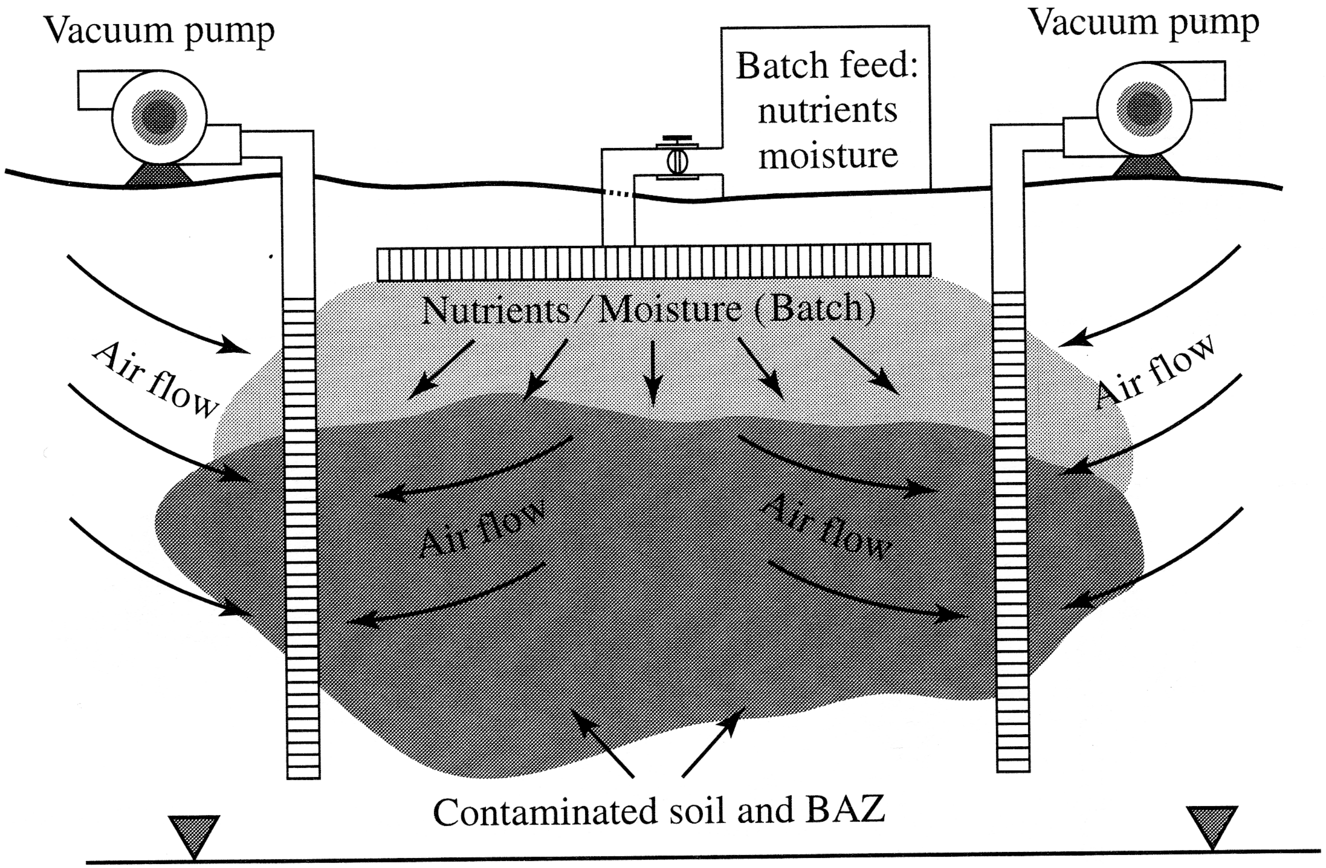
- Removal of contaminants from soil without excavation and treatment at the surface
- Main strategy is bioventing: Process of applying air or oxygen to soil to stimulate aerobic degradation of contaminants.
- Applicable to contaminants in the vadose zone



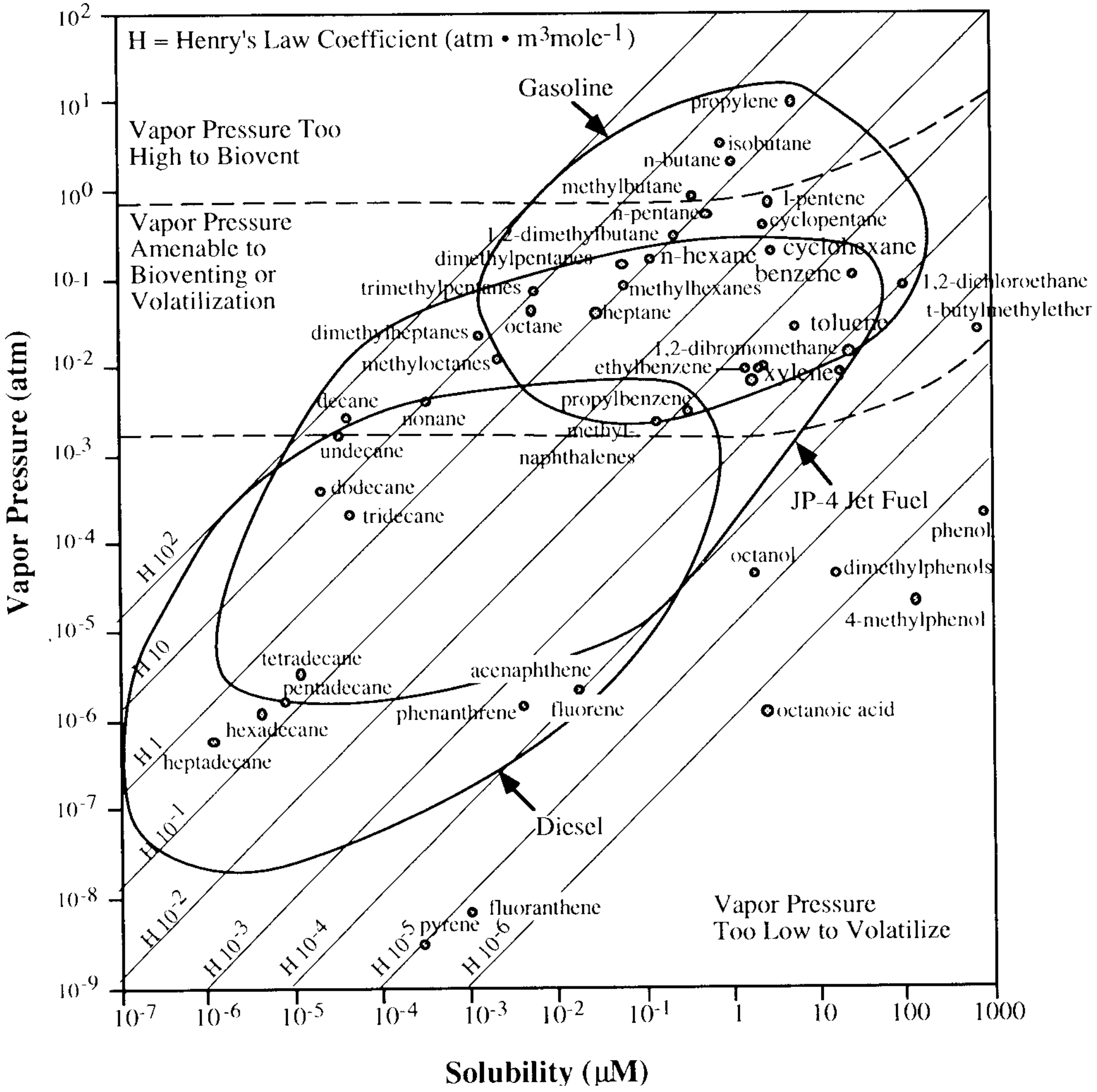
Injection Bioventing



extraction bioventing



Contaminants suitable for this technology



Best application: contaminant readily biodegraded aerobically and not very volatile

Oxygen utilization rate

- For petroleum hydrocarbons, 1.4 to 1.6 kg O_2 per kg of hydrocarbon
- Effective range of air addition must be within a certain range= O_2 utilization rate
- This value is often determined from pilot-scale tests
- Estimate biodegradation rate from O_2 utilization rate requires stoichiometric relationship with hydrocarbon (hexane used as representative hydrocarbon)

$$C_6H_{14} + 9.5\ O_2 \rightarrow 6\ CO_2 + 7\ H_2O$$

$$k_B = \frac{k_O * 100 * \varepsilon_a D_{O_2} C}{\rho_{wb}}$$

Where:

k_B= biodegradation rate (mass carbon /mass wet soil per day) (directly measured by in situ respiration test)

k_O= oxygen utilization rate (vol O_2/vol air% per day)

ε_a= air filled porosity (vol. air /vol. soil)= ε (volume void/volume soil) – θ (volume of water/volume of soil)

= 1,330 mg O_2/L O_2

D_{O2}= density of O_2 (assuming 21.5% O_2 content) (mass O_2/volume O_2)

C= ratio of mass of C in hydrocarbon to O_2 needed for mineralization (based on stoichiometry- usually around 0.3) (mass C/mass O_2)

ρ_{wb}= wet bulk density (mass wet soil/volume soil)

In class problem

Calculate the O_2 utilization rate for hexane (C_6H_{14}) of a sandy vadose zone based on the biodegradation rate of hexane obtained from respiration tests with this material.

ε_a= 0.2

ρ_{wb}= 1.95 g/cm^3

k_B= 0.6 g C/(kg wet soil.day)

Flow rate needed

$$Q = \frac{k_O V \varepsilon_a}{C_{O_2}}$$

Where:
Q= air flow rate (volume/time)
k_O= oxygen utilization rate (vol O_2/vol air % per time)
ε_a= air filled porosity (volume air/volume soil)= ε (volume void/volume soil) – θ (volume of water/volume of soil)
V= volume of contaminated soil (volume)
C_{O2}= oxygen content of air (vol O_2/vol air %)

Radius of influence

$$R_I = \sqrt{\frac{QC_{O_2}}{\pi h k_o \varepsilon_a}}$$

Where:
R_I= radius of influence (distance)
Q= air flow rate (volume/time)
C_{O2}= oxygen content of air (vol O_2/vol air %)
k_O= oxygen utilization rate (vol O_2/vol air % per time)
ε_a= air filled porosity (volume air/volume soil)= ε (volume void/volume soil) – θ (volume of water/volume of soil)
h= aerated thickness (distance)

Hill AFB site (UT)

Problem

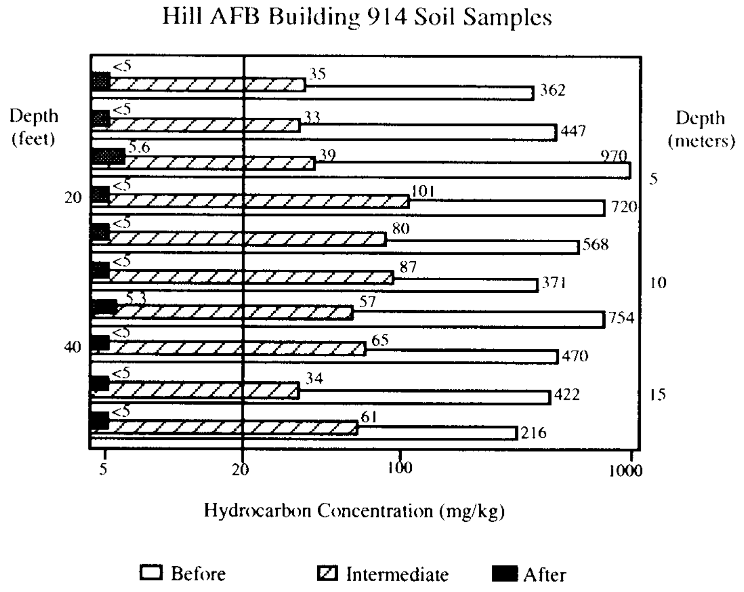
- 100,000 L of JP-4 jet fuel spilled in soil (20 m deep)
- Mixed sand and gravel and occasional clay layer
- High elevation desert with groundwater table at 200 m
- Soil moisture 6 %
- Soil samples: up to 20,000 mg/kg of JP-4 but average 400 mg/kg- uneven distribution as a function of depth

Approach

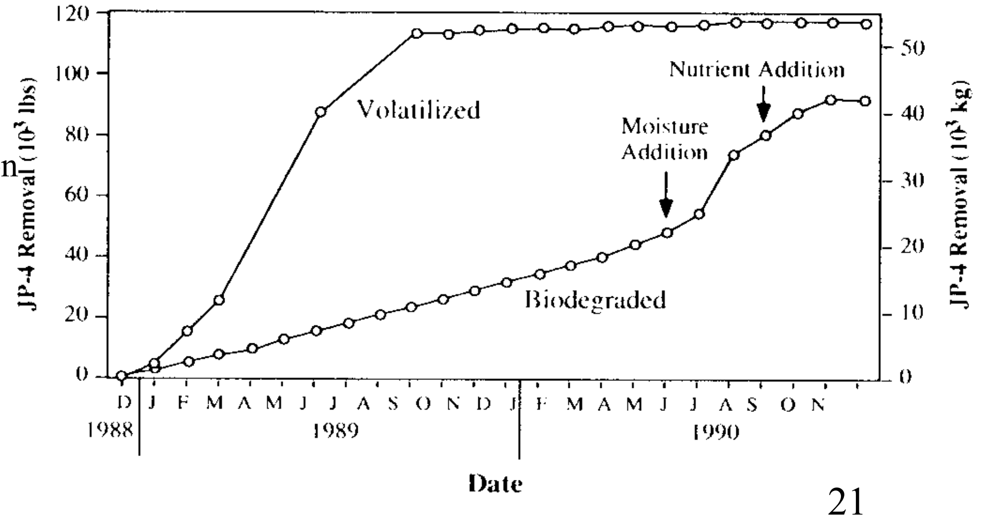
- Vent wells drilled to 20 m depth, screened 3-18m
- Background well in uncontaminated area
- Air extraction started Dec 1988
- Off-gas treated on site
- Flow rate 2,500 m^3/hr
- Dec 1988-Nov 1990: a million m^3 soil gas extracted
- In Nov 1989, flow rate to 500-1,000 m^3/hr remove off gas treatment.
- Lab studies showed moisture and nutrient additions needed

Results

- No response to nutrient addition, but response to moisture addition
- Volatilization limited after reduced flow rate



Results of soil analysis at Hill AFB before and after venting. (Each bar represent the average of 14 or more samples) (Dupont, et al., 1991).



Cumulative hydrocarbon removal from the Hill AFB soil venting site

Tyndall AFB site (FL)

Problem

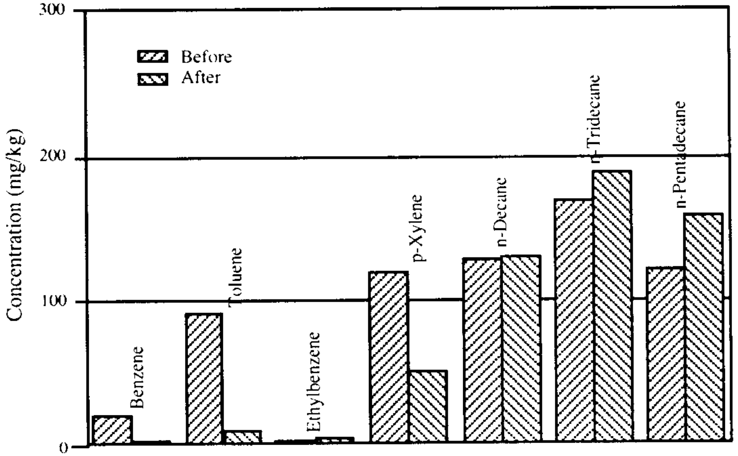
- Nature and volume of spill unknown
- Fine- to medium-sized quartz grains
- Moist subtropical environment with groundwater 0.5-1.5m

Approach

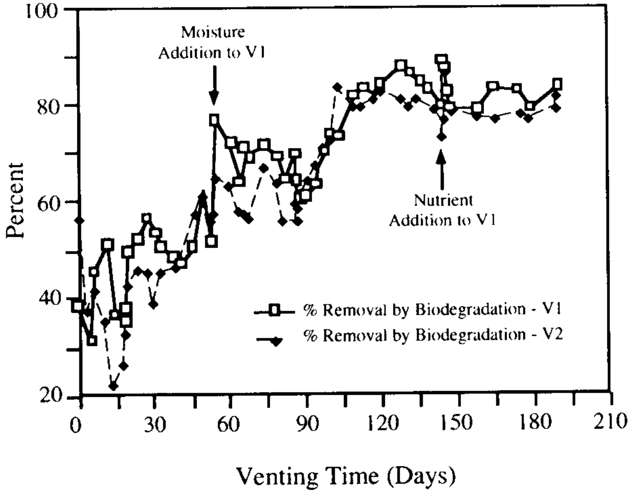
- Four test cells: 2 in contaminated area (V1 and V2) and other two in background
- 5,100 and 7,700 mg hexane eq./kg soil in V1 and V2
- Dewatered (GW level to 2m)
- Airflow: one air-filled void volume per day injected

- **Results**
- Biodegradation and volatilization rates faster than at Hill AFB
- Warm temperatures, high moisture content
- After 200 days, 2,900 mg/kg hydrocarbons removed (40% reduction)
- BTEX removed most efficiently (>90 %)
- Biodegradation rates twice as high at 25°C than at 18 °C (Hoff-Arrhenius equation)
- Effect of moisture and nutrient: minimal

V2: received moisture and nutrients from beginning
V1: nothing for 8 weeks, then moisture for 14 weeks then both for 7 weeks



Results of soil analysis from Plot V2 at Tyndall AFB before and after venting, (Each bar represents the average of 21 or more soil samples. Miller et al., 1991).



Cumulative percent hydrocarbon removal at Tyndall AFB for Sites V1 and V2 (Miller et al., 1991).

Limitations of technology

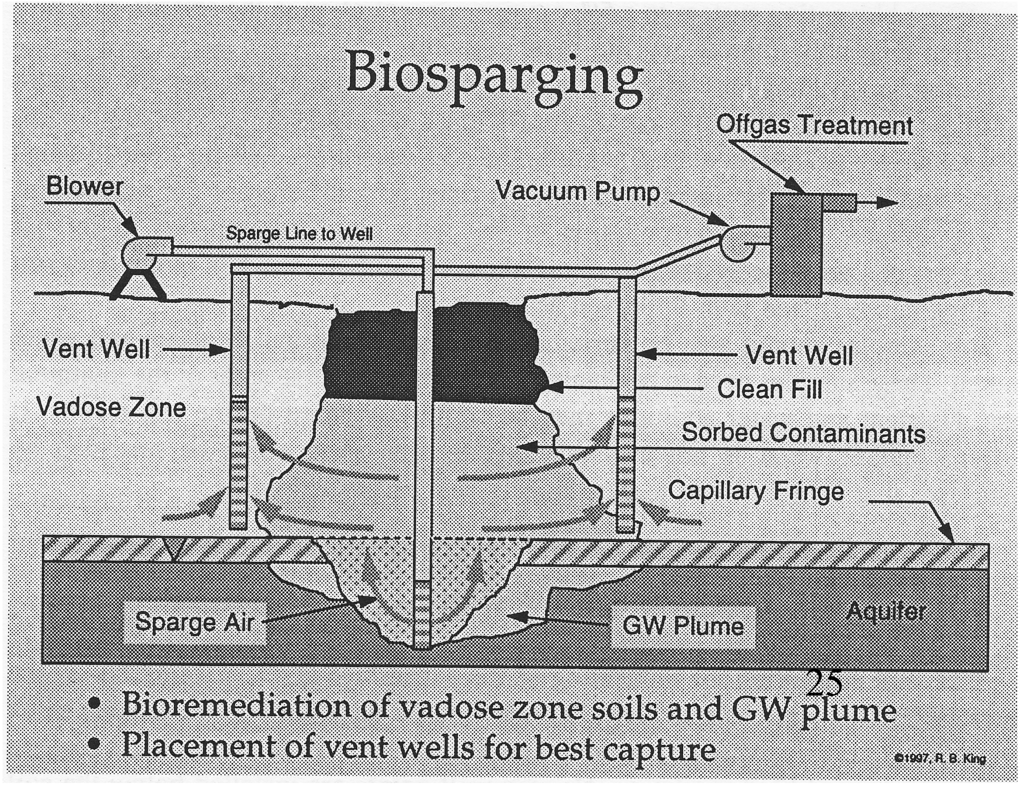
- Time required for remediation: dependent on biodegradation which can require several years
- Mixture of contaminants: sites contaminated with mixtures of contaminants may not be suitable for bioventing
- Estimate of emissions: determination of need or lack of need for off-gas treatment major cost variable. Difficult to estimate a priori.

Biosparging

What is biosparging?

- Injection of air below the water table.
- Transient, air-filled porosity by displacing water in sediment matrix.
- Air pressure needed is determined by the need to overcome resistance of soil matrix to air flow.
- Vapor phase generated travels to vadose zone where biodegradation also occurs
- Less volatile fuels (diesel, kerosene) are targeted
- Larger-chain hydrocarbons even if slower deg. rate than medium chain but less volatile
- Two actions:
  - (a) removes volatiles
  - (b) provides atm O_2 to enhance biodegradation

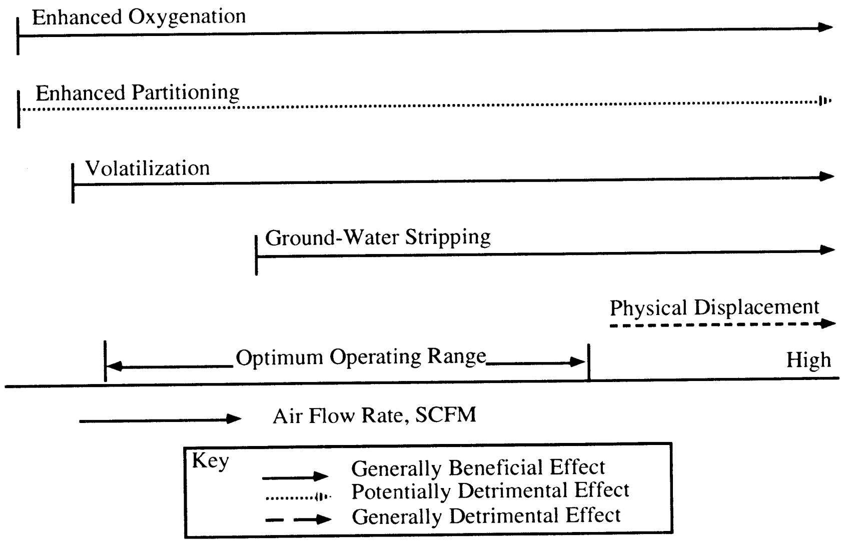
- Effectively removes contamination below the water table
- Distinct from bioventing which only targets vadose zone
- Successful at treating petroleum hydrocarbons



- Bioremediation of vadose zone soils and GW plume
- Placement of vent wells for best capture

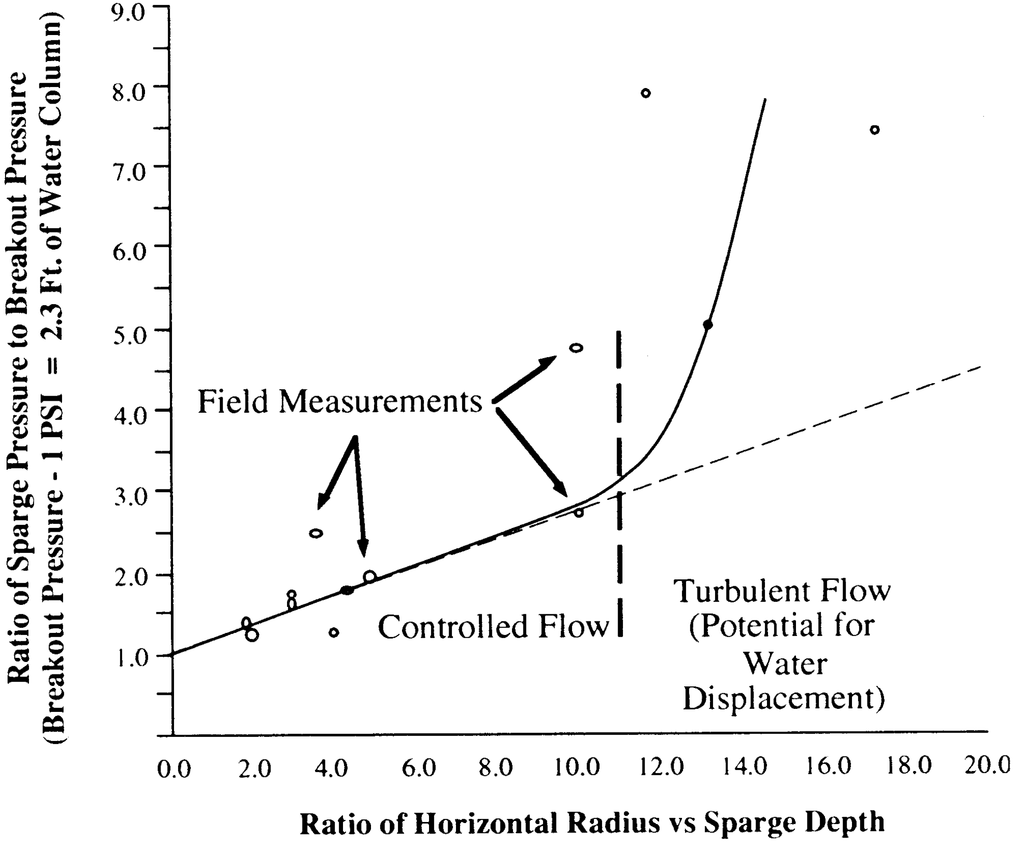
Principles of technology

- Enhanced oxygenation: air travels through aquifer and dissolves in water. Oxygenated water stimulates biodegradation
- Enhanced dissolution: air traveling in aquifer causes turbulence and mixing => better partitioning of contaminant into water. This can promote biodegradation
- Volatilization: Adsorbed contaminants will pass into gas phase and be carried to vadose zone. Can remove significant amount of contaminant.
- Ground-water stripping: contaminants with high enough Henry's law constant will volatilize into air.
- Physical displacement: at high air flow rates, water can be displaced. Contamination can spread if not controlled.



Limitations of biosparging

- Type of contaminant: must be volatile and soluble
- Structural homogeneity: if impervious layer, air confined and contamination could spread laterally
- Permeability: should be sufficient to allow air to move vertically and horizontally
- Depth limitations: * minimum 1.5 m saturated thickness (otherwise, air short-circuit around sparge point)
  * maximum 10m saturated depth (otherwise can' t control where air goes)
- Depth to water: at least 1.5 m so can install a vapor extraction system

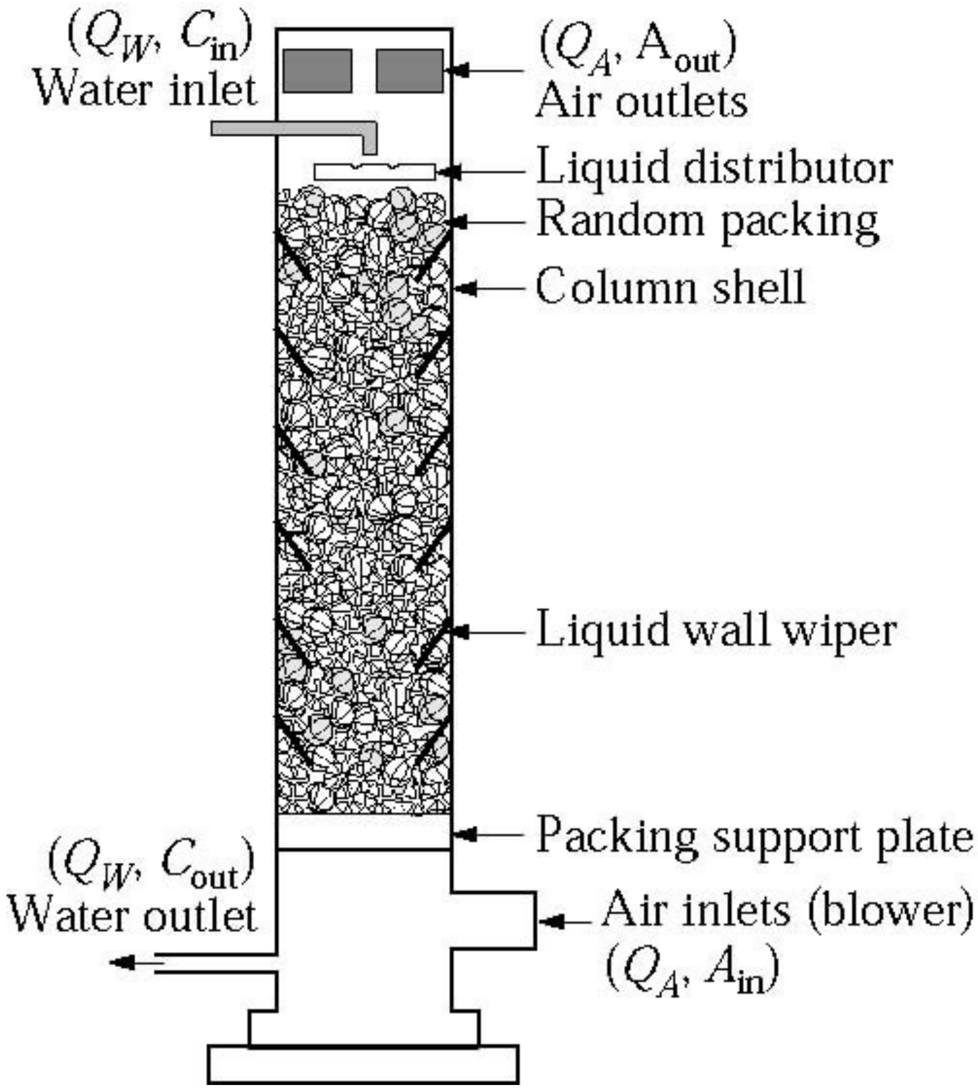


- Increase in pressure beyond a threshold does not yield a higher radius of influence.

Treatment of groundwater at surface: Air stripping

Air stripping

- Mass transfer process that enhances the volatilization of compounds from a liquid phase into a vapor phase by actively passing air through water
- Shown to be a cost-effective method for removing VOCs from contaminated water
- Most effective for low (<200 mg/L) concentrations
- Stripping basins or stripping towers (most common)



$$R = K_H'(Q_A / Q_w)$$

Where R= stripping factor
Q_A= airflow rate (m^3/s)
Q_W= water flow rate (m^3/s)

Air stripping

- The rate at which a contaminant is transferred from water to air is represented by the overall transfer rate coefficient K_La (s^{-1}).
- For preliminary design purposes, K_La can be evaluated from the Onda correlations:

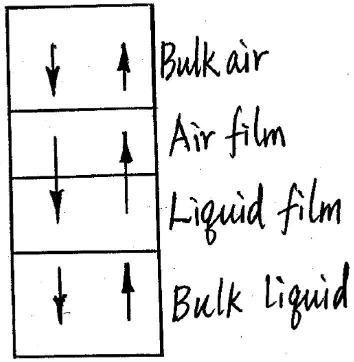
k_L= liquid phase mass transfer (m/s)

k_G= gas phase mass transfer (m/s)

a= area to volume ratio (m^2/m^3)

K_La= overall transfer rate coefficient (s^{-1})

$$\frac{1}{K_La} = \frac{1}{K_H' k_G a} + \frac{1}{k_L a}$$



A volatile organic must be transferred from air to water following the 2-film theory:

- Bulk liquid to liquid film
- Liquid film to air film
- Air film to bulk air

Simplified $K_L a$

$$K_L a = \alpha\, D_L \left(\frac{L}{\mu_L}\right)^{1-n} \left(\frac{\mu_L}{\rho_L D_L}\right)^{0.5}$$

$K_L a$ (s^{-1})

Where

α and n are constants that depend on the packing material

D_L= liquid diffusion coefficient (m^2/s) (see below)

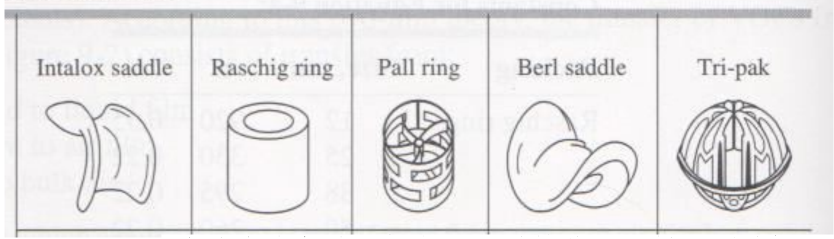
L= liquid mass loading rate [kg.$(m^2.s)^{-1}$]= mass of water per cross section and time

$L=Q_w*\rho_L/S$

S= cross-section of tower (m^2)

μ_L= viscosity of water [kg/(m.s)= $1.002*10^{-3}$ at 20ºC]

ρ_L= density of water (kg/m^3)= 998.2 at 20ºC



Packing	Size (mm)	α	n
Raschig Rings	12	920	0.35
	25	330	0.22
	38	295	0.22
	50	260	0.22
Berl Saddles	12	490	0.28
	25	560	0.28
	38	525	0.28
Tile	75	360	0.28

D_L can be estimated using

$$D_L = \frac{5.06 * 10^{-10} T}{\mu_L V_m^{0.6}}$$

Where

D_L in cm^2/s

μ_L= viscosity of water [kg/(m.s)= $1.002*10^{-3}$ at 20ºC]

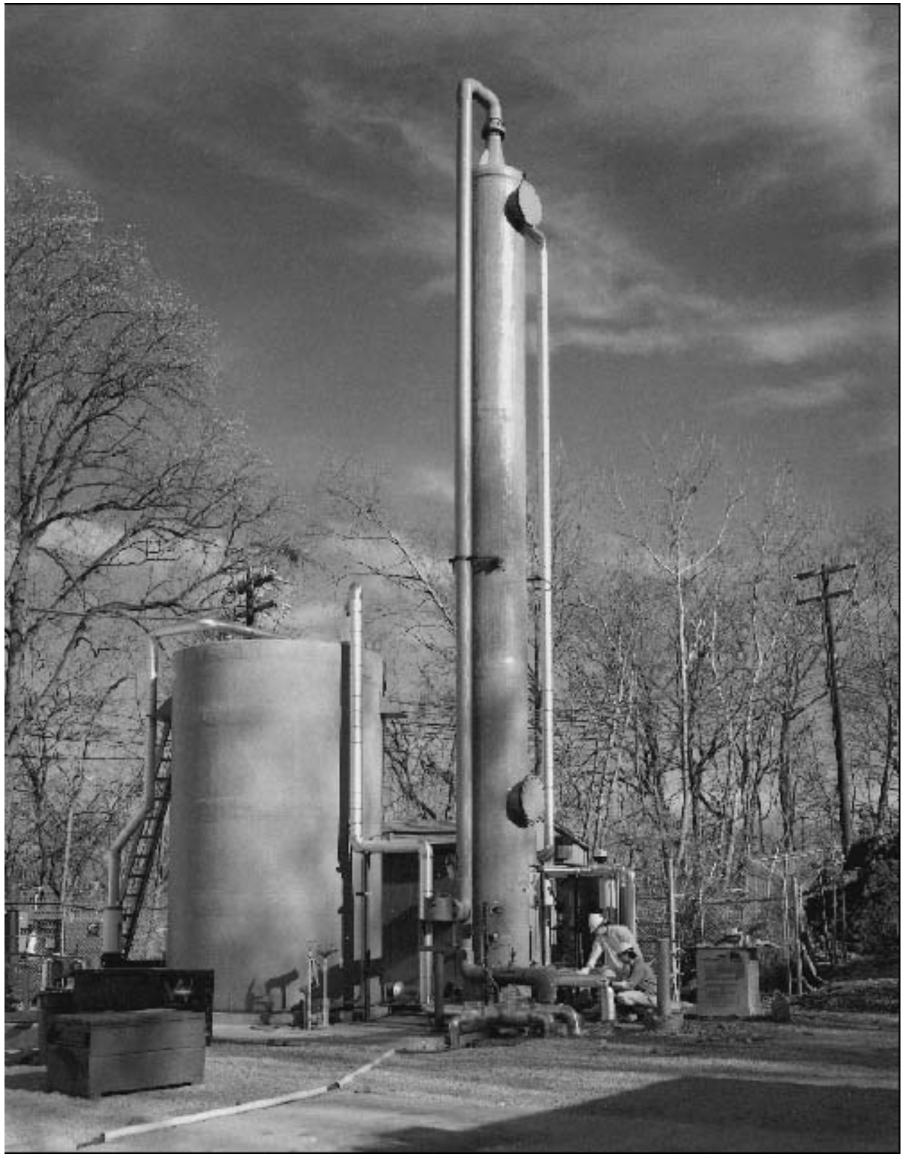
T=Temperature (K)

V_m= molar volume of contaminant (cm^3/mol)

Air stripping

HTU=height of transfer unit (m)

$$HTU = \frac{L_M}{M_{water} * K_L a}$$



Where:

L_M= liquid molar loading rate mol/(m^2.s)= L/MW(water)

MW(water)=molecular weight of water (18 g/mol)

M_{water}= molar volume of water=55.6 mol/L

$K_L a$= overall transfer rate coefficient (s^{-1})

NTU= number of transfer units= Z/HTU

Z=height of tower (m)

$$NTU = \left(\frac{R}{R-1}\right)\ln\left(\frac{(C_{in}/C_{out})(R-1)+1}{R}\right)$$

R= stripping factor [-] (usually in the range 2-10)

C_{in}= concentration in the influent water (mol /L)

C_{out}= concentration in the effluent water (mol /L)

Air stripping example

A groundwater is contaminated with ethylbenzene

C_{in}= concentration in the influent water = 1 mg/L= 1 g/m^3

C_{out}= concentration in the effluent water = 35 μg/L

Q_W= water flow rate= 7.13 L/s

K_H'= 0.27 [-]

K_La= 16 s^{-1}

Select the column diameter and air to water ratio

d=0.61 m

Q_A/Q_w=20

Determine:

L, R, HTU, NTU, Z

Treatment of vapor phase at the surface: Biofiltration

Vapor-phase bioremediation

- Vapor phase contaminants found in off-gases from soil and groundwater remediation, industrial and agricultural processes, wastewater treatment
- Include: petroleum hydrocarbons, halogenated and unhalogenated solvents, hydrogen sulfide, ammonia and odor control
- Contaminant transferred to liquid phase to be available for degradation through primary bacterial metabolism or cometabolism
- Diffusion and uptake of nutrients and oxygen
- Two types:
  - Suspended growth (contaminated air for aeration of sludge)
  - Packed beds (biofilter)
- Three steps:
  - Gas-liquid transfer
  - Diffusion through the biofilm to acclimatized organisms
  - Microbial transformation of contaminants

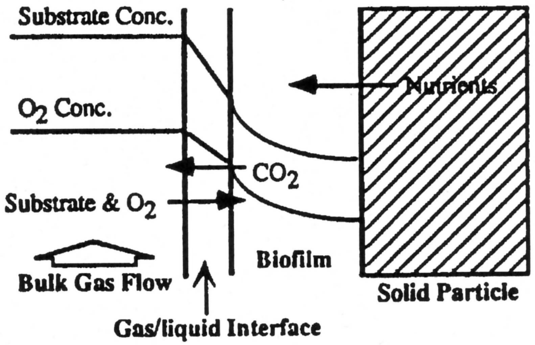


FIG. 1. Pore Space Schematic

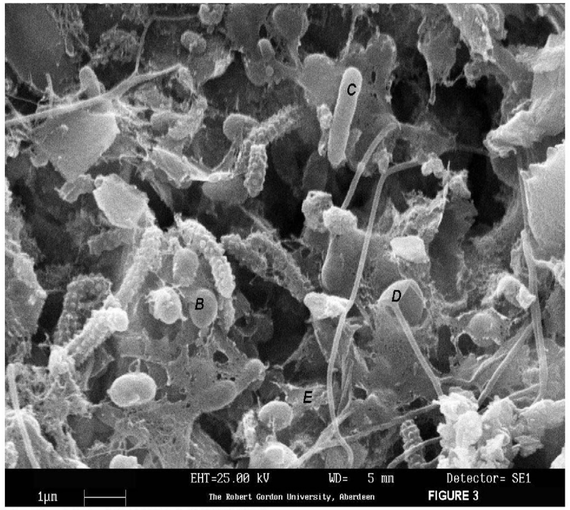
Biofilters

- Closed packed-bed reactor through which air is blown or drawn
- Microbial communities grow on surface of packing material
- Drawing air usually yields the best flow distribution
- Gas streams with low concentration biodegradable and soluble VOC well suited
- Sometimes polishing step

Biofilms

- Microorganisms
- Polysaccharides
- Bound water
- Liquid film exists around microbes for them to live and extract nutrients from liquid phase
- Very thin film
- Operate biofilter at 50-60% moisture by weight
- With compost packing (6-10 m^2/g), liquid film are 0.5-5 μm thick

http://www.bioline.org.br/showimage?bf/photo/bf01001c.jpg



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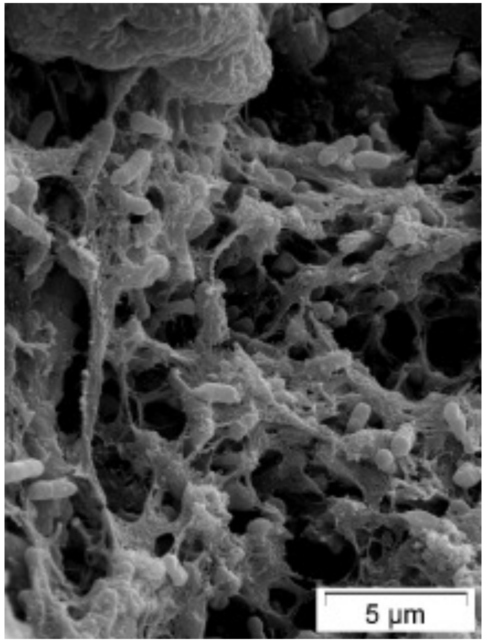
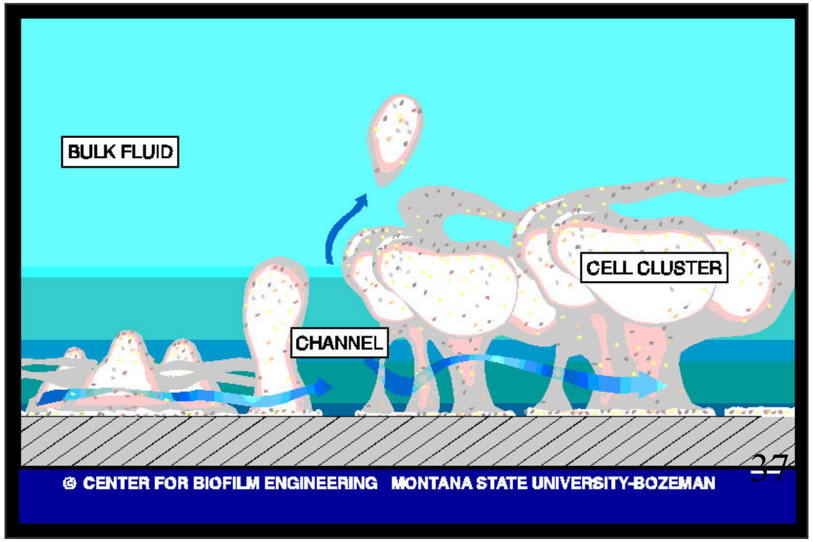
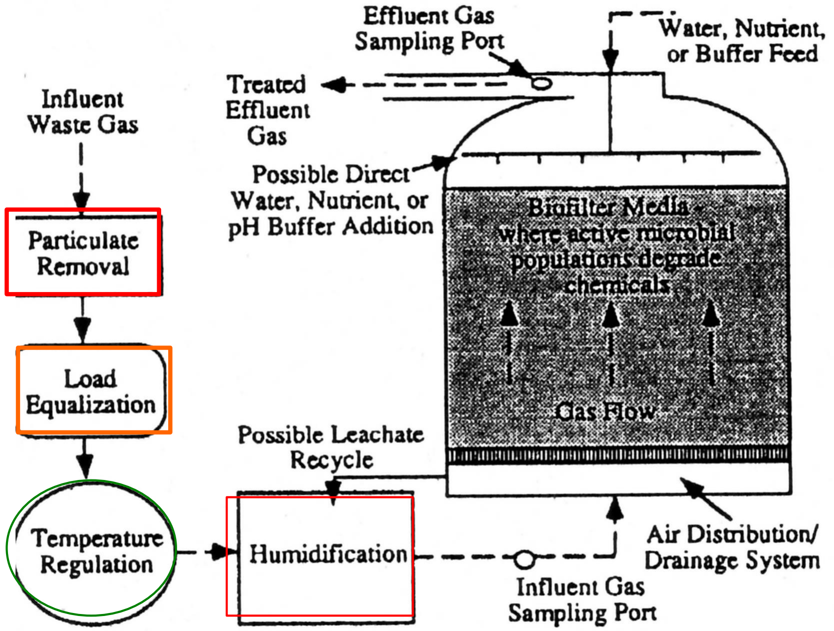




Pretreatment

- Particle removal- protects from clogging
- Load equalization- dampen peak loading
- Temperature regulation- need to be at optimal temperature for microbial activity
- Humidification- fully saturated to prevent stripping water from biofilm- most critical
- Gas distribution- uniform feed of gas into biofilter medium



Moisture content

- Most important parameter for optimal running of the biofilter (50-60%)
- Challenges:
  - High velocity, <100% relative humidity gas flow strips moisture
  - Exothermic reactions increase temperature- increases moisture carrying capacity of gas stream
- If overdry:
  - Deactivation of organisms
  - Contraction and medium cracking
  - Inability to rewet medium
- If overwet:
  - High backpressure and low gas retention time because pore space filled with H_2O
  - O_2 transfer problems due to reduced air/water interface
  - Anaerobic zone
  - Nutrients wash out

Design parameters

- Four parameters:
  - –Empty bed residence (or contact) time EBCT (s)
  - –Gas flux v (m/s)
  - –Contaminant mass loading rate R_m (g/m^3.s)
  - –Elimination capacity EC (g/m^3.s)

EBCT= V/Q V=empty bed volume m^3

Q= volumetric gas flow rate m^3/s

EBCT= 0.3-12 min depending on contaminant

v= Q/A A=bed cross-sectional area, m^2

v= h/EBCT h=height of filter bed, m

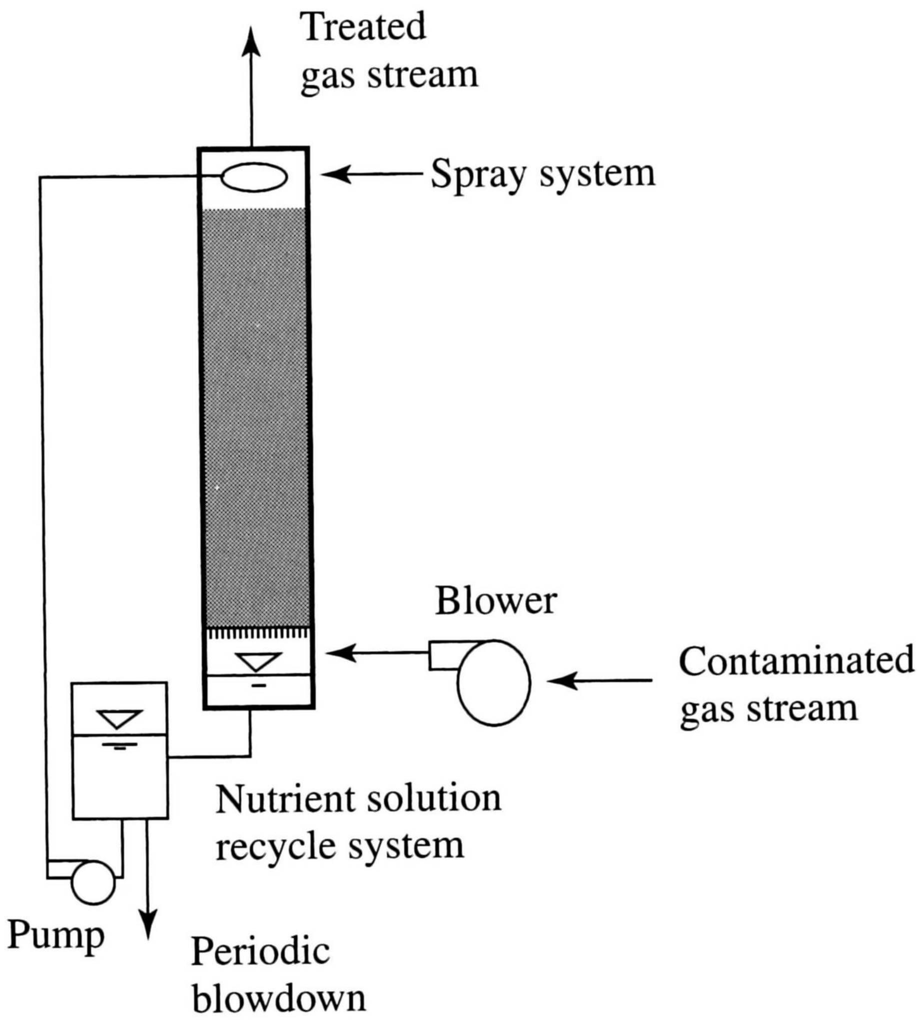
h= 1m usually

Steep concentration profiles through bed and removal takes place in first 25 cm. Greater only needed if slow reaction or mass transfer rate

$R_m=QC_i/V$ C_i= inlet gas contaminant conc. (g/m^3)

$EC= Q(C_i-C_o)/V$ C_o= outlet gas contaminant conc. (g/m^3)

Biotrickling filter



- moisture provided by spraying water continuously over top
- mobile liquid film flows over packing
- thicker liquid film than in biofilter -> slower transport through liquid phase
- compost unsuitable as media as water will accumulate and system becomes water-logged
- Size of packing material increased to allow air and liquid flow
- diatomaceous earth (crushed fossils of freshwater organisms)
- Make-up water and blowdown stream need to be disposed of

Run considerations

- Liquid spray $1 m^3/m^2$.day
- Issue with biofouling and clogging
- Problems at 1.2 kg OC/m^3 vs. no problem in biofilter with loading at 9kg OC/m^3
- Solutions:
  - Increase size of packing material but will lower surface area and removal rates
  - Periodic backwashing
  - Directional switching to have a uniform biomass distribution
  - Nutrient limitation