



Association of Engineering Geologists
1992-Annual Meeting
Hosted by the AEG
Southern California Section

**Groundwater Monitoring
and
Remediation Techniques
Short Course**

Monday - October 5, 1992 - 8 Hours Duration
Sheraton Long Beach Hotel, 333 E. Ocean Boulevard, Long Beach, California

Instructors

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Certificate of Appreciation



The Southern California Section of the Association of Engineering Geologists

*Serving Engineering, Environmental and
Groundwater Geologists Since 1957*

Appreciates

Robert Evangelista

for participating as an instructor of the Short Course

Groundwater Monitoring and Remediation Techniques

at the

Annual Association's Meeting
in Long Beach, California
October 5th, 1992

Kelly E. Rowe
Chairman, AEG
Southern California Section

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Treatment Parameters

- Flow Rate
- Chemicals of Concern
- Influent Concentration
- Discharge Requirements



Flow Rate

- **Flow Rate is a Design Variable**
- **Must Evaluate the Effect of Flow Rate on the Total Cost of the System and on the Time that is Needed for Clean-Up**



Flow Rate Factors

First:

- **Is the Flow Rate Necessary to Stop and Reverse the Movement of the Contamination Plume?**
- **Is it Desirable or Cost Effective to Use Groundwater Control and Containment Methods, Such as Slurry Wall, to Stop the Movement of a Plume?**



Flow Rate Factors

Second: What is the Amount of Groundwater Entering the Site?

- Groundwater for Up Gradient
- Surface Water from Rain and Run-off
- Confining Layer Below Aquifer Can Have Cracks and Fissures

May Be Able to Cap Surface with Impermeable Layer or Provide Good Drainage Away From Site to Reduce Surface Water



Flow Rate Factors

Third: Speed of the Clean-Up

- A Complicated Relationship Between Pumping Rate, System Design, and Remediation Time
- Must Decide Between the Cost of Increasing the Treatment System Size and the Cost Savings of Decreasing Clean-Up Time



Flow Rate Factors

Speed of the Clean-Up

What is the Relationship Between System Flow and Clean-Up Time?

- **Necessary to Identify the Source or Sources of Contamination**
- **Next, Stop the Source(s) for Contributing to the Plume. May Need to Slow Clean-Up to Use Flushing Methods to Mobilize Contaminants into the Plume**
- **Seasonal Variation in Groundwater Levels May Occur. Contamination Remaining in the Unsaturated Zone During the Low Water Season May Require Slow Treatment Rate Over Several High Water Season.**



Other Flow Rate Factors

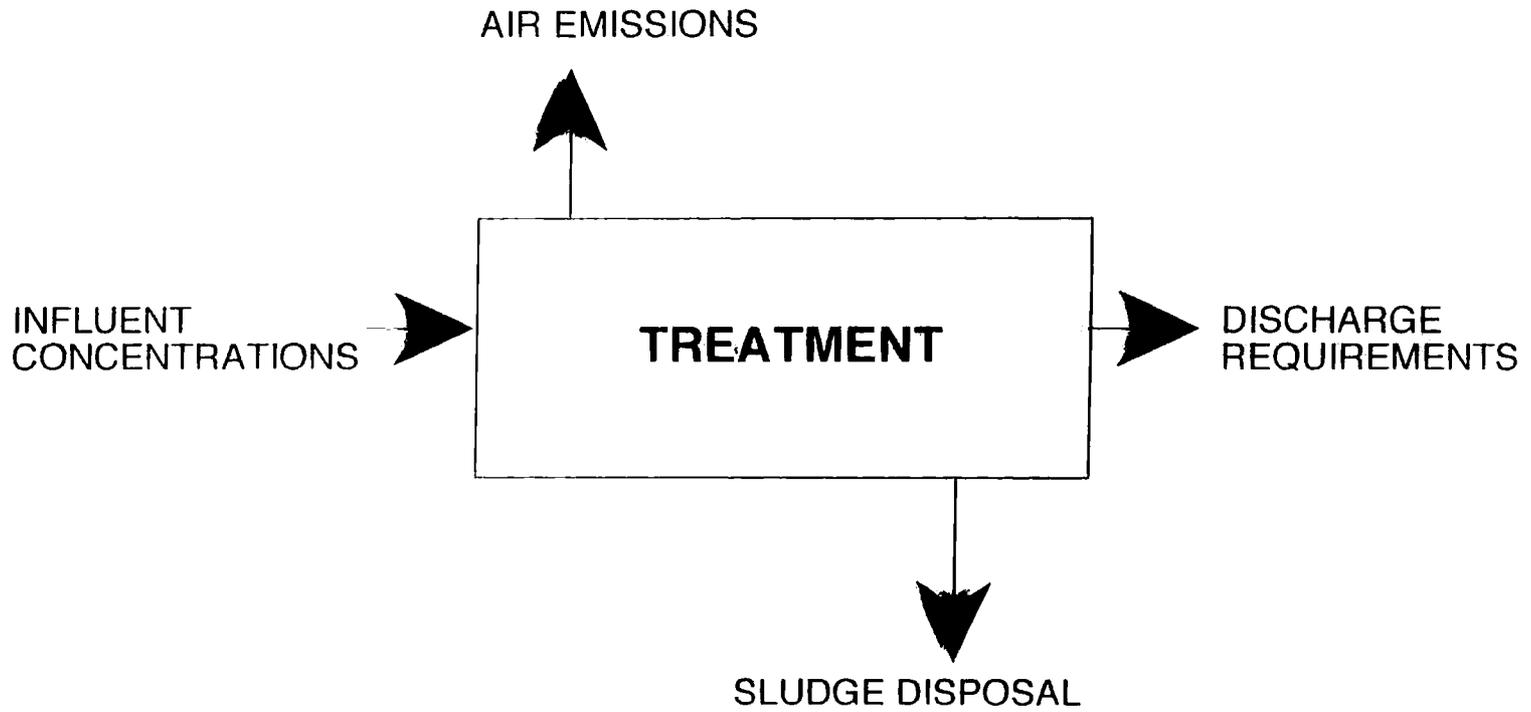
The number of recovery wells or trenches used and their effectiveness at recovering the plume and remediating the site

A recovery system located closer to the leading edge of the plume will require less water (flow) to capture the contaminants but clean water will also be recovered

More flow will be required if some of the water is to be used to flush the unsaturated zone of contaminants. Although this technique may reduce the overall remediation time, increasing the total water to the site will increase the flow to the treatment system



Parameters For Defining A Treatment System



Influent Concentration

Major factors affecting the concentration of contaminants

- The distance of the well from the original entrance of the contaminants to the aquifer
- The amount of material reaching the aquifer
- The solubility of the contaminants in water
- The relative density compared to water
- The biological and chemical transformation of the contaminants



Influent Concentration

Minor factors affecting the concentration of contaminants

- Rate of groundwater flow
- Mixing characteristics in the aquifer
- The combined effect of the above factors on concentration



Discharge Requirements

System design depends on the final disposition of the treated groundwater

- *Surface Water Body.* Regulated by the National Pollution Discharge Elimination System (NPDES) program. Determine if the discharge is direct or indirect, a regulated categorical discharge, requires bioassay testing, requires monitoring and reporting, and if the body is a sensitive environmental setting.
- *Another Treatment System - a POTW or an industrial wastewater treatment system.* This is the preferred discharge for treated groundwater. An advantage of a POTW is accessibility to sewer; an advantage of an industrial treatment system is that allowable contaminant concentrations may be higher than other discharge options.



Discharge Requirements

System design depends on the final disposition of the treated groundwater

- *Direct Use.* Must have very low effluent concentrations. Probably have to meet Federal drinking water standards.
- *Ground or Aquifer.* Strategically place recharge system to move plume. May be able to flush contaminants in the unsaturated zone. Any treated water reinjected outside the zone of influence should be at background concentrations



The Remediation Project

The influent concentration will change over the life of the project. The design must account for this cycle.

As we reach the last years of the project, the amount of contamination removed is minimal. May want to shut down the treatment system and actively monitor the groundwater until contaminant levels reach cleanup criteria by the biodegradation from naturally occurring bacteria.

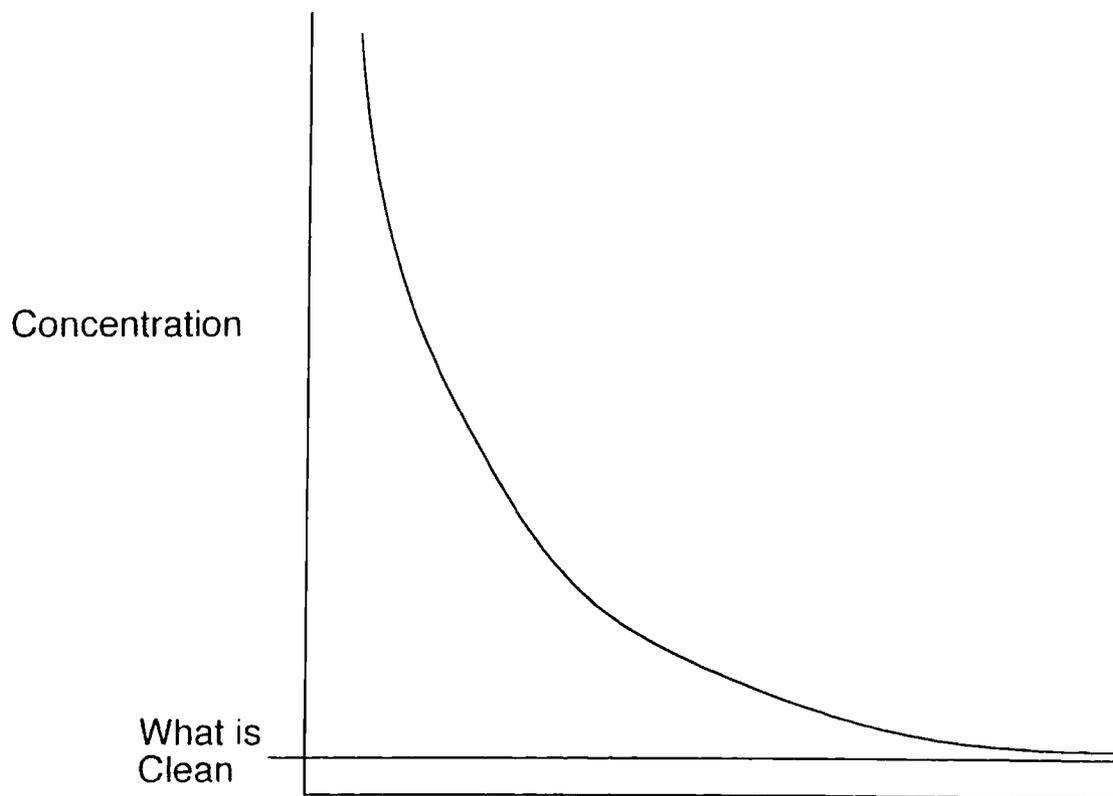
How clean is clean? Established by:

- Risk assessment
- Drinking water standards
- Permit requirements
- Analytical detection limits





Life Cycle Concentration of a Remediation Project



The Design Methodology for the Remediation Project

- **Time effect on influent parameters**
- **Capital costs**
- **Operator expense**



Time Effect on Influent Parameters

Flow

The amount of water being reused may vary during the project

- Water may be reused to increase hydraulic head and remediate the plume
- Water may be reused to flush contaminants from the unsaturated zone
- Water may be reused for in situ contamination
- Drought may lower flow



Time Effect on Influent Parameters

Concentration

Removal of contaminants by the treatment system and the dilution effect of clean water entering the site produce a steady decline in the concentration of the groundwater

- The design of certain technologies are based on a minimum concentration. For example, some bioprocesses depend on the settling properties of the bacteria. However, as the influent concentration declines, the mean cell age increases and the bacteria lose their settling properties and may be difficult to separate from the process.
- Operating cost may decline as concentration declines.



One formula for calculating costs would be:

$$C = \frac{\text{Cap}}{|1 - (1 + i)^{-n}|/i}$$

where

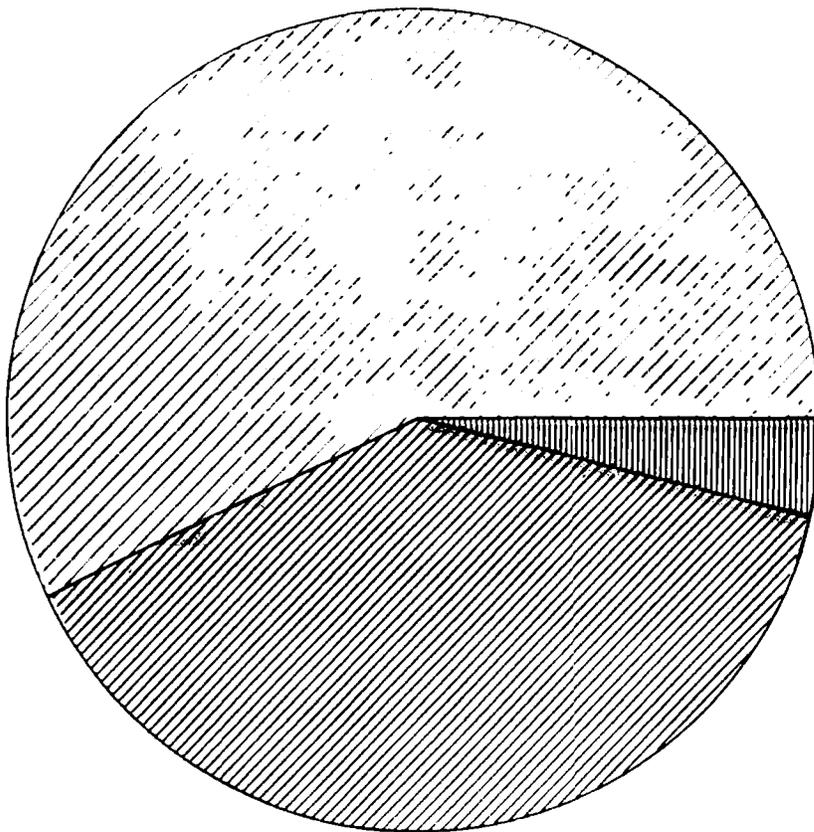
C is cost per time period n

Cap is capital cost

i is the interest rate

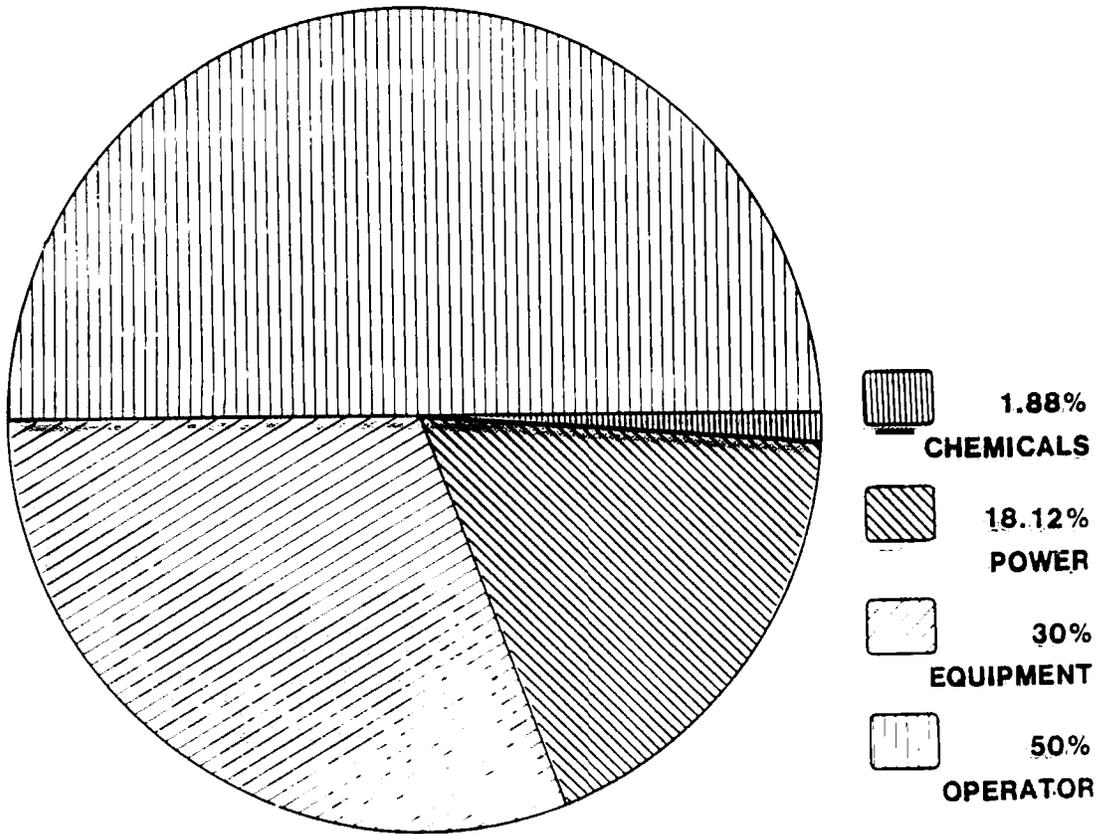
n is the period of time





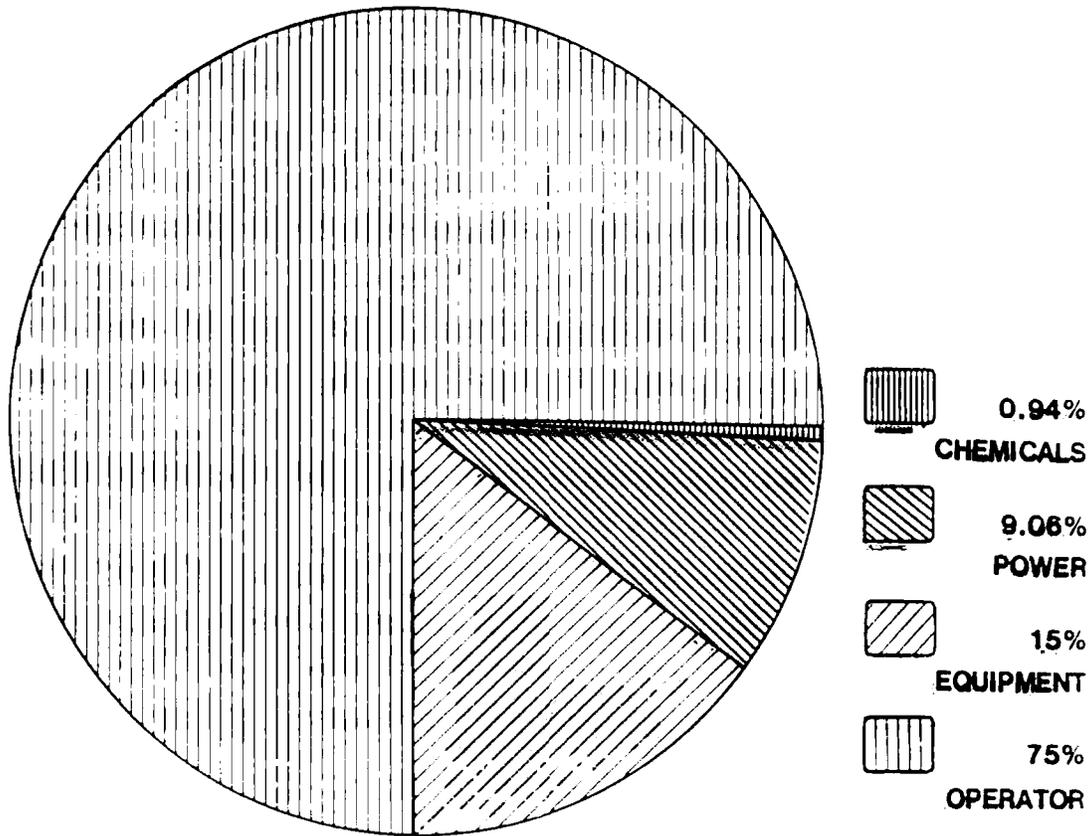
Ratio of daily costs with no operator attention.





Ratio of daily costs with 8 hr/day of operator attention.





Ratio of daily costs with 24 hr/day of operator attention.



Air Stripping

A Mass Transfer Technology Whereby Volatile Organic Compounds (VOCs) are Transferred From the Liquid Phase to the Vapor Phase.

Advantages:

- Simplicity of Operation
- Low Capital Costs
- Low Operations and Maintenance Costs

Limitations:

- Strippable Compounds Such as Chlorinated Solvents, Lightweight Aromatics
- High Iron Content Usually Causes Fouling Which Lowers Removal Efficiency and Increases Maintenance Costs

Costs:

- \$0.05 to \$0.25 / 1000 gal. Depending on Contaminants and No Air Stream Treatment
- Up to \$2.00 / 1000 gal. with Air Stream-Treatment

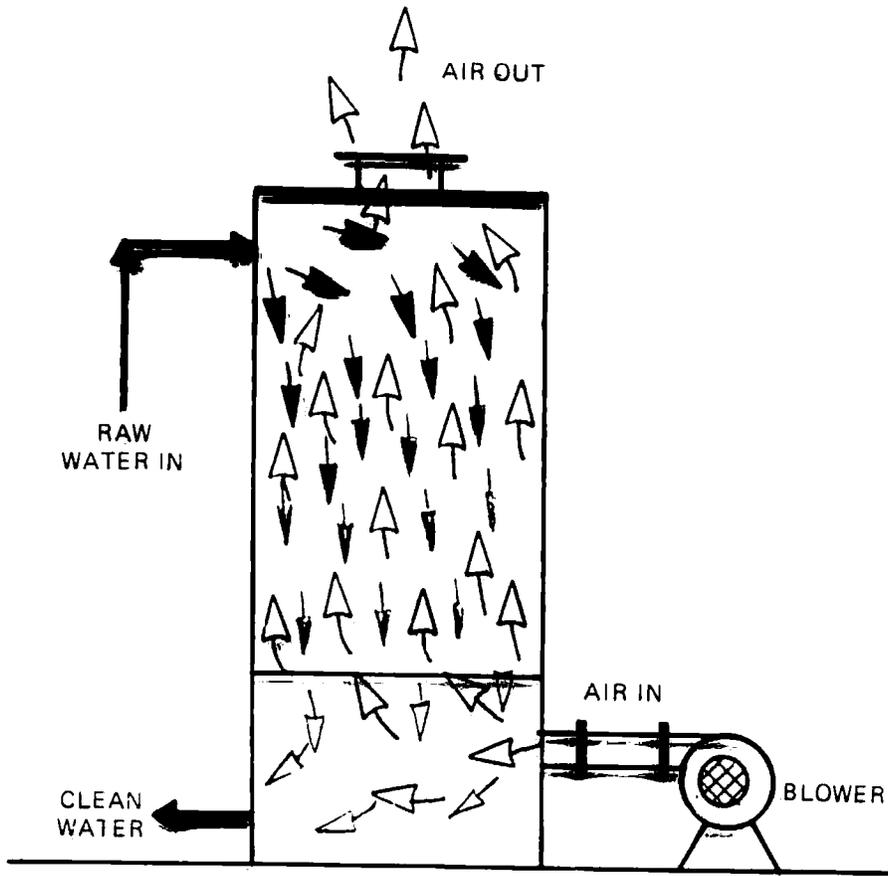


Air Stripping

Packed Tower

In a Packed Tower Air Stripper, Air and Water are Run Counter-Current Through a Media, Called Packing, Which Enhances Air/Liquid Contact. The Packing a Greater Surface Area of Liquid to Air Creating a Greater Transfer of Volatile Organics From the Falling Water to the Rising Air. The Packing also Mixes the Water so the VOCs are not Limited by Internal Diffusion Through the Water.





Packed tower air stripper.



Air Stripping

Variables for Sizing a Packed Column:

- Tower Height
- Tower Cross-Section
- Air to Water Ratio
- Water Temperature

Tower Cross-Section Area is a Strong Function of Groundwater Flow Rate. The Area is Determined by the Flow Rate and the Liquid Loading Rate (Measure in GPM/ft².) Liquid Loading Rate Ranges From 15 to 35 GPM/ft².

Tower Height is a Strong Function of Removal Efficiency. The Greater the Required Efficiency, the Taller the Tower.



Air Stripping

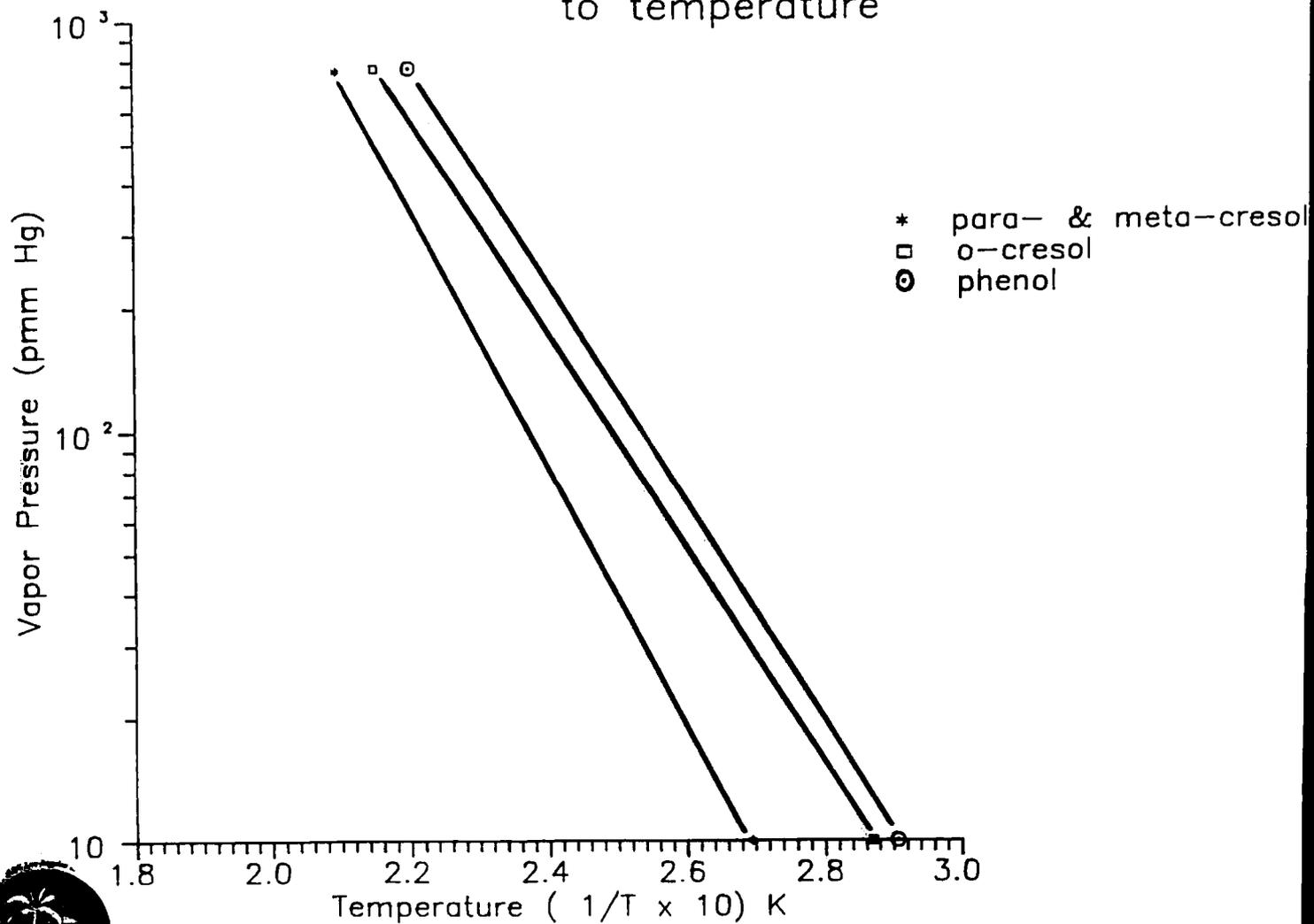
Air to Water Ratio is a Function of Contaminant Removal. The More Volatile a Component, the Lower the Volume of Air Required to Strip It.

Air : Water :: 10 : 1 to 200 : 1

Inlet Water Temperature Affects the Volatility of a Component. Groundwater Temperature May Be Increased by Pre-Heating Inlet Water or by Direct Stream Injection. Temperatures May Be Raised to 140 to 180°F. The Limitation of High Temperature is Higher Operating Cost.



Relation of vapor pressure to temperature



KEY ORGANIC CHEMICAL CHARACTERISTICS FOR TREATMENT SYSTEM DESIGN

(Primary Source: Groundwater Treatment Technology,
with updates by K. Sullivan as found)

CHEMICAL	Solubility	Spec. Grav	Henry's	Adsorp.	Bio. Deg.
1. Acetone	Infinite	0.79	0.05	Trace	D
2. Benzene	1780	0.88	240	76	D
3. Carbon Tetrachloride	800	1.59	1300	185	N,R
4. Chloroform	8000	1.48	170	1.6	N,D
5. Methylene Chloride	20,000	1.33	134	2.7	D
6. Chlorobenzene	500	1.11	228	190	D
7. Ethyl Benzene	152	0.87	323	210	D
8. Hexachlorobenzene	0.11***	2.04	33	NA	N
9. Ethylene Chloride	8690	1.24	61	4	R
10. 1,1,1-Trichloroethane	4400	1.34	200	155	N,R
11. 1,1,2-Trichloroethane	4500	1.44	41	159	R
12. Trichloroethylene	1100***	1.46	450	140	R
13. Tetrachloroethylene	150***	1.62	1100	345	N,R
14. Phenol	82,000**	1.07	0.1	31.2	D
15. 2-Chlorophenol	28,500	1.26	1.74	93.1	D
16. Pentachlorophenol	14	1.98	0.13	805	R,D
17. Toluene	515	0.87	320	147	D
18. Methyl Ethyl Ketone	353,000*	0.81	0.5	1.5	D
19. Naphthalene	32***	1.03	22	376	D
20 Vinyl Chloride	1.1***	0.91	359,000	Trace	R

Notes:

Solubility = mg/L @ 20 degC (*=10 degC, **=15 degC, ***=25 degC)

Specific Gravity (Water = 1.0)

Henry's Constant = atm-m³water/m³air

Adsorption Capacity = mg Compound/g Carbon (@ 500 ppb)

Adsorption Estimates supplied by Mr. Bob Byron, TIGG Corporation

Biodegradability (D=degradable, R=refractory, N=non-degradable)

N.B. Most values are derived for ideal, 'clean', single-compound solutions.
Multi-contaminant systems may behave differently

Revised
6/87



The mass transfer equations for an air/water stripping system are:

$$Z = \text{HTU} \times \text{NTU}$$

$$\text{HTU} = L'/K_{la}$$

$$\text{NTU} = (R/(R - 1)) \times \ln [((C_{inf}/C_{eff}) \times (R - 1) + 1)/R]$$

where:

$$R = (H \times G)/(L' \times P)$$

and

HTU = Height of transfer unit (feet)

NTU = Number of transfer units (unitless)

H = Henry's law constant (atm)

G = Gas loading rate (cfm)

L' = Liquid loading rate (gpm/sq. ft.)

P = Operating pressure (atm)

Z = Packing height (feet)

C_{inf} = Influent concentration ($\mu\text{g/l}$)

C_{eff} = Effluent concentration ($\mu\text{g/l}$)

K_{la} = Overall mass transfer coefficient (sec^{-1})

R = Stripping factor (unitless)

(Note: Unit conversion factors are not shown in the above equations. Units should be consistent.)



Air Stripping

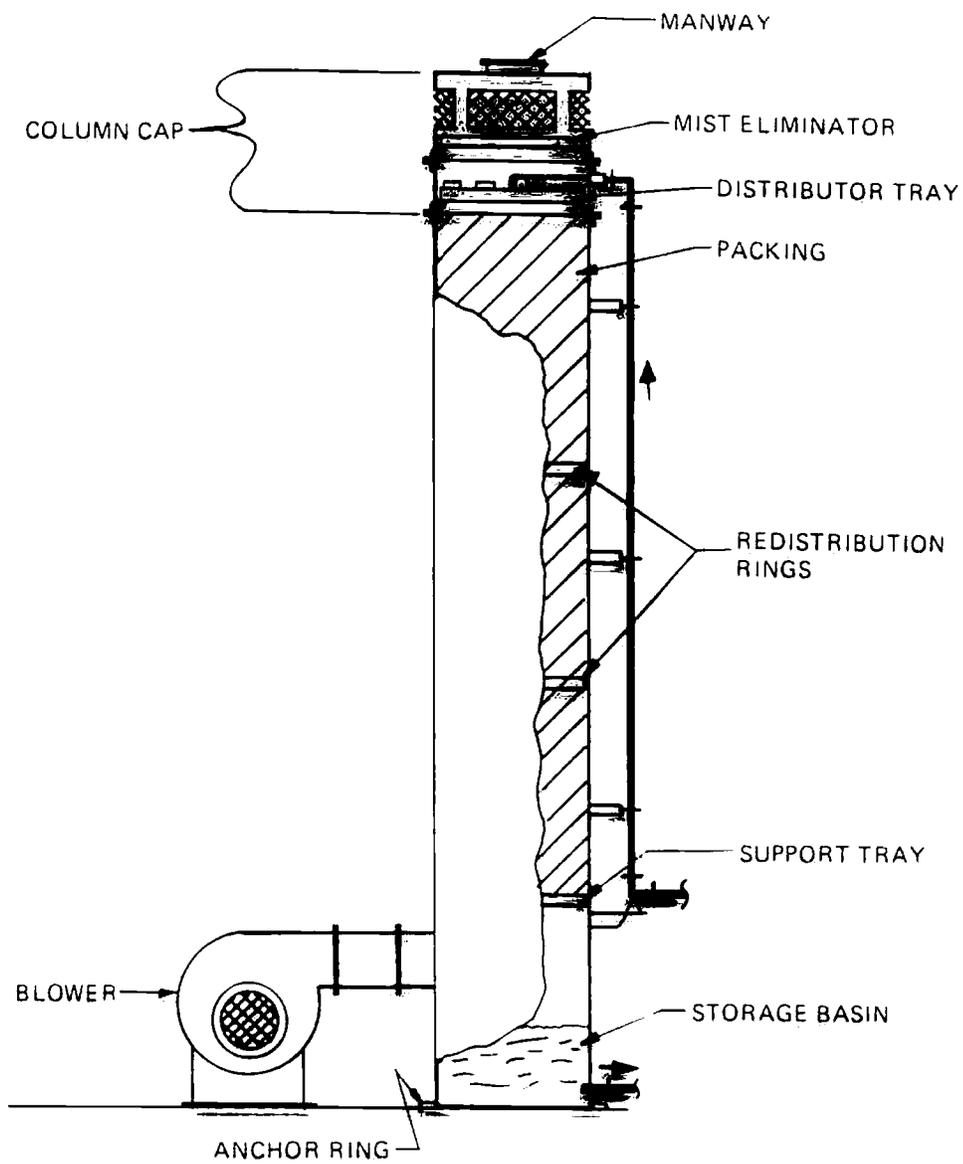
The Key Variables to Define in the Mass Transfer Equations Are:

- *Henry's Law Constant (H)*
- *Overall Mass Transfer Coefficient (K_{ea})*

The Henry's Law Constant Can Be Obtained From Reference Books.

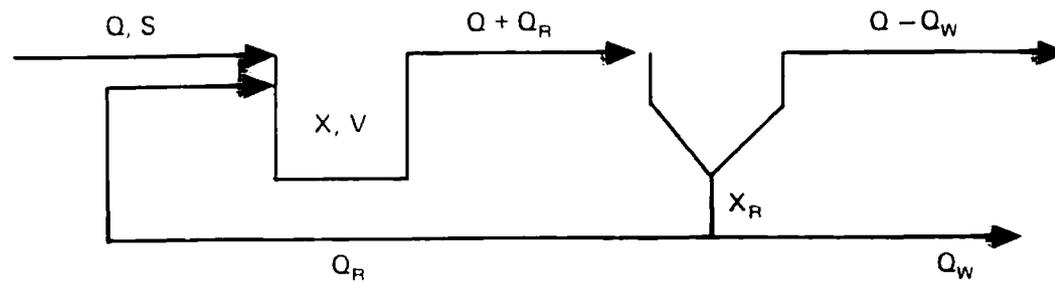
The Mass Transfer Coefficient is a Function of Tower Design and Packing Type. It Expresses the Overall Efficiency of the Tower. Best to Select a Mass Transfer Coefficient Based on Field Data From a Pilot Test. Testing Should Cover a Range of Liquid Loading Rates and Air to Water Ratios While Measuring the Resulting Effluent Concentration. The Mass Transfer Equations are Solved for K_{ea} .





Packed tower components.





- Q = Flow
- Q_R = Recycle Flow
- Q_W = Sludge Wastage Flow
- X = Mixed Liquor Suspended Solids (MLSS)
- X_R = Clarifier Underflow Solids Concentration
- X_E = Effluent Solids Concentration
- V = Volume of Aeration Basin
- S = Organic Concentration

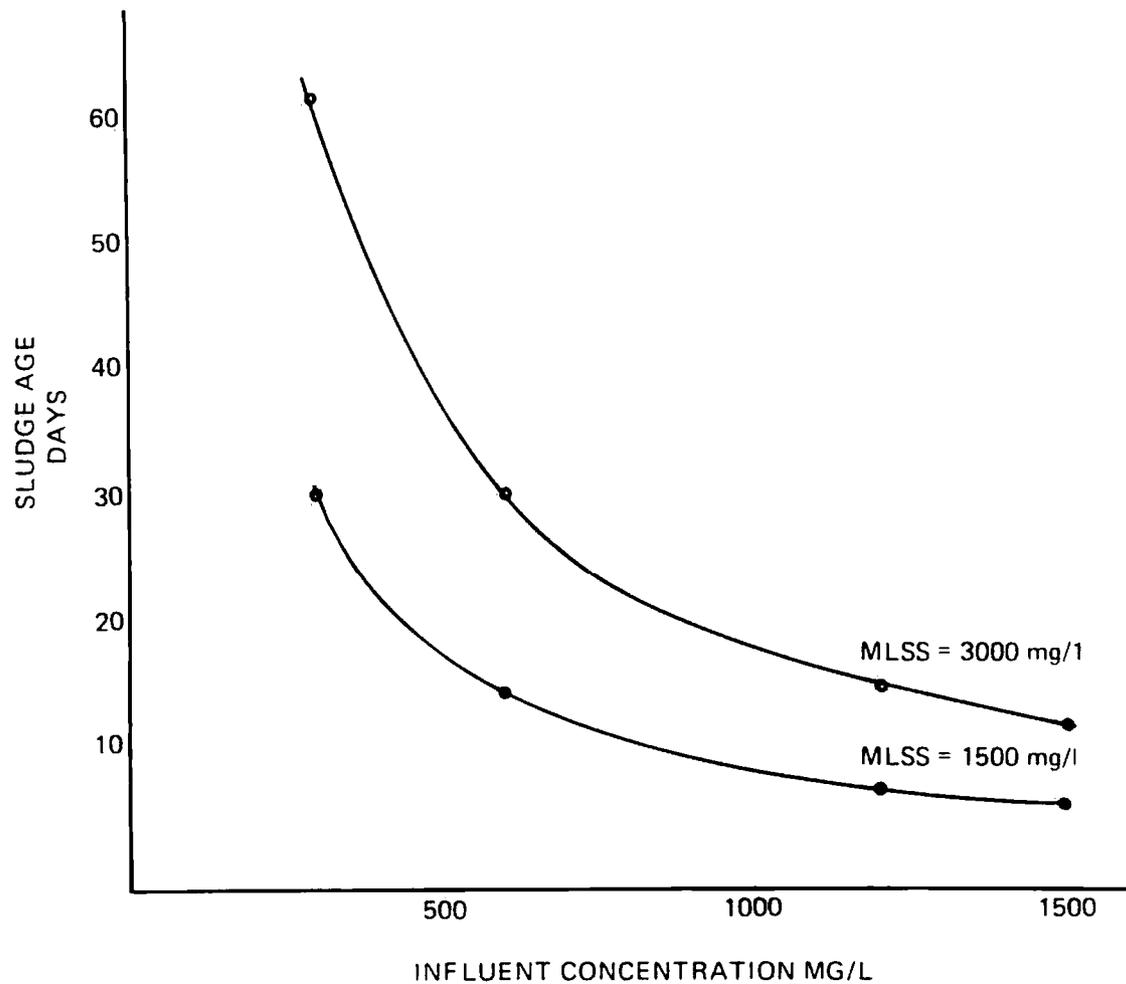
Activated sludge treatment system.



sludge age

$$A = (X \times V) / (Q \times S \times Y)$$

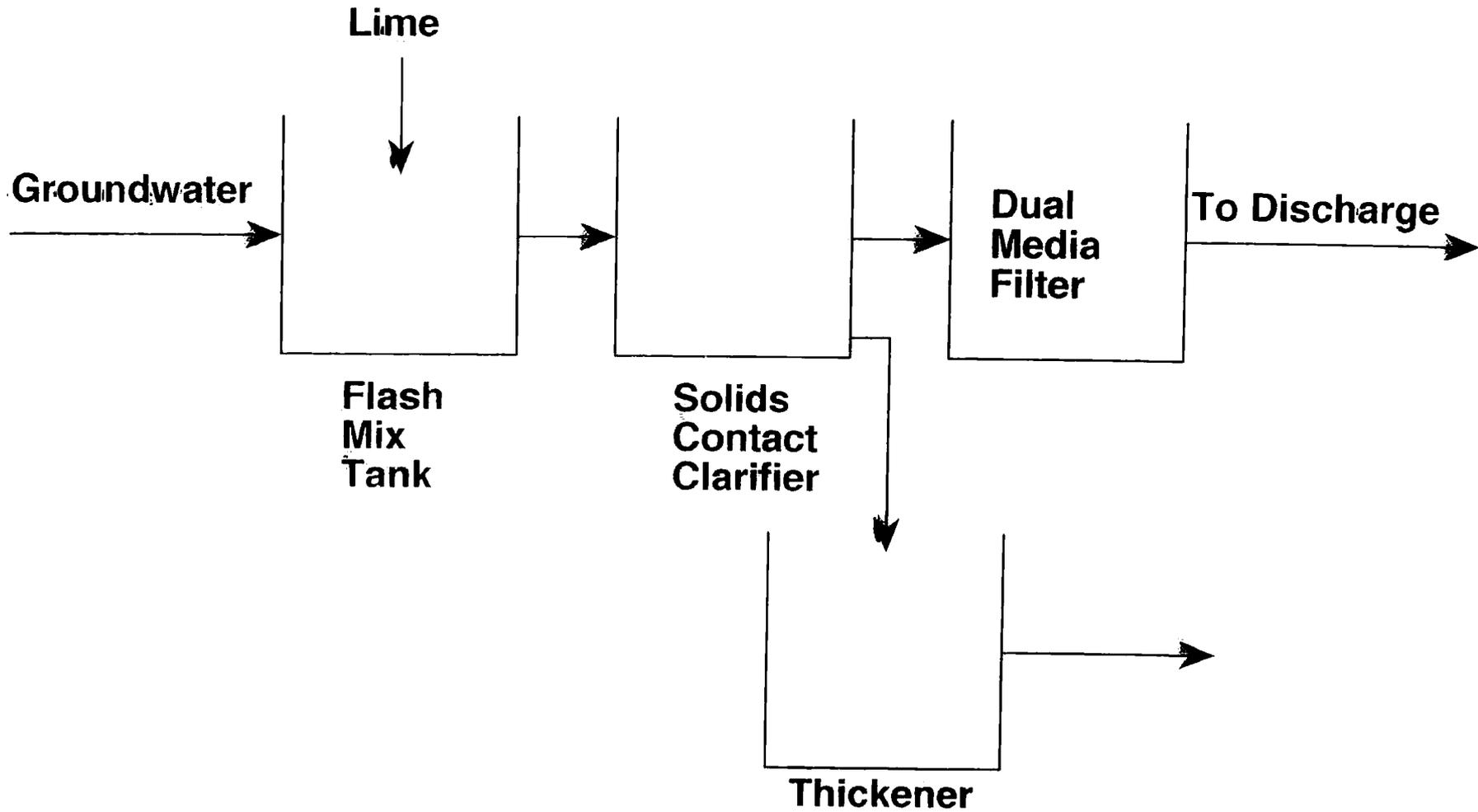




. Sludge age with life cycle influent concentrations.



Treatment Plant Design for a Heavy Metal

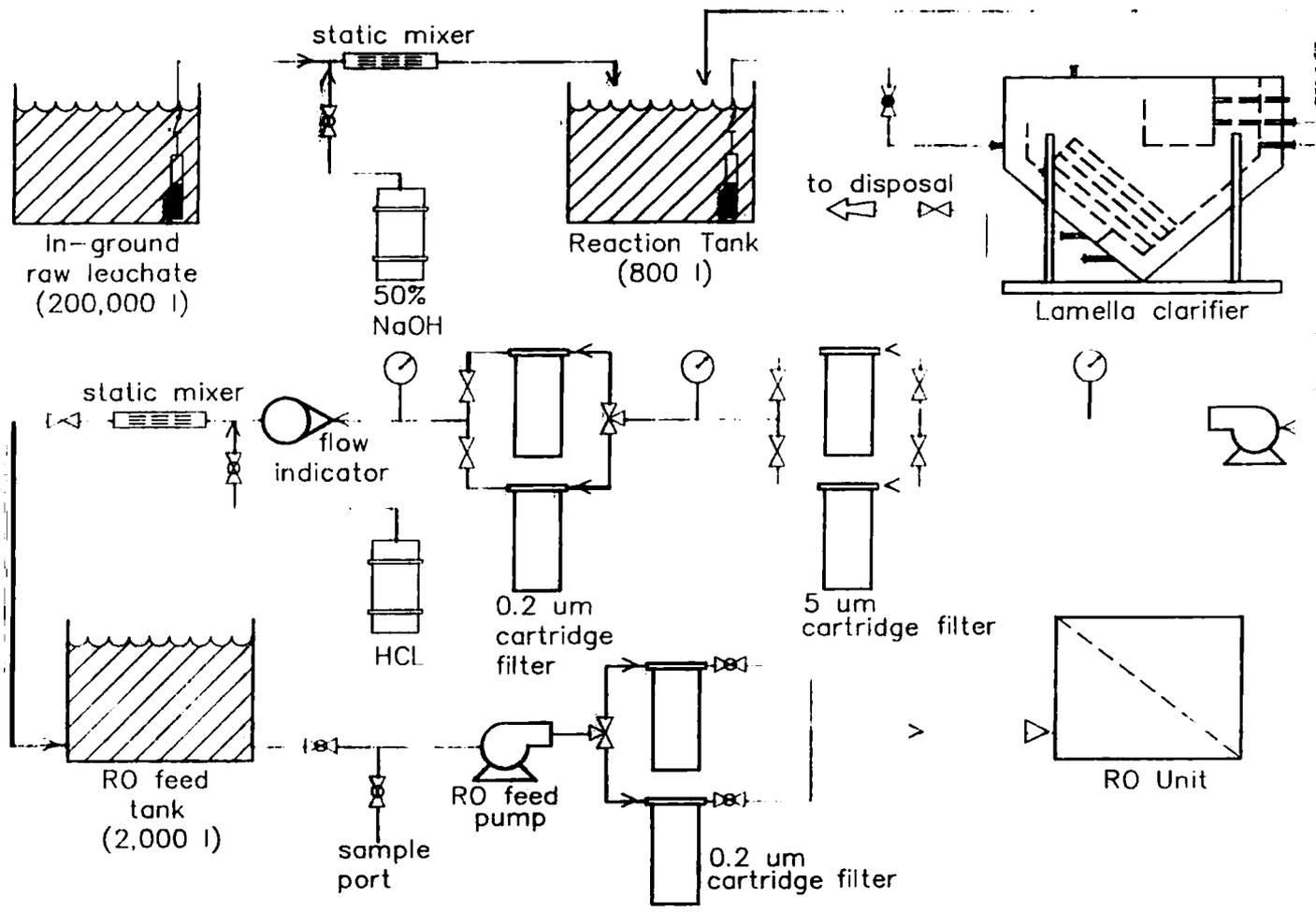


Reverse Osmosis

The Technology Uses A Semi-Permeable Membrane to Separate a Solute, Chemical Compound or Ion, From a Solvent or Groundwater. The Solvent Flows Through the Membrane, Under a Hydrostatic Pressure Greater Than the Osmotic Pressure, While the Larger Compounds are Rejected and Retained Behind the Membrane.

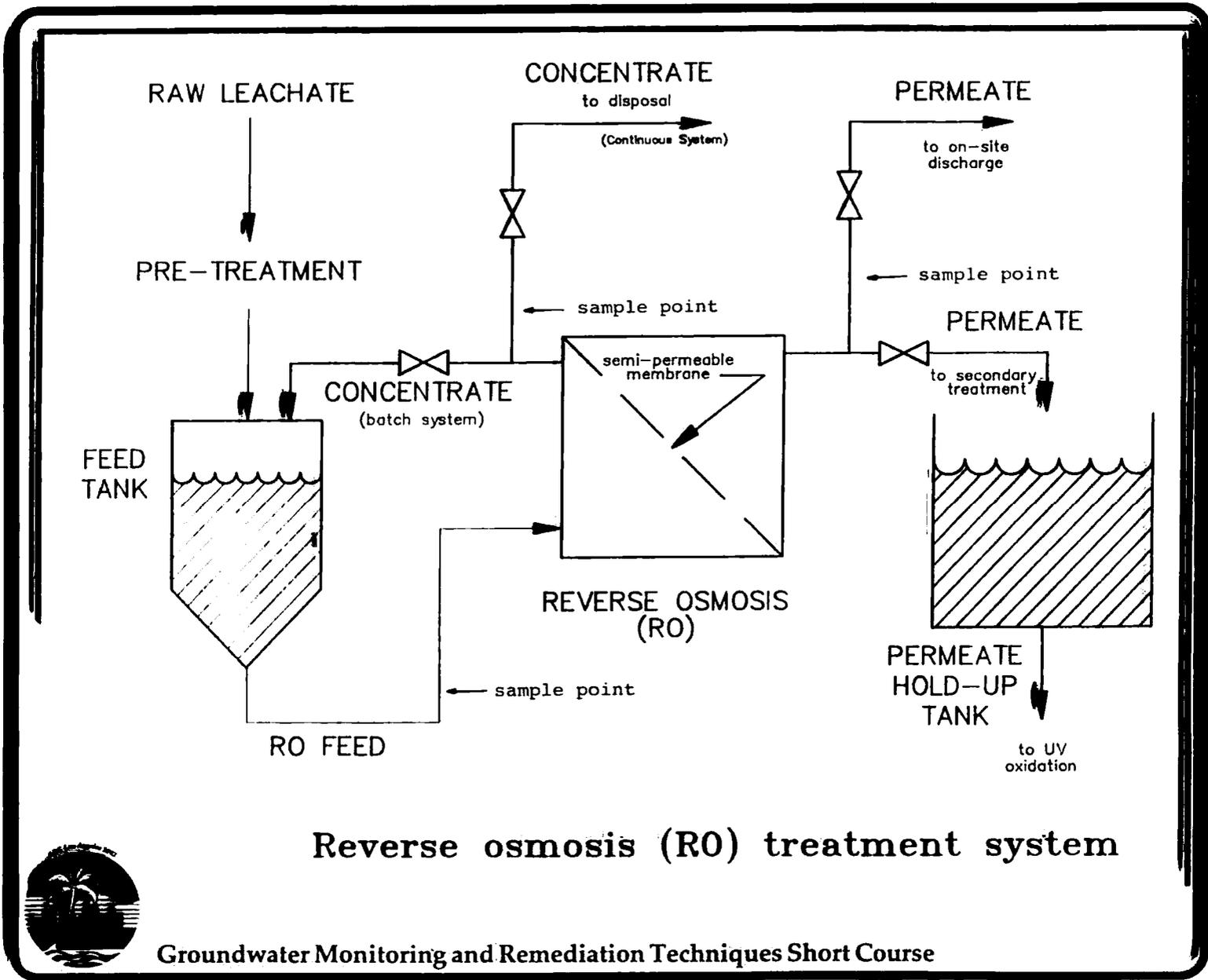
The Inlet Stream is Separated into Two Outlet Streams: the Permeate Which Contains the Treated Groundwater and the Retentate or Concentrate Which Contains Elevated Concentrations of the Chemicals of Concern. The Volume of the Retentate is Much Less Than the Inlet Volume and the Concentration of the Chemicals of Concern are Greater Than the Inlet Concentration; Therefore, Reverse Osmosis is a Volume Reduction Technology.

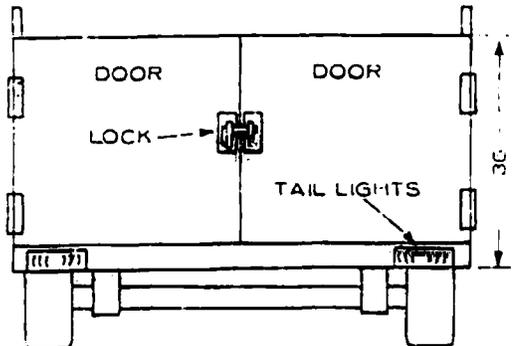
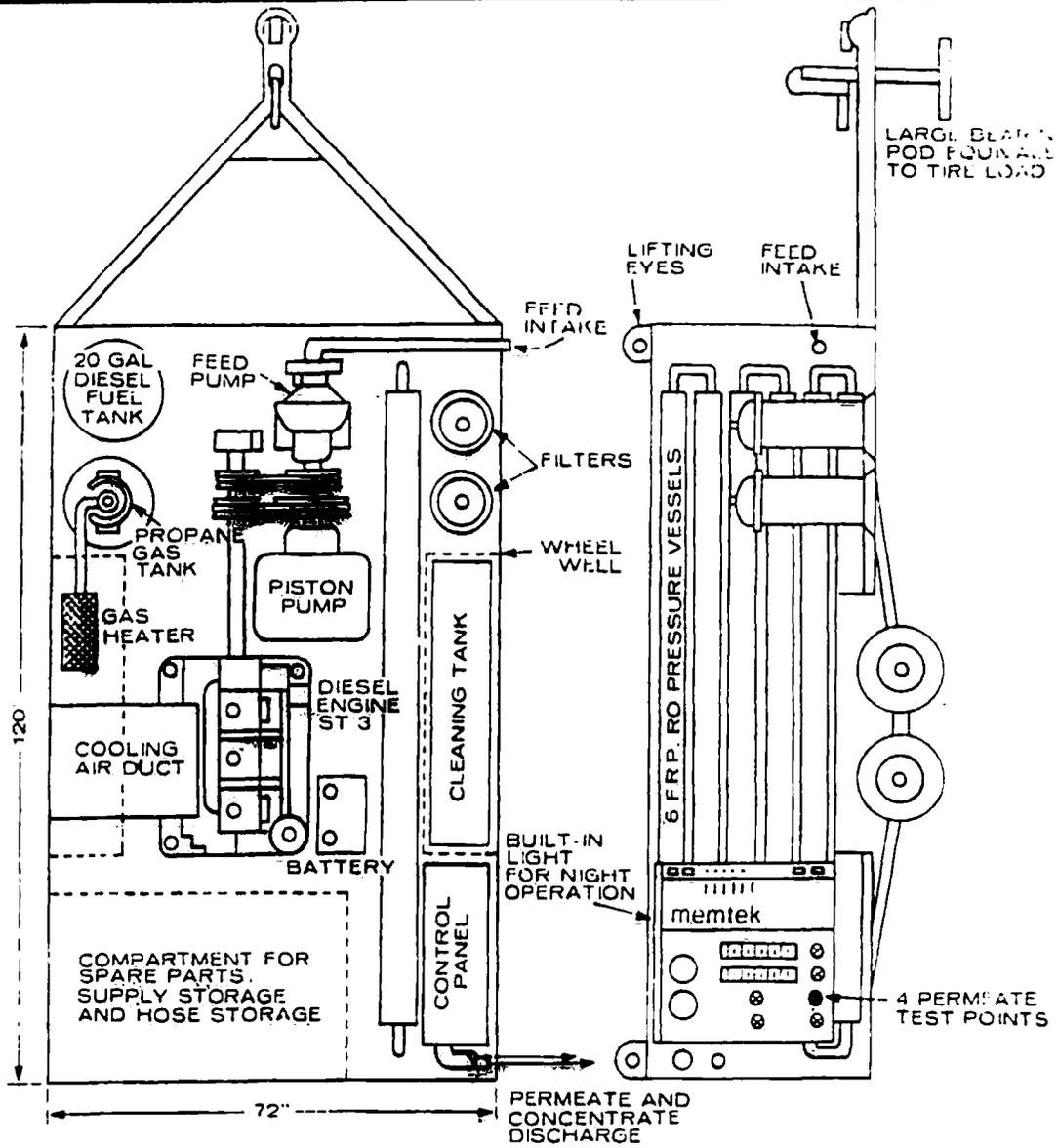




Reverse osmosis (RO) pretreatment system





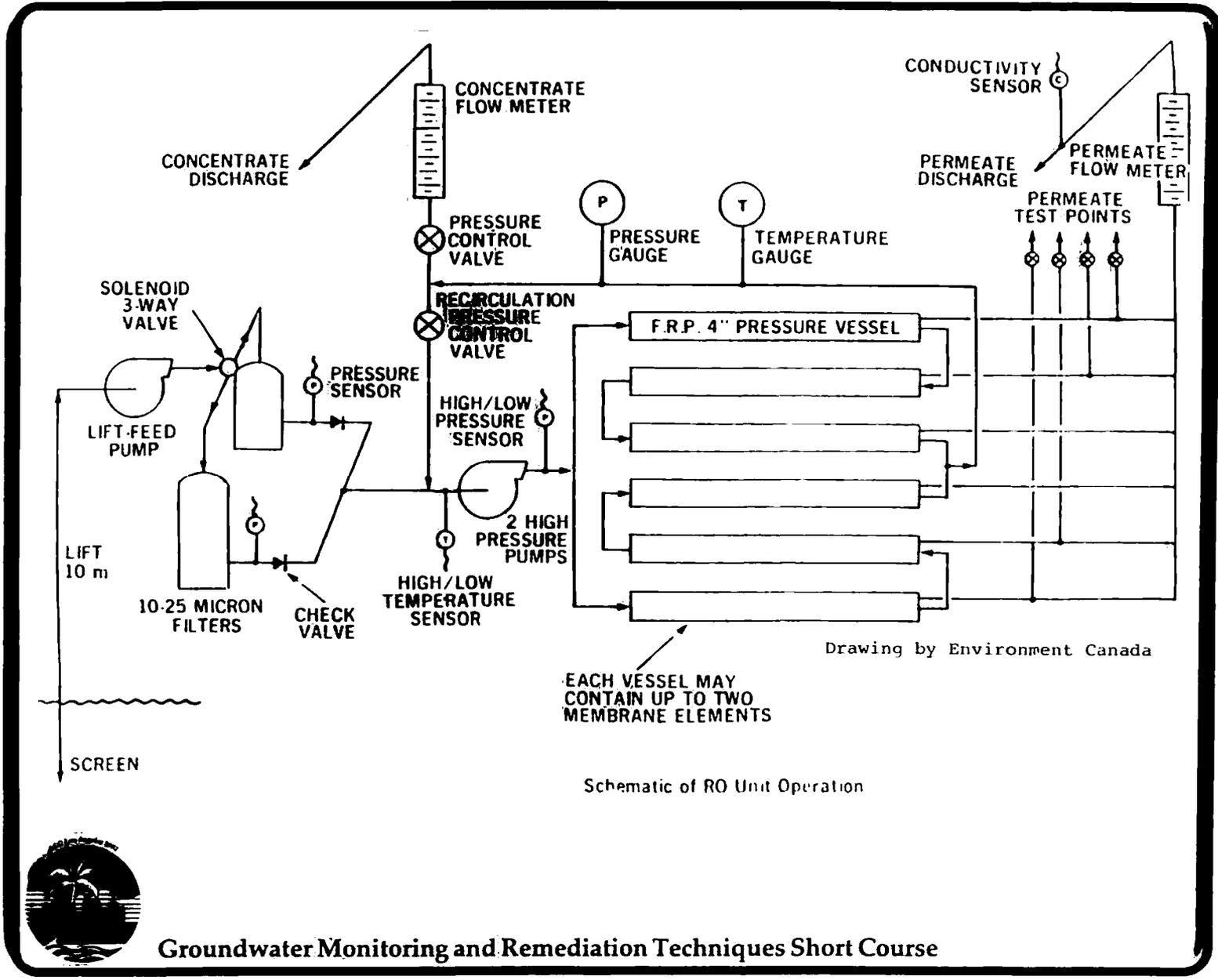


NOTE. SKIN AND DOORS FOR CONTROL PANEL FILTER HOUSINGS, CLEANING TANKS AND FUEL TANKS OMITTED FOR CLARITY

Drawing by Environment Canada

Reverse Osmosis Unit Layout





EACH VESSEL MAY CONTAIN UP TO TWO MEMBRANE ELEMENTS

Schematic of RO Unit Operation



Reverse Osmosis

Membrane Separation Efficiency (E), in Terms of Chemical Rejection, is:

$$E = 1 - (C_P/C_F)$$

Where: C_P = Chemical Concentration in Permeate
 C_F = Chemical Concentration in Feed

Groundwater Recovery Fraction (R) is:

$$R = Q_P/Q_F$$

Where: Q_P = Permeate Flow
 Q_F = Feed Flow



Reverse Osmosis

Advantages:

- Removes High Levels of Inorganic Salts and Heavy Metals
- Removal of Large Non-Polar Organic Compounds
- Removal of Most Polar Organic Compounds
- Can Be Used to Recycle Some Compounds

Limitations:

- Does Not Destroy Chemicals of Concern
- Does Not Remove All Organics
- Membrane Fouling Reduces Flow of Permeate, May Reduce Separation Efficiency, and Increase Operating and Maintenance Costs
- Groundwater May Require Pre-Treatment and System May Have to be Accurately Operated to Reduce Fouling



Reverse Osmosis

Operation and Maintenance Costs:

- Membrane Cleaning
- Membrane Replacement
- Unit Maintenance
- Monitoring
- Power Consumption

O & M Cost per 1000 Gallons to Remove THM from Groundwater:

\$0.68 for 700 GPM

\$0.55 for 1700 GPM

\$0.79 for 700 GPM

Total Cost per 1000 Gallons to Remove Agricultural Chemicals from Groundwater:

Flow	RO	GAC	Air Stripping
7	\$5.00	\$4.05	\$1.30
70	\$3.30	\$2.05	\$0.57
700	\$1.95	\$1.00	\$0.31



PERCENT REJECTION OF CONTAMINANTS BY REVERSE OSMOSIS MEMBRANES

	UOP		DSI		TORAY		FILMTEC	
	Mean	n	Mean	n	Mean	n	Mean	n
<u>VOLATILE ORGANIC (VOA)</u>								
<u>ORGANICS</u>								
Methylene Chloride	35.7	12	48.9	11	46.9	7	50.5	11
Acetone	45.9	11	44.5	10	38.3	6	73.8	11
1,1-Dichloroethene	56.7	9	62.7	8	61.8	7	74.7	9
1,1-Dichloroethane	57.2	12	64.7	11	64.3	8	88.2	11
t-1,2-Dichloroethene	10.7	12	28.2	11	30.5	8	47.4	11
Chloroform	ND	11	ND	11	ND	8	ND	11
1,2-Dichloroethane	41.0	12	52.3	12	53.7	9	75.3	11
1,1,1-Trichloroethane	76.9	12	85.2	12	85.7	9	93.3	11
Carbon Tetrachloride	42.9	4	54.1	3	43.2	3	59.3	3
Bromodichloromethane	67.0	10	75.6	10	62.3	7	91.6	10
1,2-Dichloropropane	3.5	3	43.7	2	98.3	1	72.5	1
Cis-1,3-Dichloropropane	0	3	32.7	3	27.5	3	24.7	3
Trichloroethene	43.8	12	59.9	12	50.9	9	59.8	11
Benzene	53.5	12	57.9	12	68.2	9	83.9	11
t-1,2-Trichloroethane								



PERCENT REJECTION OF CONTAMINANTS BY REVERSE OSMOSIS MEMBRANES

	UOP		DSI		TORAY		FILMTEC	
	Mean	n	Mean	n	Mean	n	Mean	n
<u>VOLATILE ORGANIC (VOA) ORGANICS</u>								
t-1,3-Dichloropropane	ND	10	ND	11	ND	7	ND	11
Dibromochloromethane								
Methyl Isobutyl Ketone	77.7	11	85.4	11	71.6	8	73.7	11
Bromoform	74.9	10	91.5	9	69.1	8	99.5	9
Tetrachloroethene	78.5	12	61.4	12	46.2	9	66.4	11
Toluene	54.2	12	68.1	12	67.7	9	83.7	11
Chlorobenzene	36.4	12	55.5	11	59.1	8	76.7	10
Ethylbenzene	66.1	11	74.3	11	74.6	9	94.9	10
meta- and para-Xylene	74.2	11	83.9	10	84.6	7	96.3	9
ortho-Xylene	71.9	11	83.2	9	83.4	7	96.6	9
<u>SEMI-VOLATILE (BNA) ORGANICS</u>								
Phenol	54.5	10	55.7	10	52.5	7	72.1	10
Benzyl Alcohol	42.0	2	25.0	2	25.0	2	28.0	3
1,2-Dichlorobenzene	64.4	10	91.7	10	73.3	7	87.9	10
2-Methylphenol	47.3	7	73.4	6	49.0	7	77.8	9
4-Methylphenol	78.6	10	57.4	10	59.8	7	89.8	10
Isophorone	83.9	4	79.9	5	75.0	4	83.9	4
2,4-Dimethylphenol	72.3	10	69.2	10	64.0	7	88.5	10
Benzoic Acid	67.8	7	81.9	8	76.3	5	86.4	8
Naphthalene	74.2	10	80.6	9	70.2	7	88.9	9
2-Methylnaphalene	85.0	5	60.8	4	57.7	2	92.6	5



PERCENT REJECTION OF CONTAMINANTS BY REVERSE OSMOSIS MEMBRANES

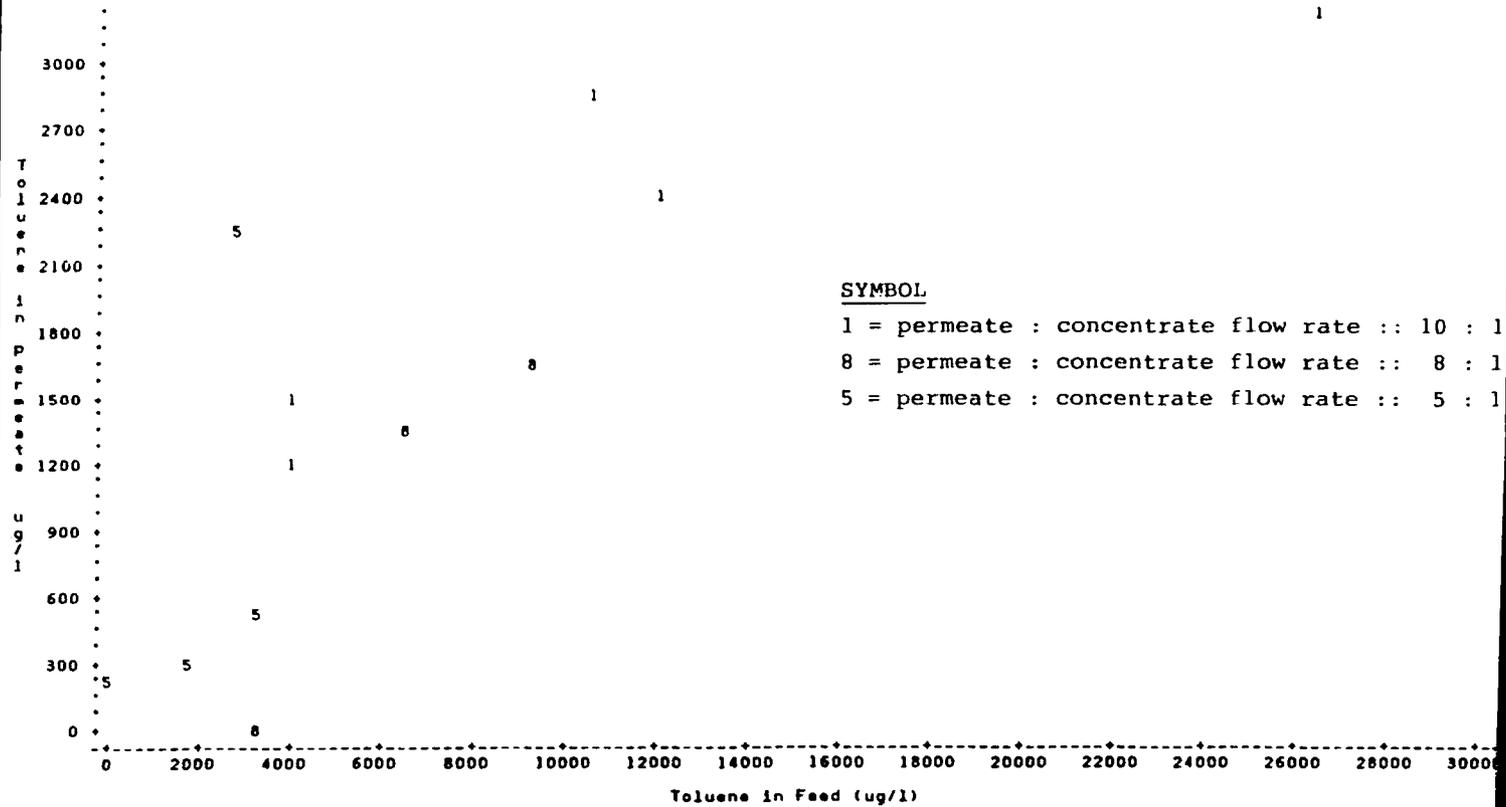
	<u>UOP</u>		<u>DSI</u>		<u>TORAY</u>		<u>FILMTEC</u>	
	Mean	n	Mean	n	Mean	n	Mean	n
Bis(2-Ethylhexyl)phthalate	78.4	10	76.4	8	54.9	6	71.1	9
Di-n-octylphthalate	50.0	6	41.7	6	63.7	3	52.3	10
Di-n-butylphthalate	37.5	2	25.0	2	56.2	6	37.5	2
<u>HEAVY METALS</u>								
Antimony	89.6	6	89.6	6	75.8	6	85.7	6
Arsenic	95.4	8	85.0	8	61.5	6	98.6	8
Beryllium	ND	1	ND	1	ND	1	ND	1
Cadmium	ND	9	ND	9	ND	6	ND	9
Chromium	ND	9	ND	9	ND	6	ND	9
Copper	84.4	1	84.4	1	84.4	1	84.4	1
Lead	10.3	9	16.9	8	10.0	8	29.1	7
Mercury	ND	1	ND	1	ND	1	ND	1
Nickel	98.3	9	92.8	9	79.6	6	88.2	9
Selenium	1.7	3	19.4	3	ND	6	15.0	4
Silver	ND	9	ND	9	ND	6	ND	9
Thallium	ND	8	ND	8	ND	6	ND	8
Zinc	45.4	9	33.6	9	27.1	6	53.3	9

ND - Means not detected.



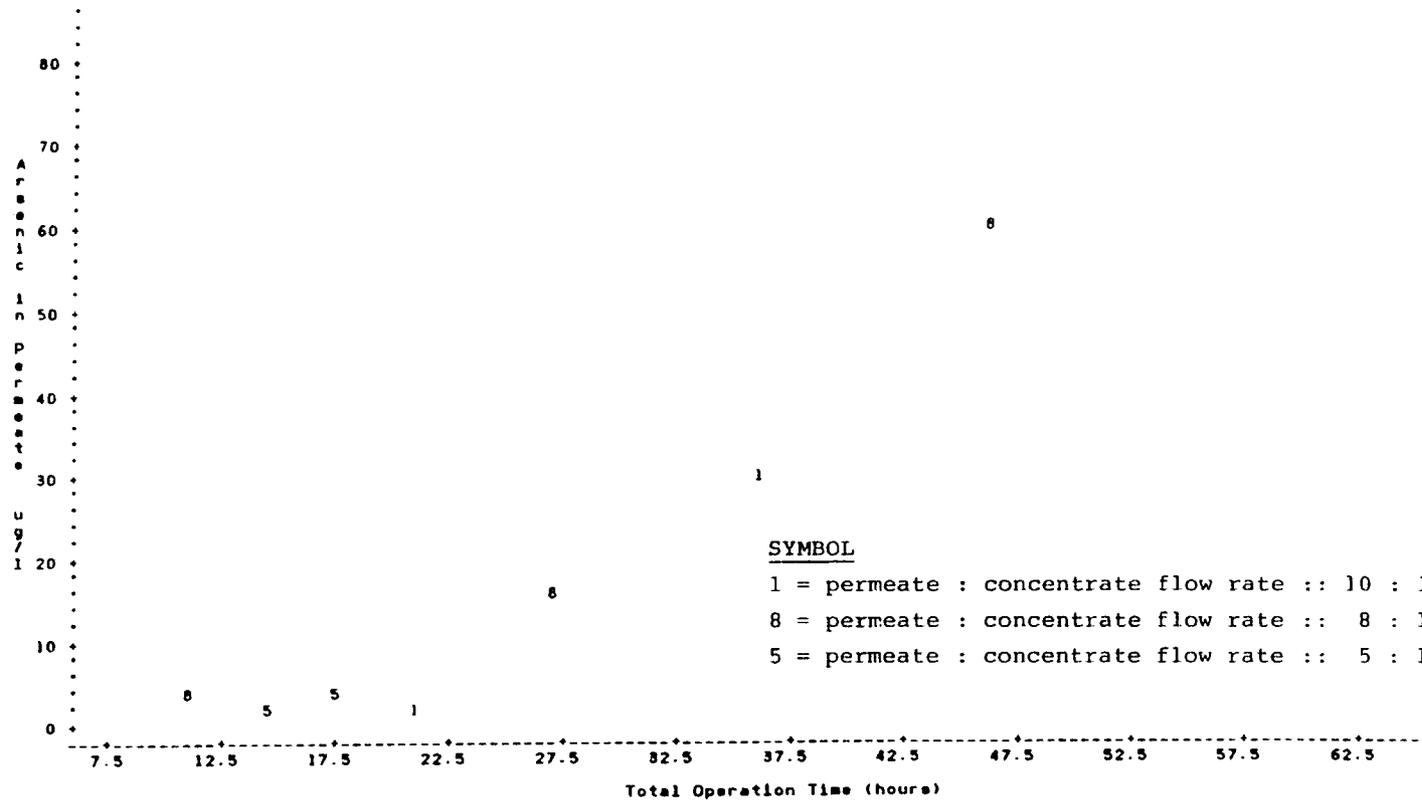
Toluene permeate concentration versus feed concentration

Type of RO Membrane=Desal



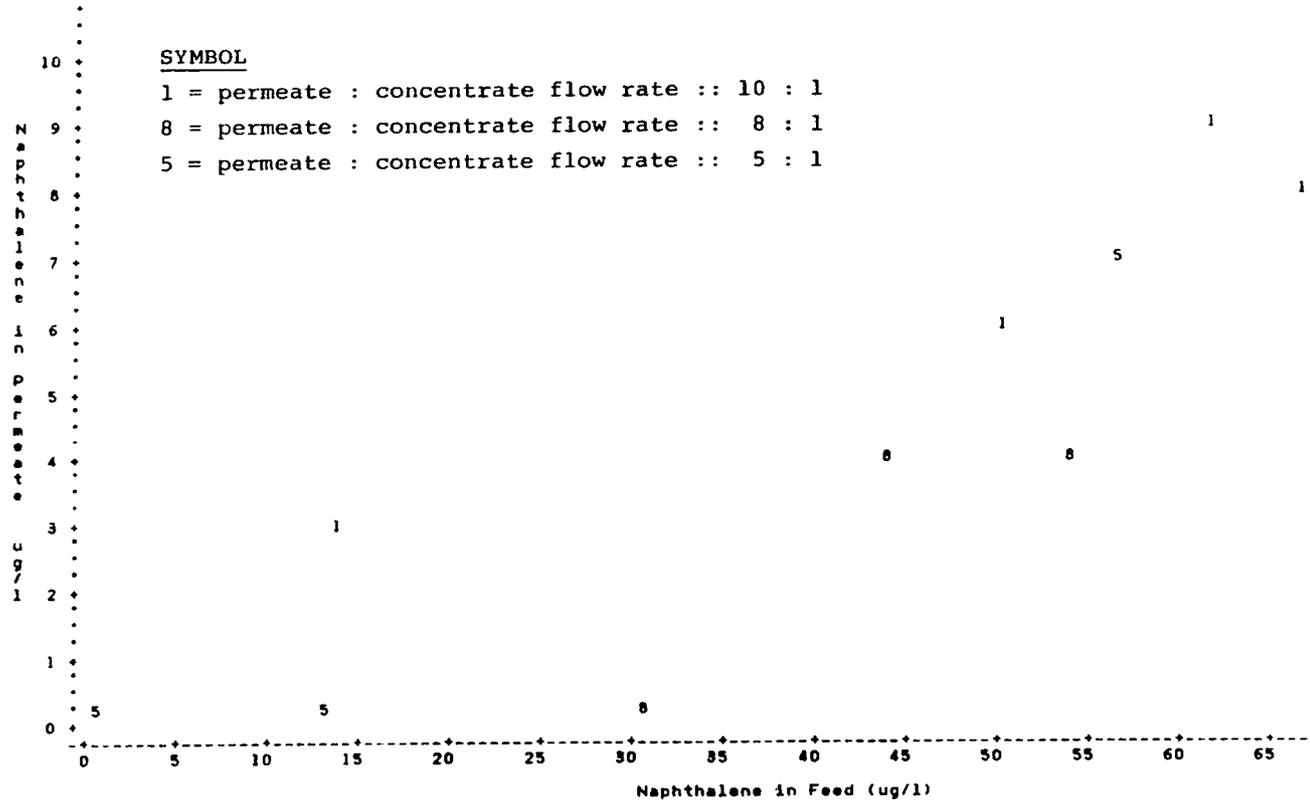
Arsenic permeate concentration versus time

Type of RO Membrane-Toray



Naphthalene permeate concentration versus feed concentration

Type of RO Membrane=Desal



Activated Carbon

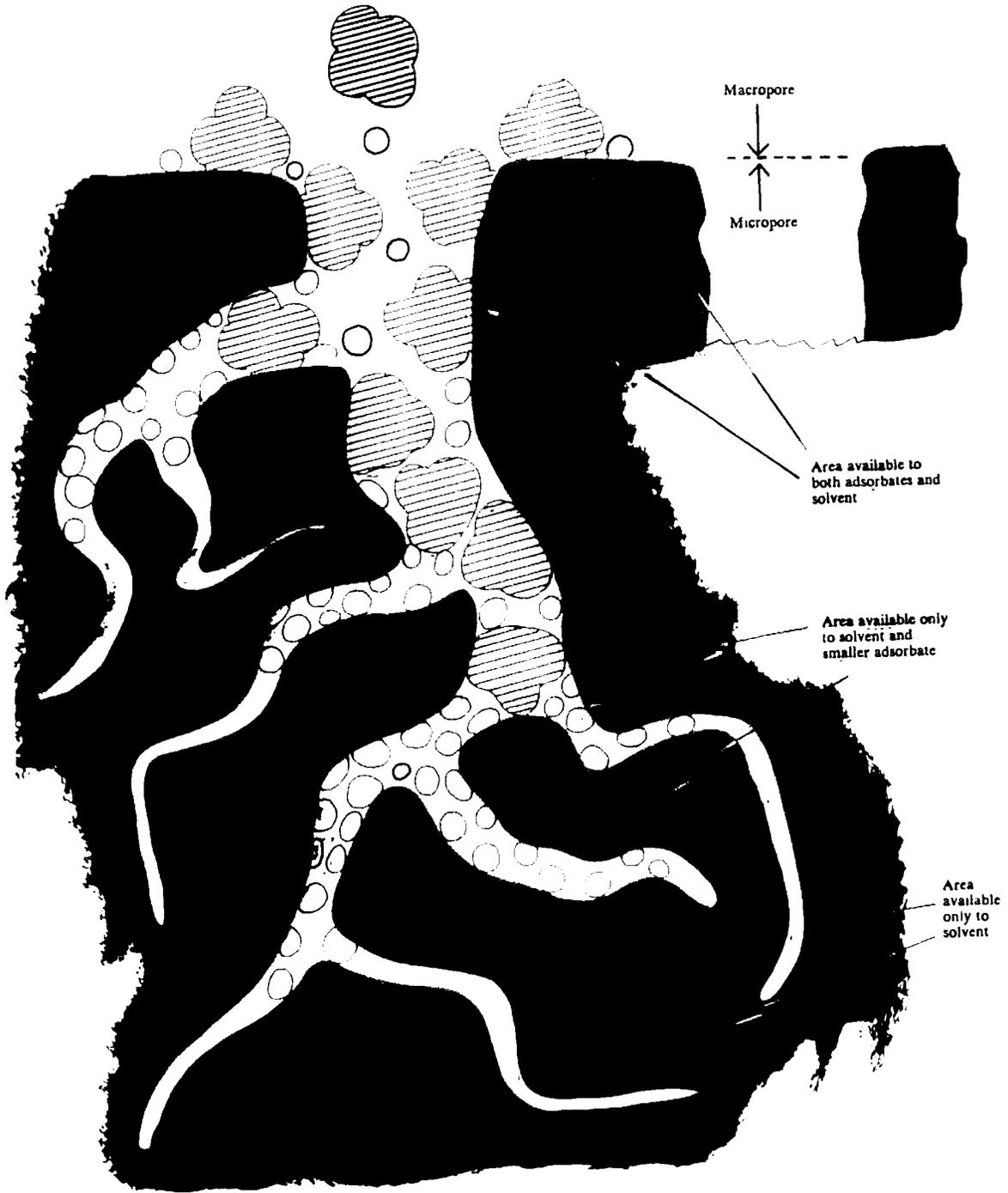
Technology uses a variety of carbons to selectively adsorb a wide range of organic and certain inorganic compounds. Cost of treatment ranges from \$0.38 to \$2.52 / 1000 gal.

Source materials are bituminous coal, coconut shell, lignite, pump mill residue and wood. The surface area, on which adsorption takes place, varies by carbon type but ranges between 500 and 1400 meters²/gm.

Most of the surface area of carbon is part of the internal structure. This structure is comprised of macropores and micropores.



CONCEPT OF MOLECULAR SCREENING
IN MICROPORES



Activated Carbon

Adsorption is a 3 step mechanism

- External diffusion of compounds through the liquid to the carbon particle
- Internal diffusion through the macropores
- Adsorption to the surface

Molecular Screening

Many of the micropores are only large enough for small molecules. The effective surface area for adsorption exists only in pores that a molecule can enter. Therefore, the surface area for adsorption of a particular compound depends on its size and the available surface area accessible to it.

The adsorptive properties of a particular carbon are expressed in terms of its compounds (adsorbate), such as iodine, methylene blue, and molasses.



Activated Carbon

Freundlich Isotherm Equation

$$x/M = KC^{1/n} \quad \text{or}$$

$$\log x/M = 1/n \log C + \log K$$

On log/log paper

$1/n$ = slope of the line

K = y intercept

x/M = is the ordinate of the graph

C = is the abscissa



Activated Carbon

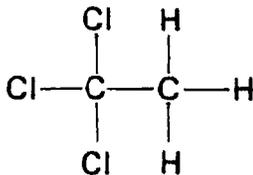
Calculation of Carbon Capacity

To calculate the capacity of carbon for a particular species, an adsorption isotherm test is performed. A fixed volume of water containing a chemical of concern is mixed with a known weight of carbon. After equilibrium is reached, the carbon is removed and the residual chemical concentration, C , is measured. The amount of adsorbed chemical, x , is the initial concentration, C_0 , minus the residual, or $x = C_0 - C$. If M is the weight of the carbon, then $x/M =$ the amount adsorbed per weight of carbon (mg/g), at a specific C_0 . The test is repeated several times for different carbon doses, M .



COMPOUND: 1,1,1-Trichloroethane

STRUCTURE:



FORMULA: C₂H₃Cl₃ MOL. WT. 133.41

FREUNDLICH PARAMETERS	pH		
		5.3	
K	2.48		
1/n	0.34		
Corr. Coef. r	0.97		
INITIAL CONC. mg/l	ADSORPTION CAPACITY, mg/gm		
1.0	2.5		
0.1	1.1		
0.01	0.51		
0.001	0.23		

CALCULATED CARBON REQUIREMENTS TO ACHIEVE INDICATED CHANGE IN CONCENTRATION (a)

SINGLE STAGE POWDERED CARBON
C_f, mg/l

GRANULAR CARBON COLUMN

C ₀ , mg/l	0.1	0.01	0.001
1.0	800	1,900	4,300
0.1		180	430
0.01			39

C ₀ , mg/l	
1.0	400
0.1	90
0.01	20

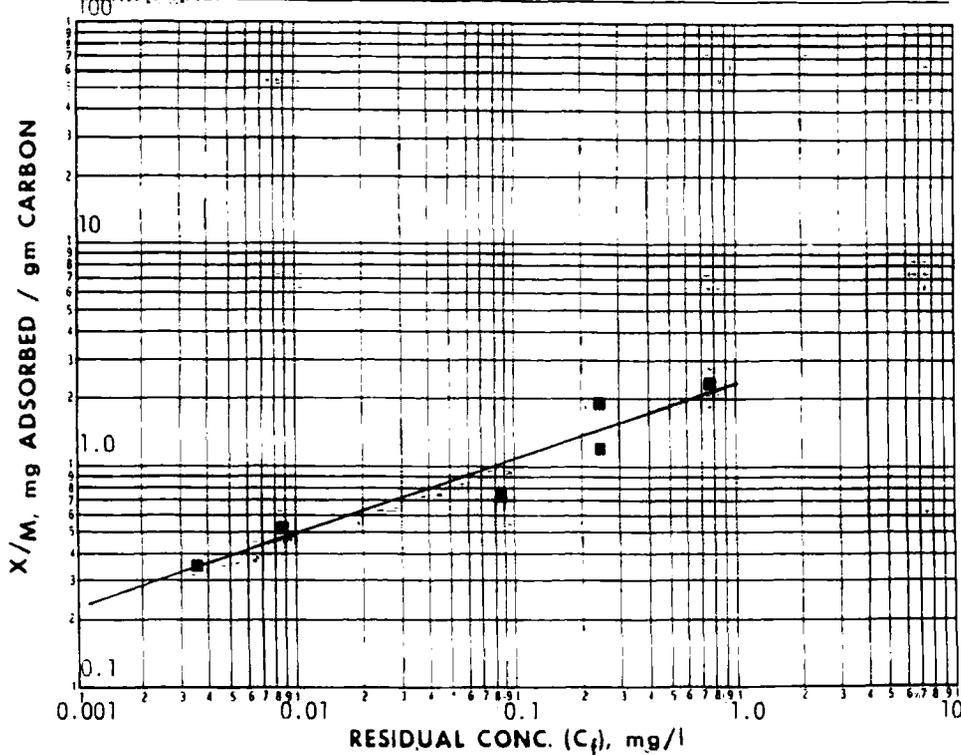
(a) Carbon doses in mg/l at neutral pH.

ANALYTICAL METHOD: G. C. - Purge and Trap

REMARKS:



COMPOUND: 1,1,1-Trichloroethane



CARBON DOSE mg/l	■ pH= 5.3			pH=			pH=		
	C_f	$C_o - C_f = X$	X/M	C_f	$C_o - C_f = X$	X/M	C_f	$C_o - C_f = X$	X/M
0	1.000								
96	0.768	0.232	2.41						
385	0.240	0.760	1.97						
577	0.238	0.762	1.32						
1154	0.084	0.916	0.794						
1923	0.00870	0.991	0.516						
2692	0.00350	0.9965	0.370						



United States
Environmental Protection
Agency

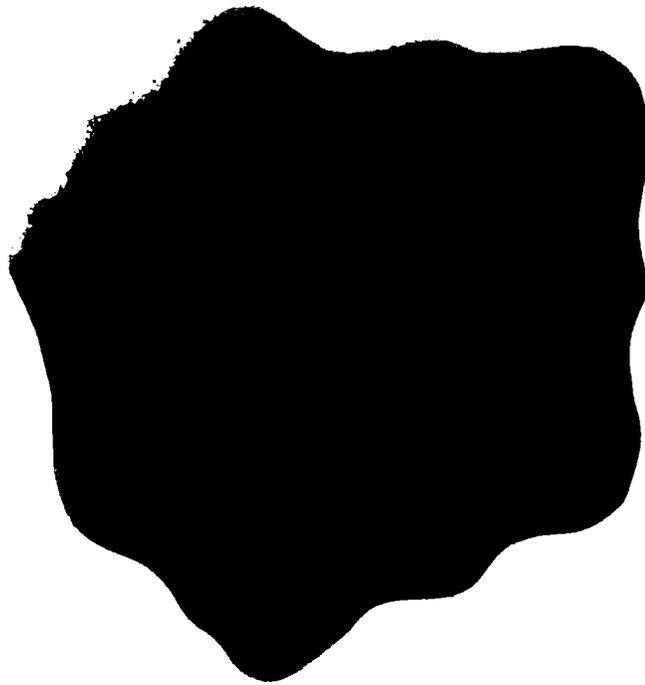
Municipal Environmental Research
Laboratory
Cincinnati OH 45268

EPA-600/8-80-023
April 1980

Research and Development



Carbon Adsorption Isotherms for Toxic Organics



Groundwater Monitoring and Remediation Techniques Short Course

Activated Carbon

To estimate the capacity of carbon, use the x/M value that corresponds to the influent concentration, C_o . This value, $x/M @ C_o$, represents the maximum amount of contaminant adsorbed per unit weight of carbon when the carbon is in equilibrium with the untreated concentration.

For complete removal of the contaminant

$$Y = C_o / (x/M @ C_o)$$

Where

Y = weight of carbon required per unit volume of contaminated liquid



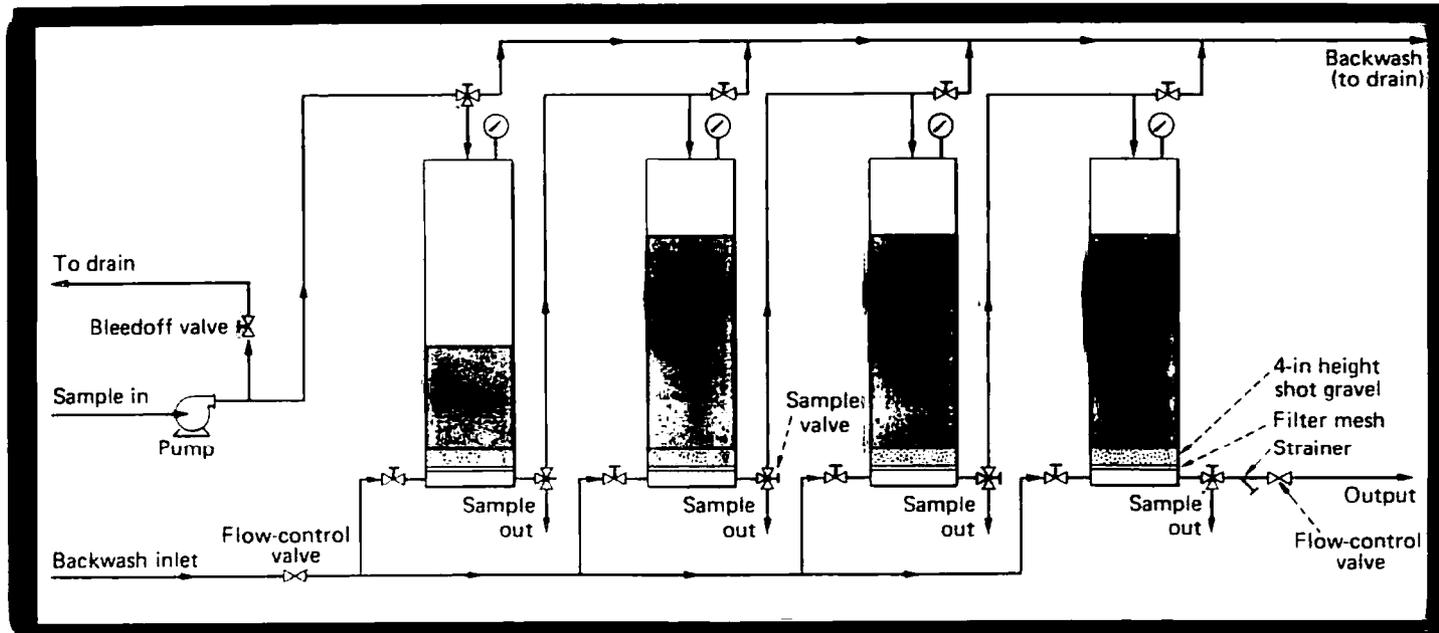
Activated Carbon

Dynamic Column Study

- Determines Optimum Operating Capacity
- Determines Contact Time
- Necessary for Adsorber Size and System Configuration

Superficial contact time ranges between 15 to 60 minutes per column. The rate of flow per unit area of column, surface loading, is in the range of 2 GPM/ft²





Laboratory series column adsorption test.

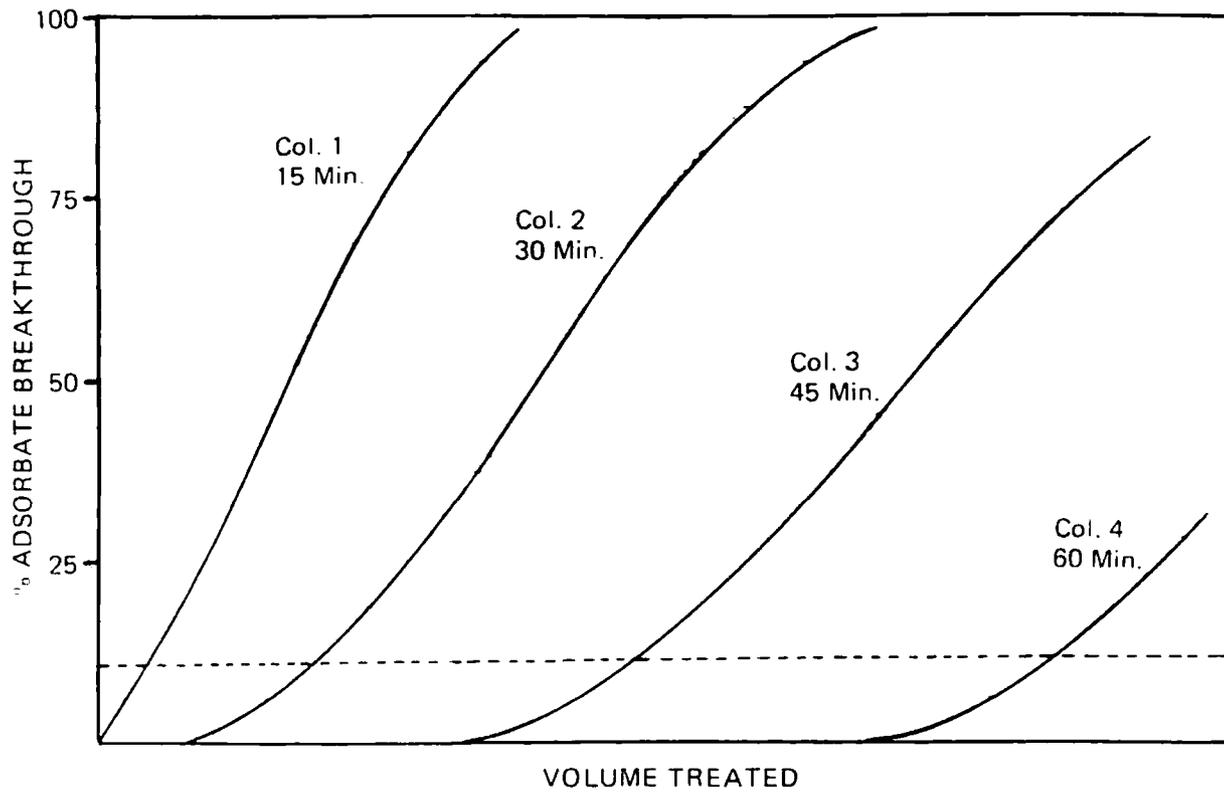


Activated Carbon

Dynamic Column Study

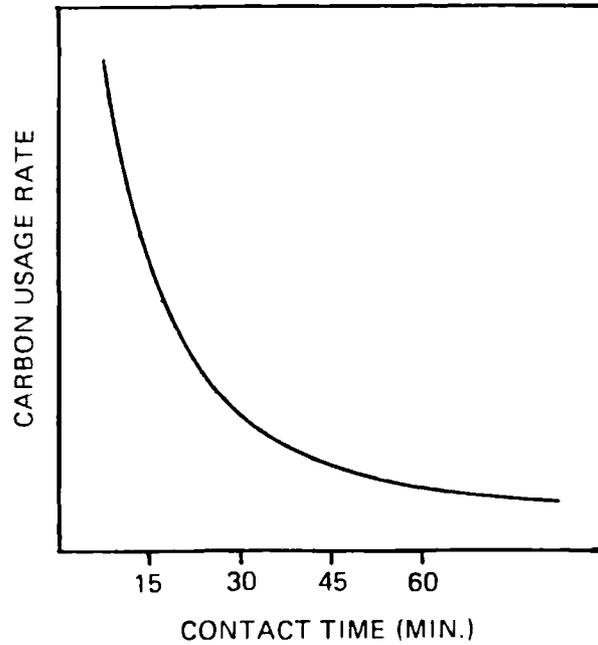
- Pump water through columns
- Take samples of effluent from each column
- Obtain a series of curves, each representing a column. The curves represent the concentration or amount of contaminants present in the effluent which have passed through the column unadsorbed.





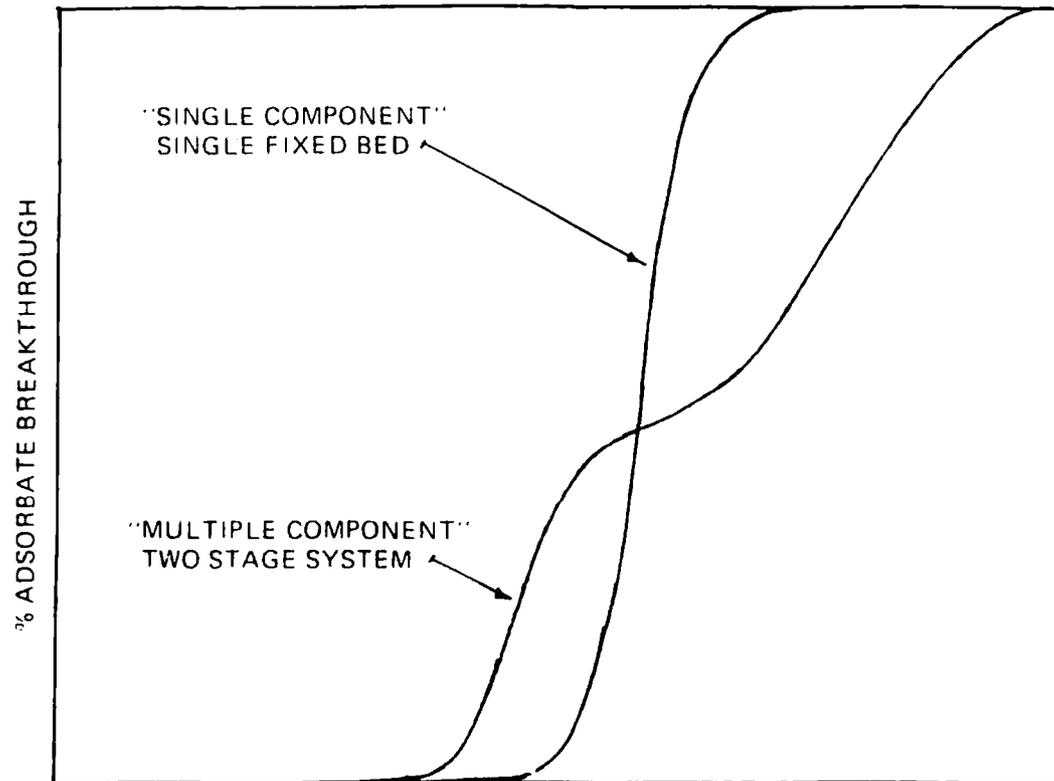
Column study results: breakthrough curves.





Optimum carbon contact time.





Mass transfer zones for two typical breakthrough curves.



ACTIVATED CARBON CLASSES OF ORGANICS COMMONLY REMOVED

In general compounds which are non-polar and of high molecular weight (in the broad range of from four to 20 carbon atoms) are readily removed from wastewater by the activated carbon.

Following classes are commonly adsorbed by carbon:

- o Aromatic Hydrocarbons (benzene, toluene, xylene)
- o Polynuclear Aromatic (naphthalene, anthracene, biphenyls)
- o Chlorinated Aromatics (chlorobenzene, polychlorinated biphenyls, aldrin, endrin, toxaphene, DDT)
- o Phenolics (phenol, cresol, resorcinol and polyphenyls such as tannin and lignin derivatives)
- o Chlorinated Phenolics (trichlorophenol, pentachlorophenol)
- o High Molecular Weight Aliphatic and Branch Chain Hydrocarbons (gasolene, kerosene)
- o Chlorinated Aliphatic Hydrocarbons (carbon tetrachloride, perchloroethylene)
- o High Molecular Weight Aliphatic Acids and Aromatic Acids (tar acids, 2,4-dichlorobenzoic acid, sulfonated lignins, benzoic acid)
- o High Molecular Weight Aliphatic Amines and Aromatic Amines (aniline, toluene diamine)
- o High Molecular Weight Ketones, Esters, Ethers and Alcohols (hydroquinone, polyethylene glycol)
- o Surfactants (alkyl benzene sulfonates, linear alcohol sulfates)
- o Soluble Organic Dyes (methylene blue, Indigo carmine, Benzopurpurin 4B Phthalocyanines)

Source Calgon Bulletin



AMENABILITY OF TYPICAL ORGANIC COMPOUNDS TO ACTIVATED CARBON ADSORPTION

Compound	Molecular weight	Aqueous solubility (%)	Concentration (mg/l)		Adsorbability	
			Initial (C.)	Final (C.)	g compound/ g carbon	Percent reduction
Alcohols						
Methanol	32.0	∞	1,000	964	0.007	3.6
Ethanol	46.1	∞	1,000	901	0.020	10.0
Propanol	60.1	∞	1,000	811	0.038	18.9
Butanol	74.1	7.7	1,000	466	0.107	53.4
n-Amyl alcohol	88.2	1.7	1,000	282	0.155	71.8
n-Hexanol	102.2	0.58	1,000	45	0.191	95.5
Isopropanol	60.1	∞	1,000	874	0.025	12.6
Allyl alcohol	58.1	∞	1,010	789	0.024	21.9
Isobutanol	74.1	8.5	1,000	581	0.084	41.9
t-Butanol	74.1	∞	1,000	705	0.059	29.5
2-Ethyl butanol	102.2	0.43	1,000	145	0.170	85.5
2-Ethyl hexanol	130.2	0.07	700	10	0.138	98.5
Aldehydes						
Formaldehyde	30.0	∞	1,000	908	0.018	9.2
Acetaldehyde	44.1	∞	1,000	881	0.022	11.9
Propionaldehyde	58.1	22	1,000	723	0.057	27.7
Butyraldehyde	72.1	7.1	1,000	472	0.106	52.8
Acrotoin	56.1	20.6	1,000	694	0.061	30.6
Crotonaldehyde	70.1	15.5	1,000	544	0.092	45.6
Benzaldehyde	106.1	0.33	1,000	60	0.188	94.0
Paraldehyde	132.2	10.5	1,000	261	0.148	73.9
Amines						
Di-N Propylamine	101.2	∞	1,000	198	0.174	80.2
Butylamine	73.1	∞	1,000	480	0.103	52.0
Di-N Butylamine	129.3	∞	1,000	130	0.174	87.0
Allylamine	57.1	∞	1,000	686	0.063	31.4
Ethylenediamine	60.1	∞	1,000	893	0.021	10.7



AMENABILITY OF TYPICAL ORGANIC COMPOUNDS TO ACTIVATED CARBON ADSORPTION

Compound	Molecular weight	Aqueous solubility (%)	Concentration (mg/l)		Adsorbability*	
			Initial (C _i)	Final (C _f)	g compound/ g carbon	Percent reduction
Diethylenetriamine	103.2	∞	1,000	706	0.062	29.4
Monethanolamine	61.1	∞	1,012	939	0.015	7.2
Diethanolamine	105.1	95.4	996	722	0.057	27.5
Triethanolamine	149.1	∞	1,000	670	0.067	33.0
Monoisopropanolamine	75.1	∞	1,000	800	0.040	20.0
Dusopropanolamine	133.2	87	1,000	543	0.091	45.7
Pyridines and morpholines						
Pyridine	79.1	∞	1,000	527	0.095	47.3
2 Methyl 5 Ethyl pyridine	121.2	sl. sol.	1,000	107	0.179	89.3
N Methyl morpholine	101.2	∞	1,000	575	0.085	42.5
N Ethyl morpholine	115.2	∞	1,000	467	0.107	53.3
Aromatics						
Benzene	78.1	0.07	416	21	0.080	95.0
Toluene	92.1	0.047	317	66	0.050	79.2
Ethyl benzene	106.2	0.02	115	18	0.019	84.3
Phenol	94	6.7	1,000	194	0.161	80.6
Hydroquinone	110.1	6.0	1,000	167	0.167	81.3
Aniline	93.1	3.4	1,000	251	0.150	74.9
Styrene	104.2	0.03	180	18	0.028	88.8
Nitrobenzene	123.1	0.19	1,023	44	0.196	95.6
Esters						
Methyl acetate	74.1	31.9	1,030	760	0.054	26.2
Ethyl acetate	88.1	8.7	1,000	495	0.100	50.5
Propyl acetate	102.1	2	1,000	248	0.149	75.2
Butyl acetate	116.2	0.68	1,000	154	0.169	84.6
Primary amyl acetate	130.2	0.2	985	119	0.175	88.0
Isopropyl acetate	102.1	2.9	1,000	319	0.137	68.1



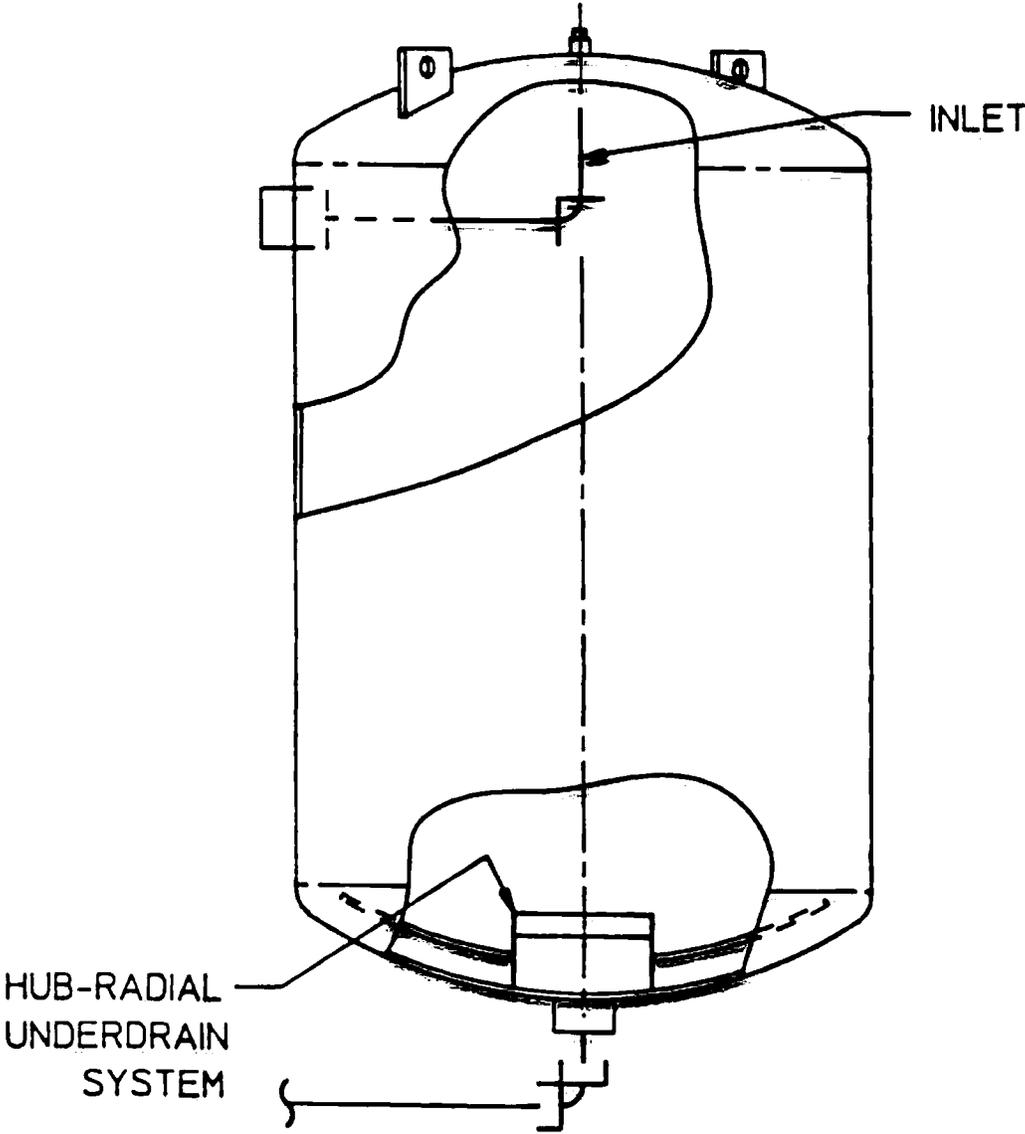
AMENABILITY OF TYPICAL ORGANIC COMPOUNDS TO ACTIVATED CARBON ADSORPTION

Compound	Molecular weight	Aqueous solubility (%)	Concentration (mg/l)		Adsorbability*	
			Initial (C _i)	Final (C _f)	g compound/ g carbon	Percent reduction
Methyl propyl ketone	86.1	4.3	1,000	305	0.139	69.5
Methyl butyl ketone	100.2	v. sl. sol.	988	191	0.159	80.7
Methyl isobutyl ketone	100.2	1.9	1,000	152	0.169	84.8
Methyl isoamyl ketone	114.2	0.54	986	146	0.169	85.2
Diisobutyl ketone	142.2	0.05	300	nil	0.060	100.0
Cyclohexanone	98.2	2.5	1,000	332	0.134	66.8
Acetophenone	120.1	0.55	1,000	28	0.194	97.2
Isophorone	138.2	1.2	1,000	34	0.193	96.6
Organic Acids						
Formic acid	46.0	∞	1,000	765	0.047	23.5
Acetic acid	60.1	∞	1,000	760	0.048	24.0
Propionic acid	74.1	∞	1,000	674	0.065	32.6
Butyric acid	88.1	∞	1,000	405	0.119	59.5
Valeric acid	102.1	2.4	1,000	203	0.159	79.7
Caproic acid	116.2	1.1	1,000	30	0.194	97.0
Acrylic acid	72.1	∞	1,000	355	0.129	64.5
Benzoic acid	122.1	0.29	1,000	89	0.183	91.1
Oxides						
Propylene oxide	58.1	40.5	1,000	739	0.052	26.1
Styrene oxide	120.2	0.3	1,000	47	0.190	95.3

* Dosage — 5 g Carbon C/l solution.



ACTIVATED CARBON
FILTER



Enhanced Oxidation

- Technology Uses “Supercharged” Oxidation to Destroy Organic Compounds into CO_2 , Water, Chlorides, and Smaller Organic Compounds (Where Incomplete Oxidation Occurs.)
- Chemical Oxidants, Such as Hydrogen Peroxide and/or Ozone, are Added to Groundwater in the Presence of UV Light to Create Free Radicals. The Free Radicals Greatly Enhance the Oxidation Rate of the Organic Compounds in the Groundwater. Advanced “Catalysts” May Be Added to Speed Reaction Rates of Refractive Compounds Such as Carbon Tetrachloride, Chloroform, And Trichloroethane.



REACTION RATES OF OZONE AND HYDROXYL
RADICALS WITH VARIOUS CLASSES OF ORGANIC COMPOUNDS

k, in L mole⁻¹ s⁻¹

COMPOUND	O ₃	OH
Olefins	1 to 450 x 10 ³	10 ⁹ to 10 ¹¹
S-containing organics	10 to 1.6 x 10 ³	10 ⁹ to 10 ¹⁰
Phenols	10 ³	10 ⁹
N-containing organics	10 to 10 ²	10 ⁸ to 10 ¹⁰
Aromatics	1 to 10 ²	10 ⁸ to 10 ¹⁰
Acetylenes	50	10 ⁸ to 10 ⁹
Aldehyde	10	10 ⁹
Ketones	1	10 ⁹ to 10 ¹⁰
Alcohols	10 ⁻² to 1	10 ⁸ to 10 ⁹
Alkanes	10 ⁻²	10 ⁶ to 10 ⁹
Carboxylic acids	10 ⁻³ to 10 ⁻²	10 ⁷ to 10 ⁹



Enhanced Oxidation

Successfully Destroyed Contaminants:

Propellants	Freon	TPH
Complexed Cyanides	BETXs	Dioxins,
Furans	MTBE	Pesticides
DDT	2,4D	Ethanol
Dinoseb	Roundup	Methanol
PAHs	Mercaptans	Hydrazines
Solvents	PCP	Chlorinated Solvents
H ₂ S	Ordnance Compounds:	Color Organic Dyes
TNT	Phenols	- DNT
PCBs	- NG	Glycol
- TMETN	Ketones	Alehydes
- TEGDN	Citric Acid	- PGDN

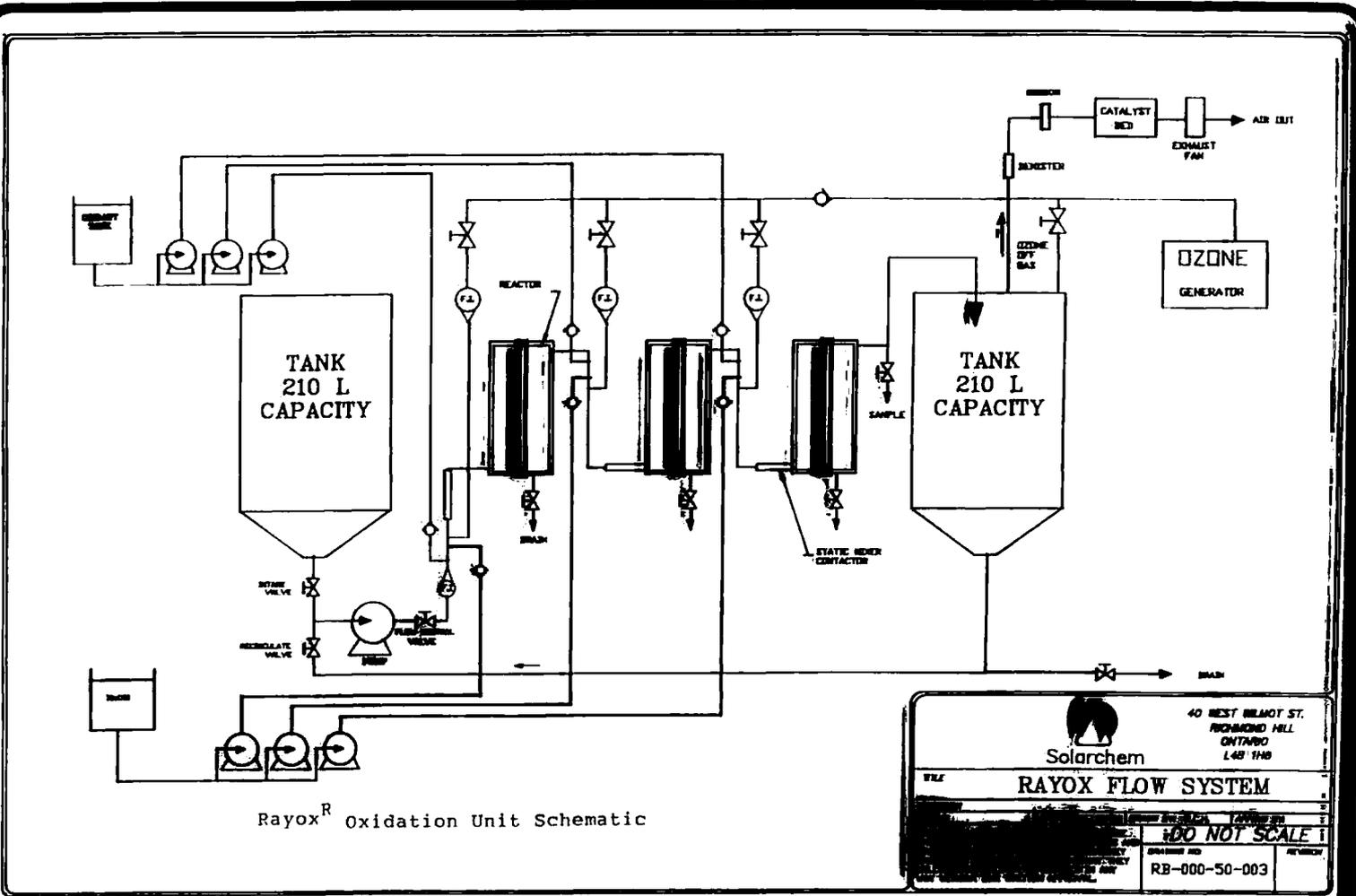


Enhanced Oxidation

Typical Treatment Systems Include:

- Annular Reactor(s) in Series
- High Intensity UV Lamp(s) at Center of Reactor
- Quartz Sleeves Surrounding Lamp(s)
- Stainless Steel Construction
- Chemical Addition Systems
- O₃ Venting System
- Tankage





Groundwater Monitoring and Remediation Techniques Short Course

Enhanced Oxidation

Advantages:

- No Toxics are Emitted to Air
- No Toxics are Adsorbed onto Media Requiring Landfilling or Regeneration
- Does Not Merely Concentrate Contaminants
- Effective for Wider Range of Contaminants Than Biotreatment
- Can Be Run Intermittently



Enhanced Oxidation

Site 1

Treatment Time (Minutes)	Chemical (ppb)
02.55	PCE704 ND ND
1,1 - DCE	263 ND ND
Freon - TF717553	
TCE	54 ND ND
1,1,1 - TCA-2920	

UV Dose:	160 Watt/l
H ₂ O ₂ Dose:	7 mg/l/min
Oxidation Time:	2.5 minutes
Flow Rate:	400 GPM
Cost/1000 gallons:	\$1.37



Enhanced Oxidation

Site 2

	Treatment Time (Minutes)	Chemical (ppb)
024 TCE	1924	57 ND
trans 1,2 -DCE	198 ND	ND

UV Dose: 160 Watt/l
H₂O₂ Dose: 10 mg/l/min
Oxidation Time: 4 minutes
Flow Rate: 40 GPM
Cost/1000 gallons: \$2.08



Enhanced Oxidation

Site 3

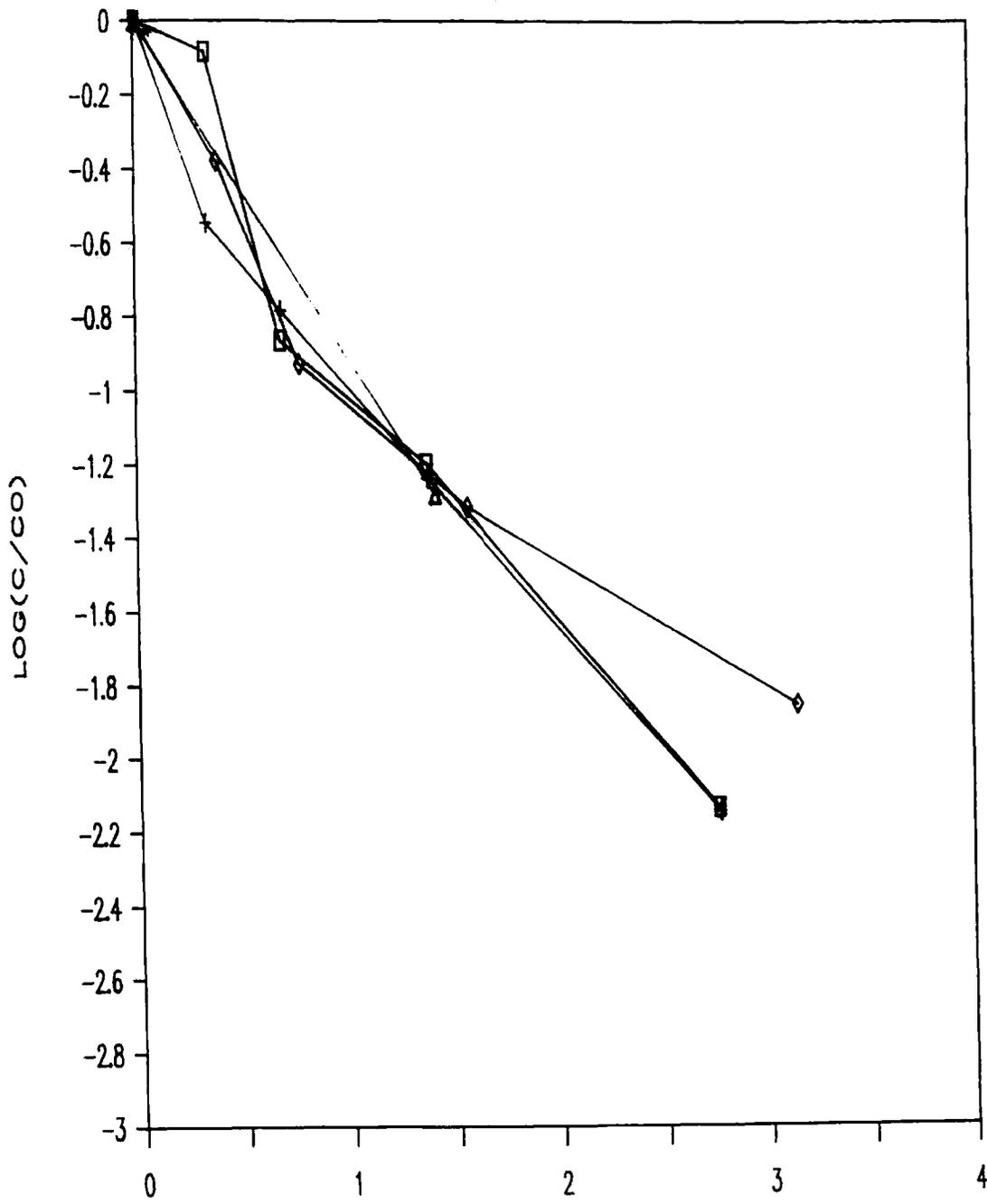
Treatment Time (Minutes)	Chemical (ppb)
01545 Chloroform 7900	2300 38
1,2 -DCA 16900110ND	Meth Chloride 3000
230 ND Carbon Tet-45	ND 1,1,1 - TCA -56
ND	

UV Dose:	160 Watt/l
H ₂ O ₂ Dose:	150 mg/l/min
Oxidation Time:	45 minutes
Flow Rate:	15 GPM
Cost/1000 gallons:	\$15.20



LEACHATE

TOTAL VOC



RUNS 6,8,9

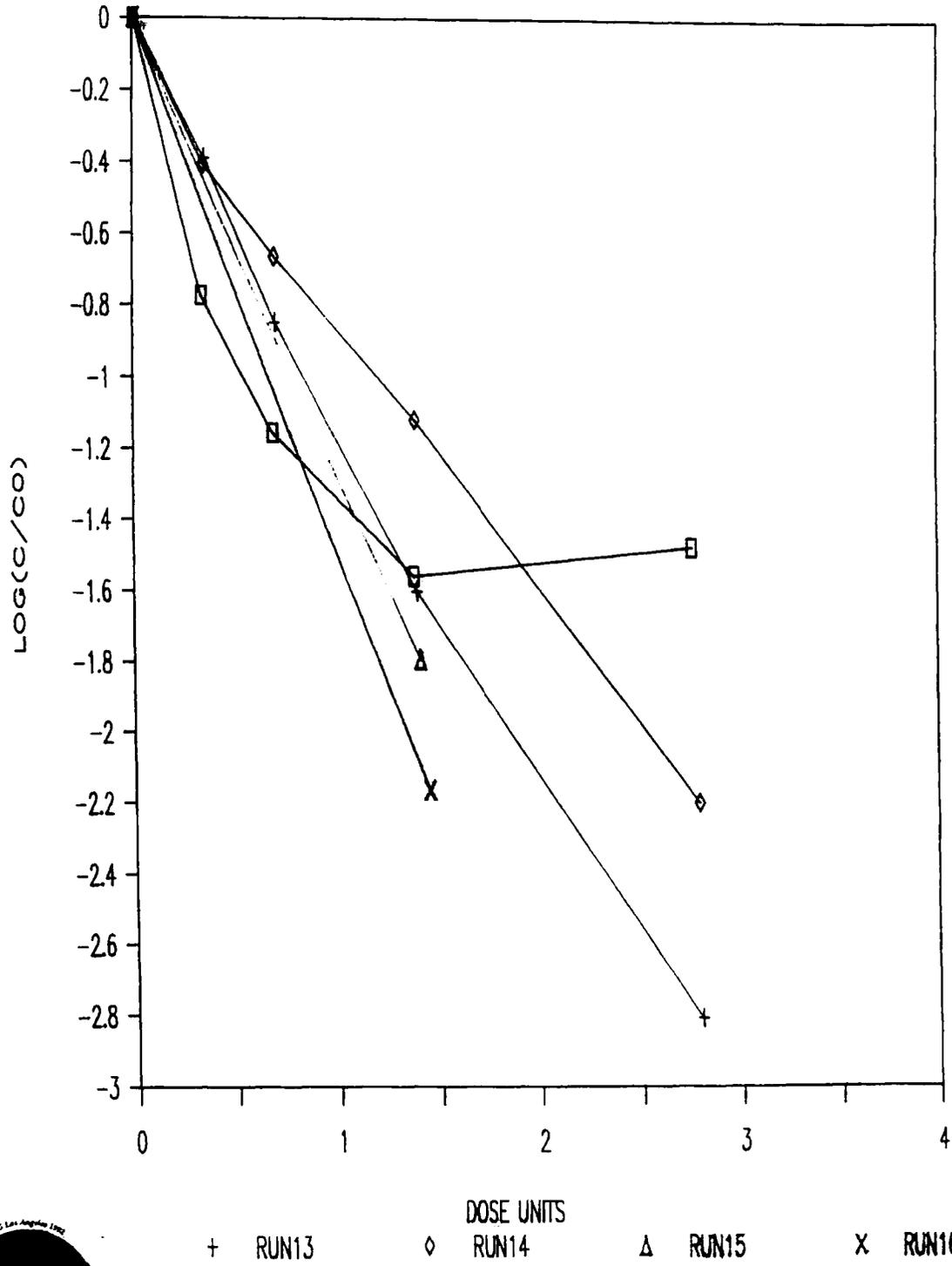
+ RUN 7

◇ RUN 10

△ RUN 11

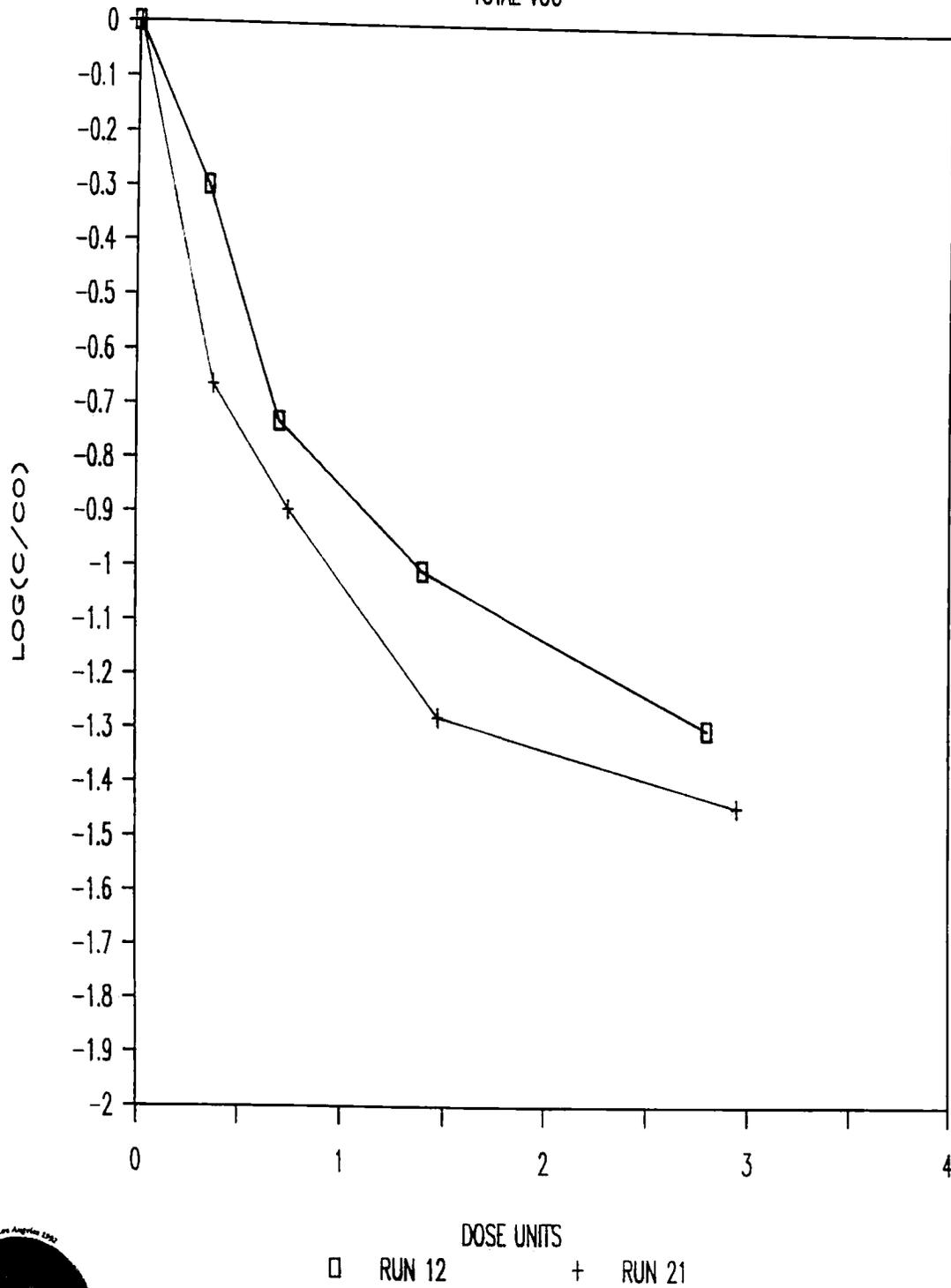
PERMEATE

TOTAL VOC



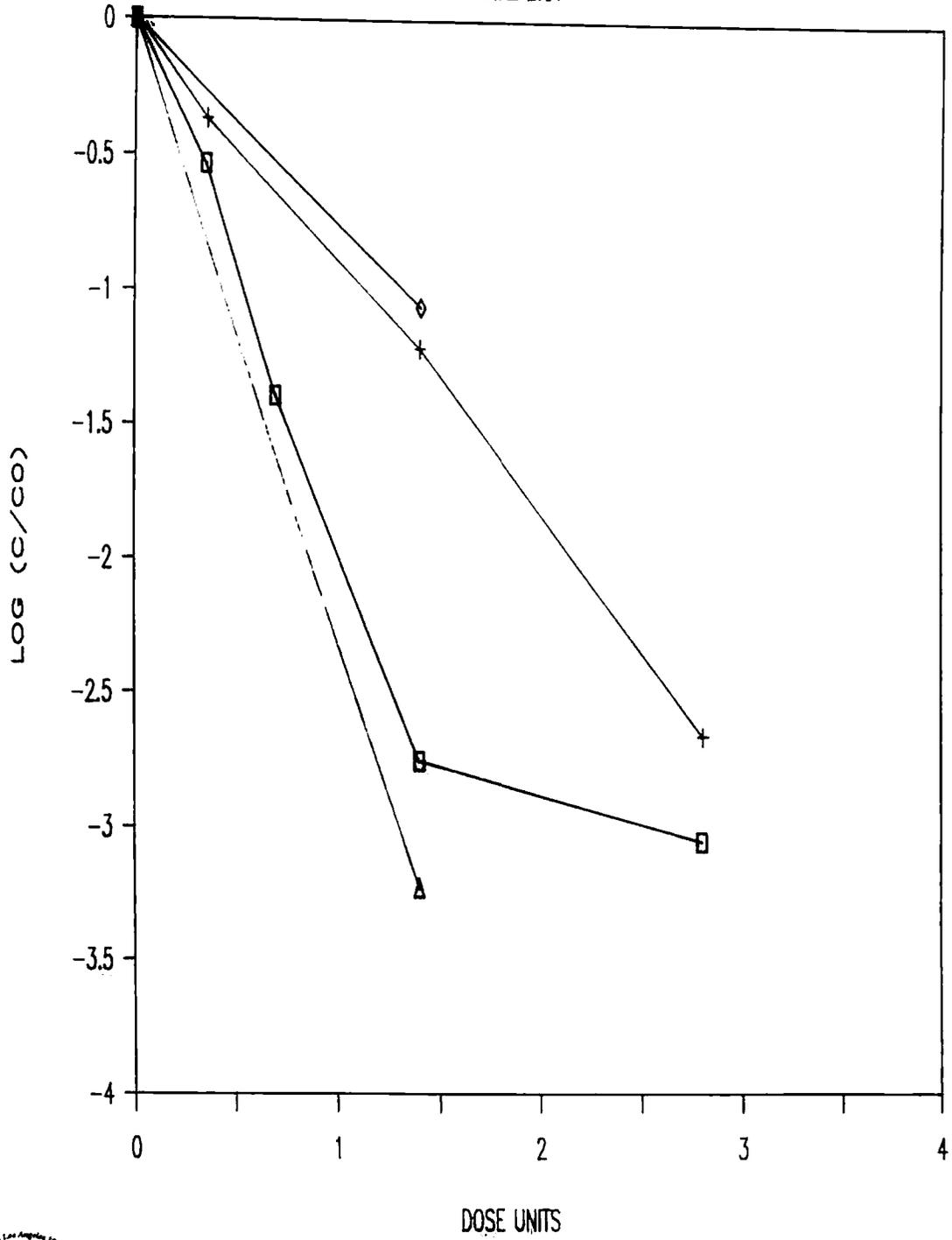
CONCENTRATE

TOTAL VOC



PERMEATE

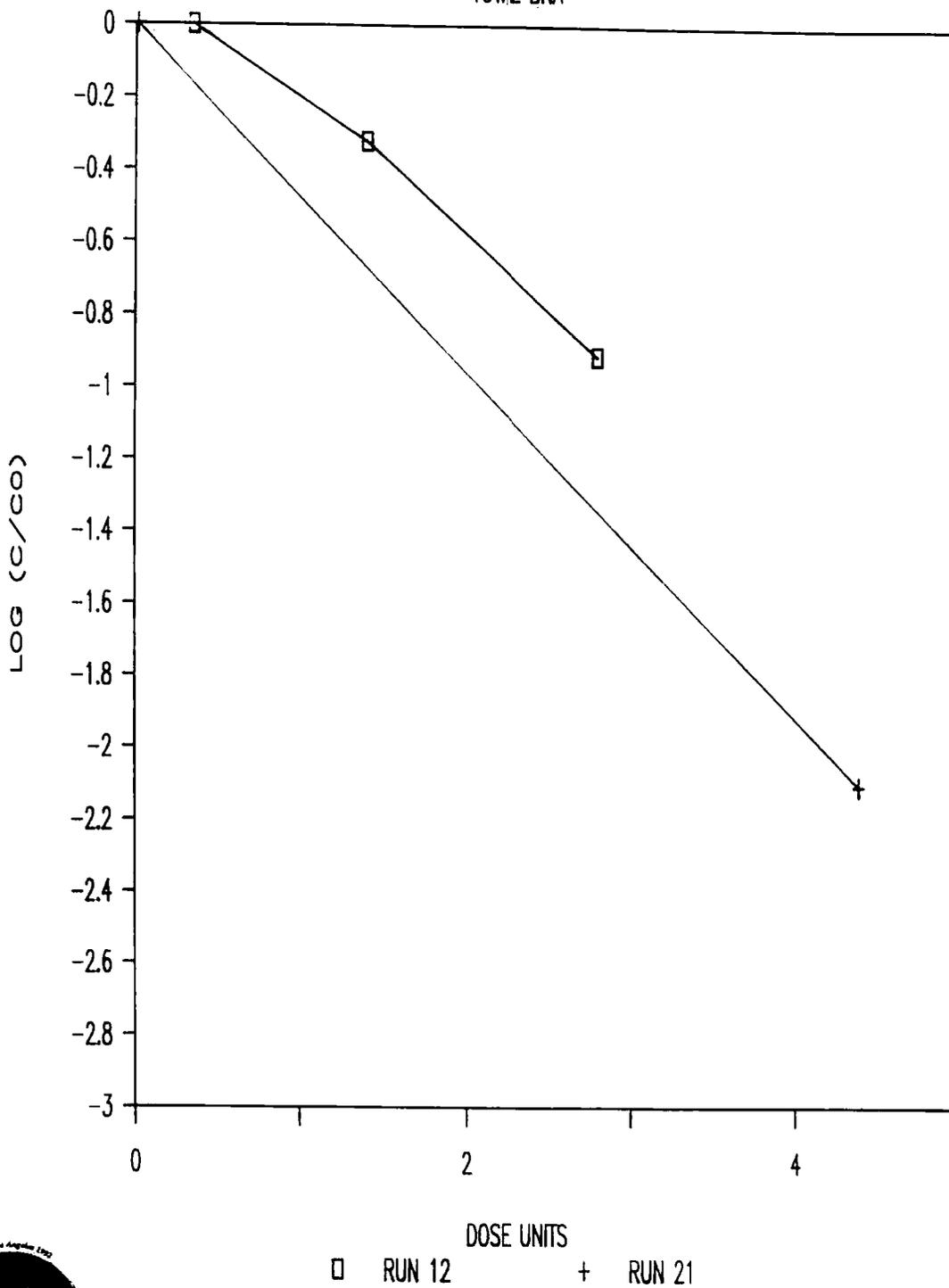
TOTAL BNA



RUN 13 + RUN 14 ◇ RUN 15 Δ RUN 16

CONCENTRATE

TOTAL BNA



Enhanced Reduction

Works on the Premise That Difficult to Oxidize Substances May Be Easy to Reduce.

Technology Uses the Hydrated Electron as a Reducing Agent to Photodegrade Refractory Substances, Such As Chloroalkanes, Aliphatic Ketones, and Some Nitro Compounds.

The Reaction Rate Constants of Hydrated Electrons are Higher Than the Rate Constants of the Free Radicals with Chloroalkanes. The Difference Increases with Increasing Number of Chlorine Atoms.

The Technology Can Be Combined With and Can Follow Enhanced Oxidation.



Comparison of rate constants for the hydroxyl radical
and the hydrated electron with chloro-organic
compounds

Pollutant	Rate Constant / $10^9 \text{M}^{-1} \text{s}^{-1}$	
	hydrated electron	hydroxyl radical
CH_2Cl_2	6.3	0.058
CHCl_3	30	~0.005
CCl_4	16	~0.001
$\text{CH}_2=\text{CCl}_2$	23	6.8
$\text{CHCl}=\text{CCl}_2$	19	4.2



Enhanced Reduction

*Photodegradation Usually Follows
First-Order Kinetics*

$$EE/O = \frac{3785 P (t / 60)}{V \log (c_i / c_f)}$$

EE/O = Electrical energy per order or the electrical energy (kWh) to reduce the concentration of a pollutant by one order of magnitude in 1000 gallons (3785 liters)

- P = lamp power in (kW)
- t = Irradiation time (minutes)
- V = Reactor volume (liters)
- c_i = Initial concentration
- c_f = Final concentration



Enhanced Reduction

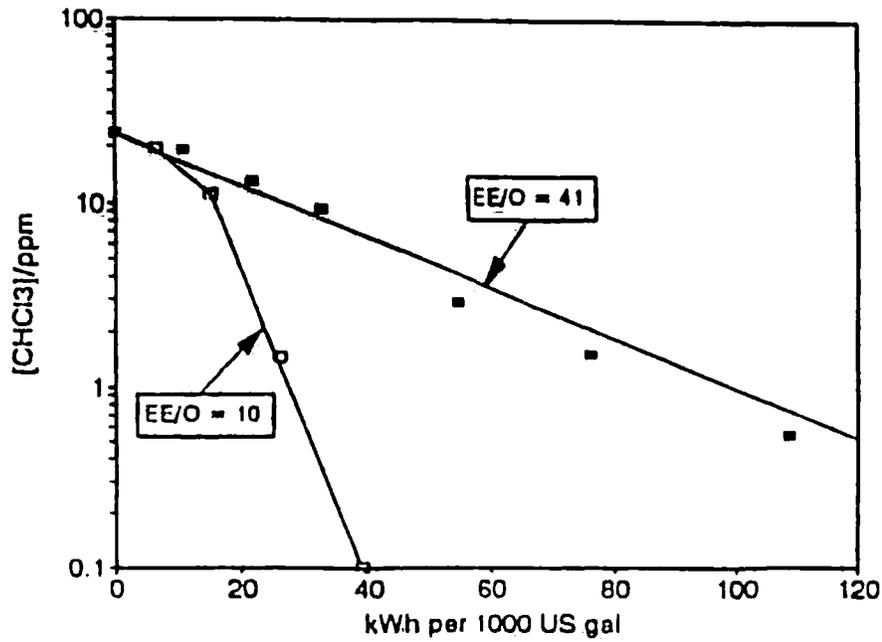
EE/O is Related to the First-Order Rate Constant, k (min^{-1}), by:

$$k = \frac{145.25 P}{V (EE/O)}$$

EE/O Values < 10 Are Very Good.



COMPARISON OF Rayox[®] AND Rayox[®] R TREATMENT OF CHCl₃



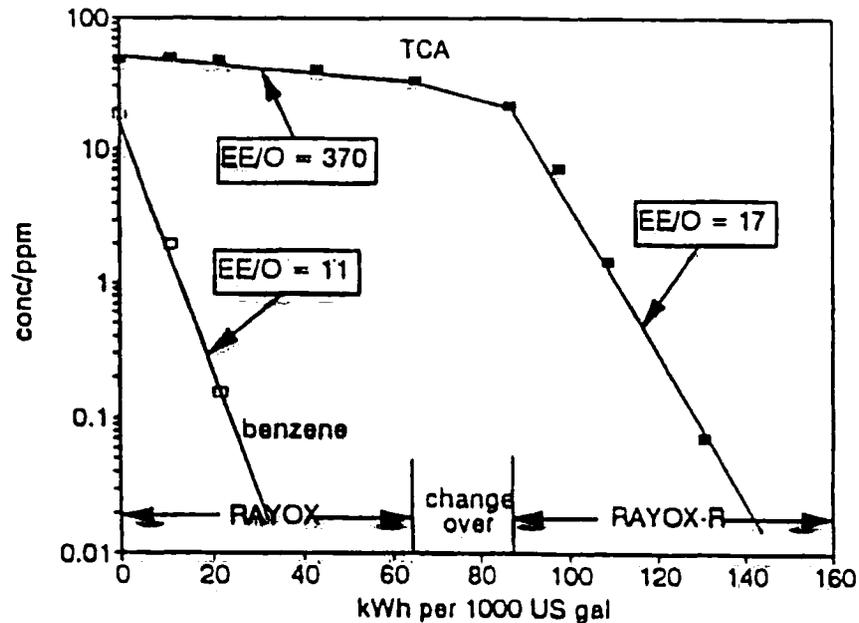


Figure 3 shows an example where a mixture of benzene (20 ppm) and trichloroethane (TCA) is subjected to a sequential Rayox® /Rayox® R treatment. In the Rayox® phase (0- 65 kWh per 1000 USgal), the benzene treats very well (EE/O = 11), while the TCA is hardly treated at all (EE/O = 370). However, after the switch-over to the Rayox® R process, the TCA treats very well (EE/O = 17).