The Effect of Volatile Organic Compounds on GAC Adsorbers

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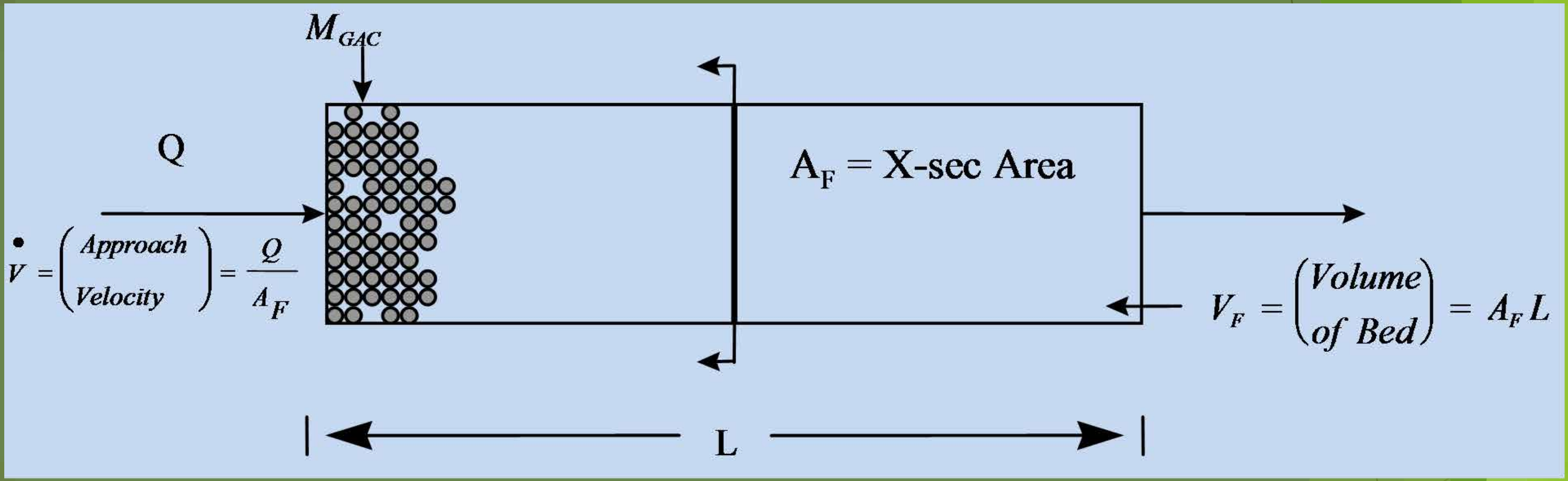
OUTLINE

- Important design parameters for fixed-bed adsorbers
- Methods for obtaining important design parameters
- Model predictions for a variety of VOCs & SOCs and water sources using the PSDM
- Analysis of VOC removal using GAC
- GAC costs for removal of VOCs.

Important Variables in Fixed-bed Adsorption

GAC Adsorber size is quantified in terms of Empty Bed Contact Time.



$$\begin{pmatrix} \text{Empty Bed} \\ \text{Contact Time} \end{pmatrix} = EBCT = \frac{V_F}{Q} = \frac{A_F L}{\dot{V} A_F} = \frac{L}{\dot{V}}$$

5 - 30 minutes

Important Variables in Fixed-bed Adsorption

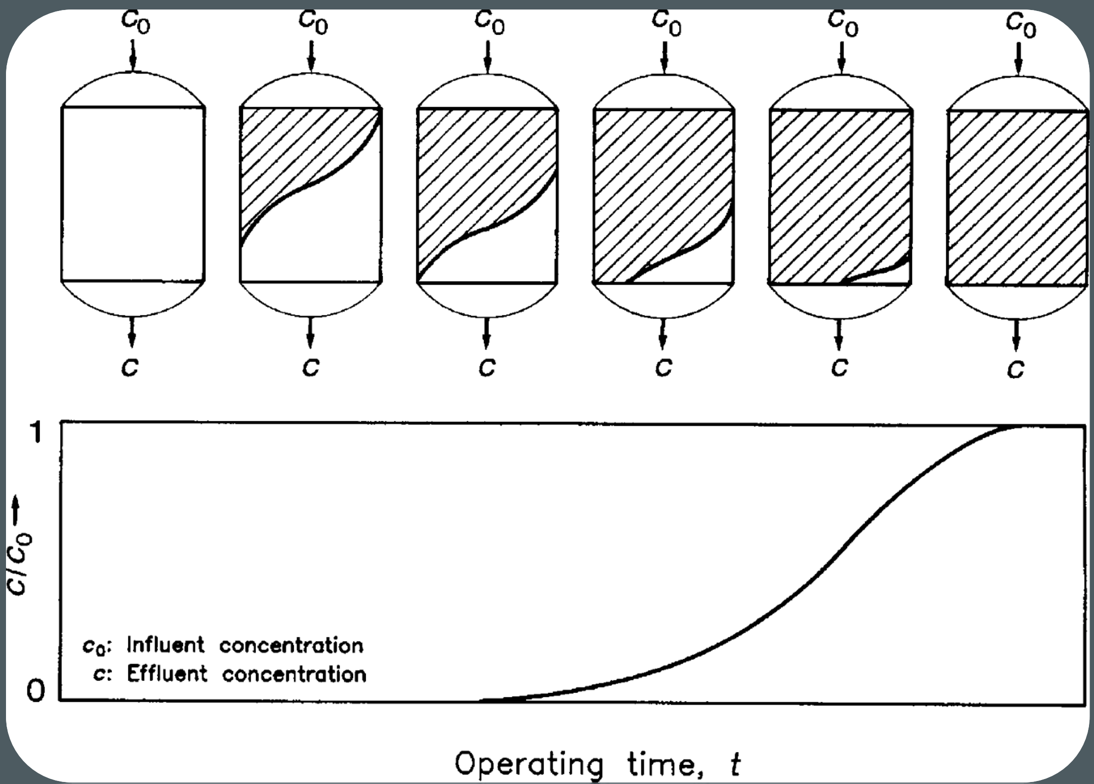
GAC Adsorber performance is quantified in terms of specific throughput. Defined as the volume fed to the adsorber divided by the mass of GAC in the adsorber.

$$\left(\begin{array}{l}\text{Specific}\\ \text{Throughput}\end{array}\right) = \frac{Qt}{M_{GAC}}$$

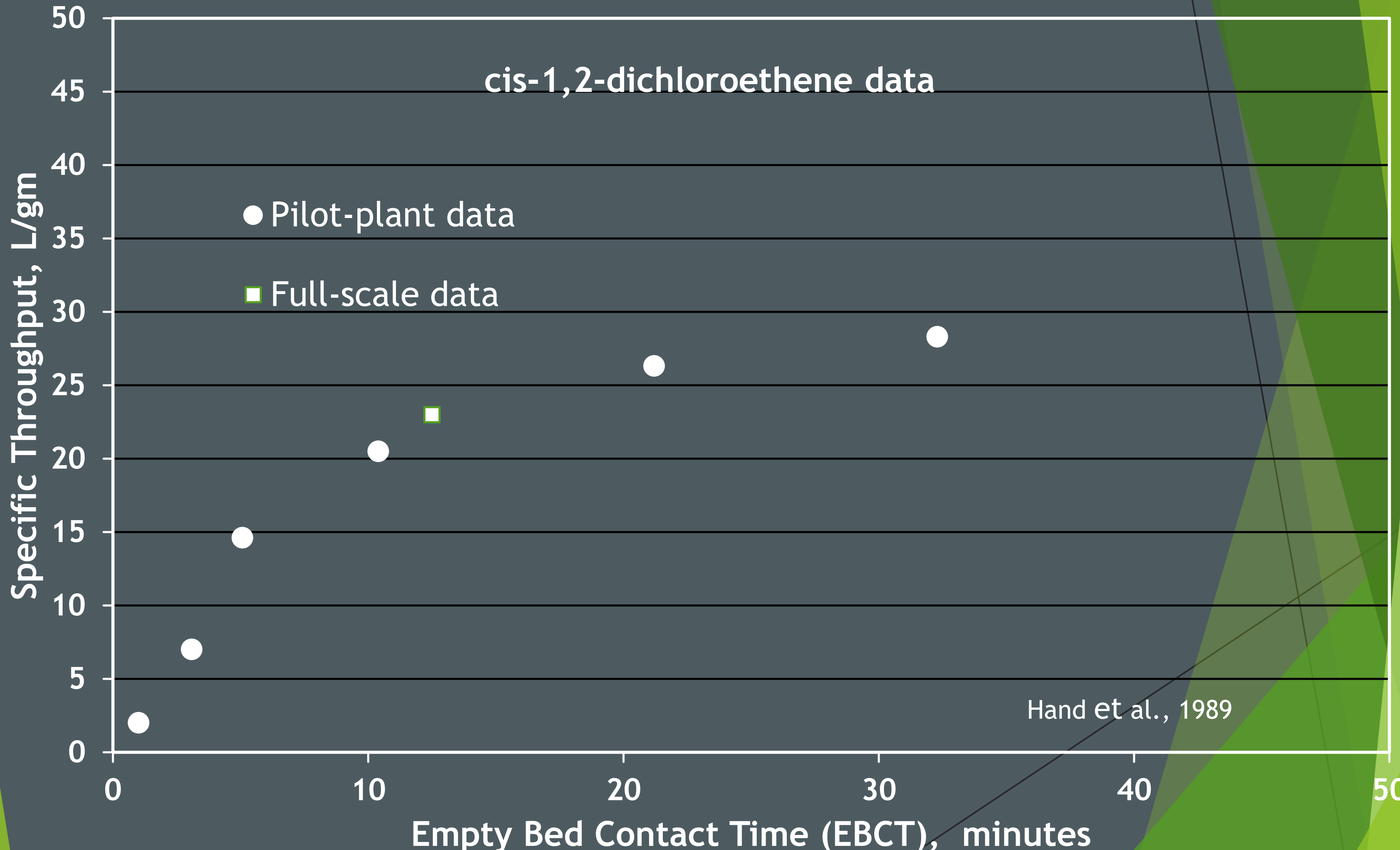
Another more common way to quantify the performance of a GAC adsorber is in terms of GAC usage rate.

$$\left(\begin{array}{l}\text{GAC}\\ \text{Usage Rate}\end{array}\right) = \frac{M_{GAC}}{Qt} = \frac{1}{\left\{\begin{array}{l}\text{Specific}\\ \text{Throughput}\end{array}\right\}}$$

Breakthrough Characteristics of Fixed-Bed GAC Adsorber



Relationship Between Specific Throughput & EBCT



Methods for Obtaining Breakthrough Characteristics

- **Full-Scale Studies**
- **Pilot-Plant Studies**
- **Rapid Small Scale Column Studies (RSSCTs)**
- **Mathematical Models**

Methods for Obtaining Breakthrough Characteristics

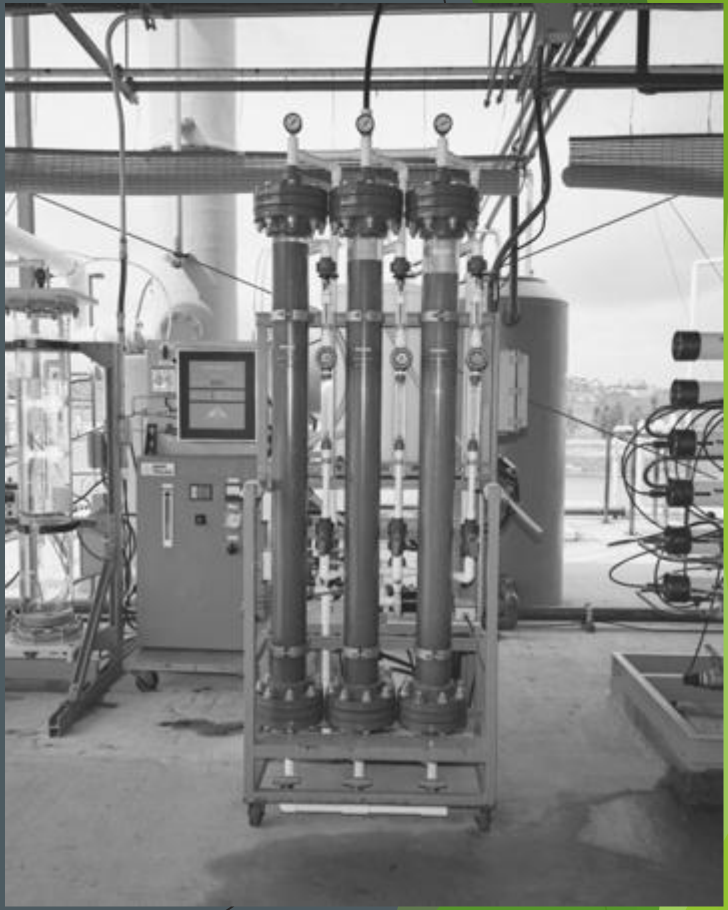
Full-Scale Studies:

- **Most effective method**
- **Most expensive**
- **Most time consuming**

Methods for Obtaining Breakthrough Characteristics

Pilot Plant Studies:

- Effective method
- Expensive
- Time consuming



Methods for Obtaining Breakthrough Characteristics

RSSCT Studies:

- Somewhat effective method
    - (Need scaling factor)
- Cost can be reasonable
- Short time (1 wk – 1 month)

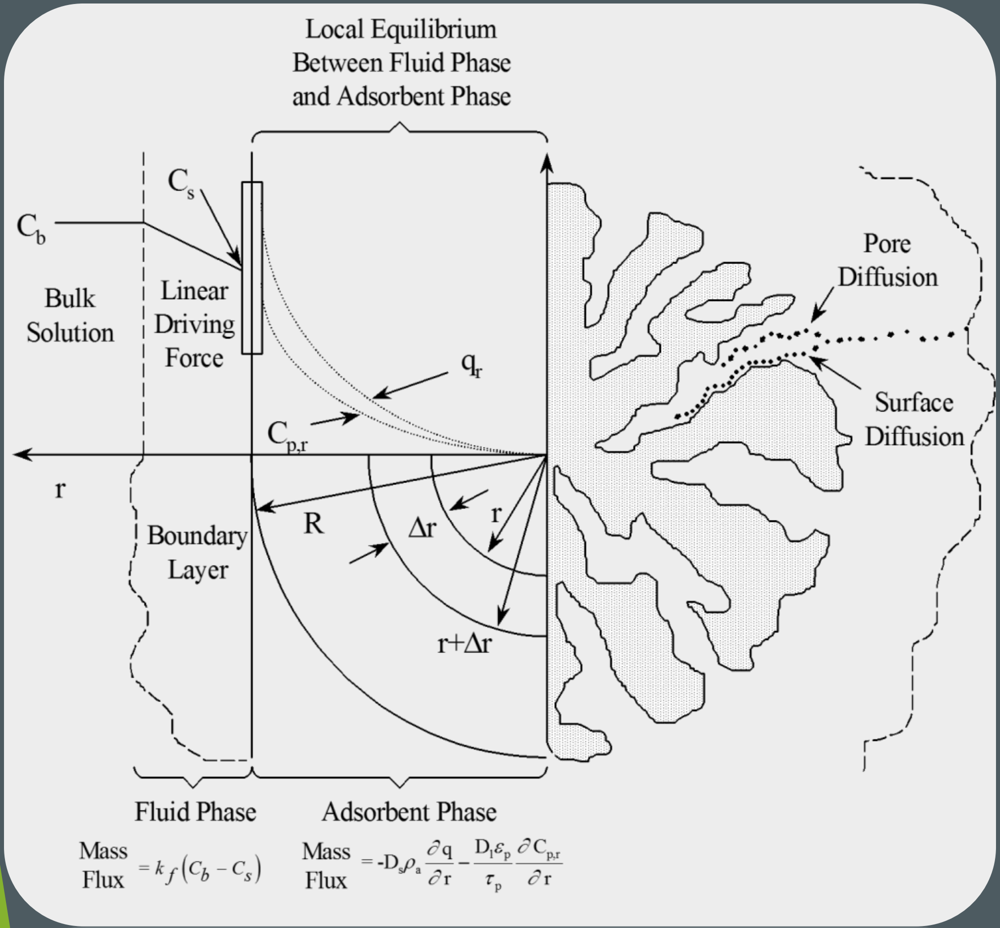
Methods for Obtaining Breakthrough Characteristics

Mathematical Model:

- Somewhat effective method
- Least Expensive
- Least Time Consuming

Pore Surface Diffusion Model (PSDM)

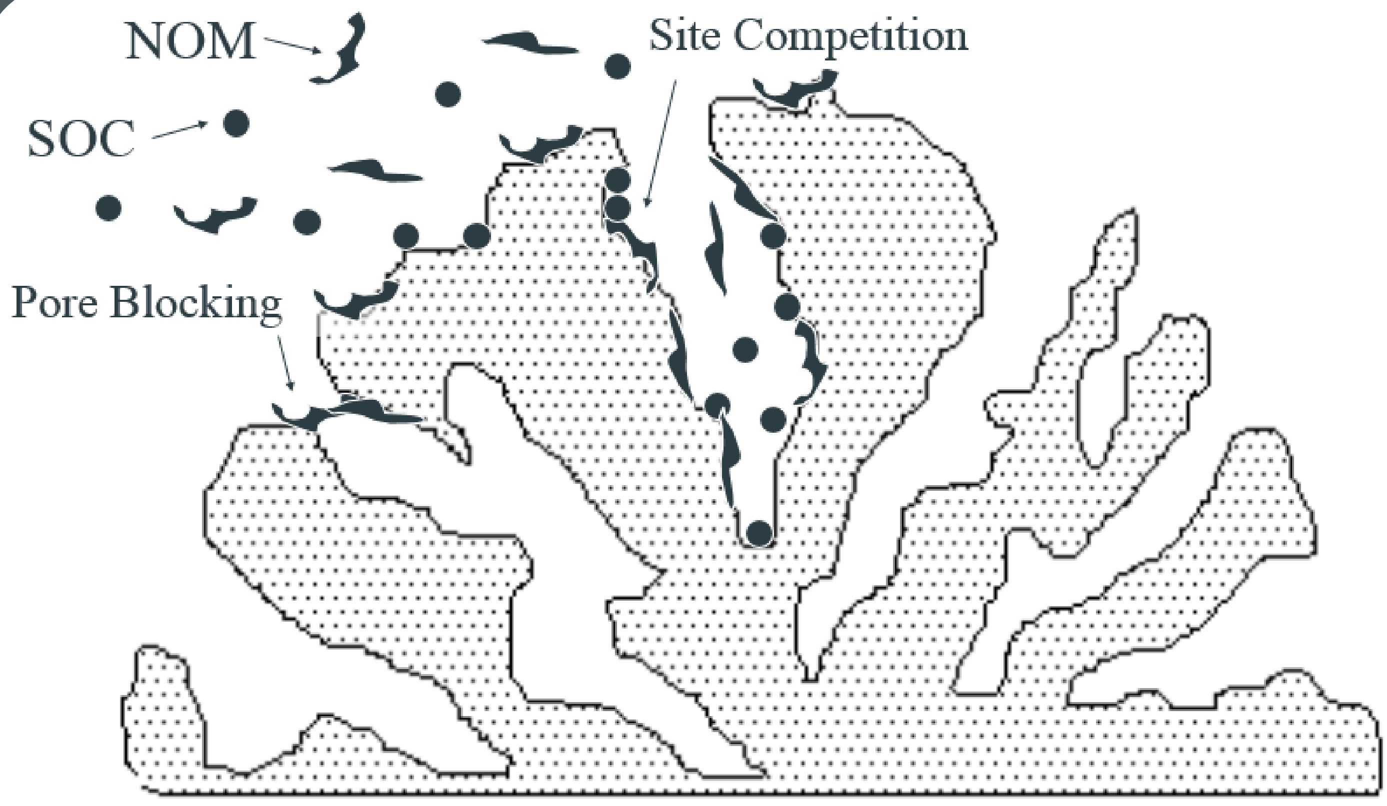
Schematic of Intraparticle Mass Transport Mechanisms:



Intraparticle Mass Transport Mechanisms & Assumptions:

- Diffusion resistance in the liquid-phase surrounding the adsorbent particles and may be described by a linear driving force approximation.
- Diffusion resistance within the adsorbent particle is described by Fick’s law. Intraparticle mass transport is by both surface and pore diffusion.
- There is no channeling.
- Ideal Adsorbed Solution Theory (IAST) describes the competitive equilibrium.

MECHANISMS of NOM Interference with VOC Adsorption



Model Parameters influenced by NOM Fouling

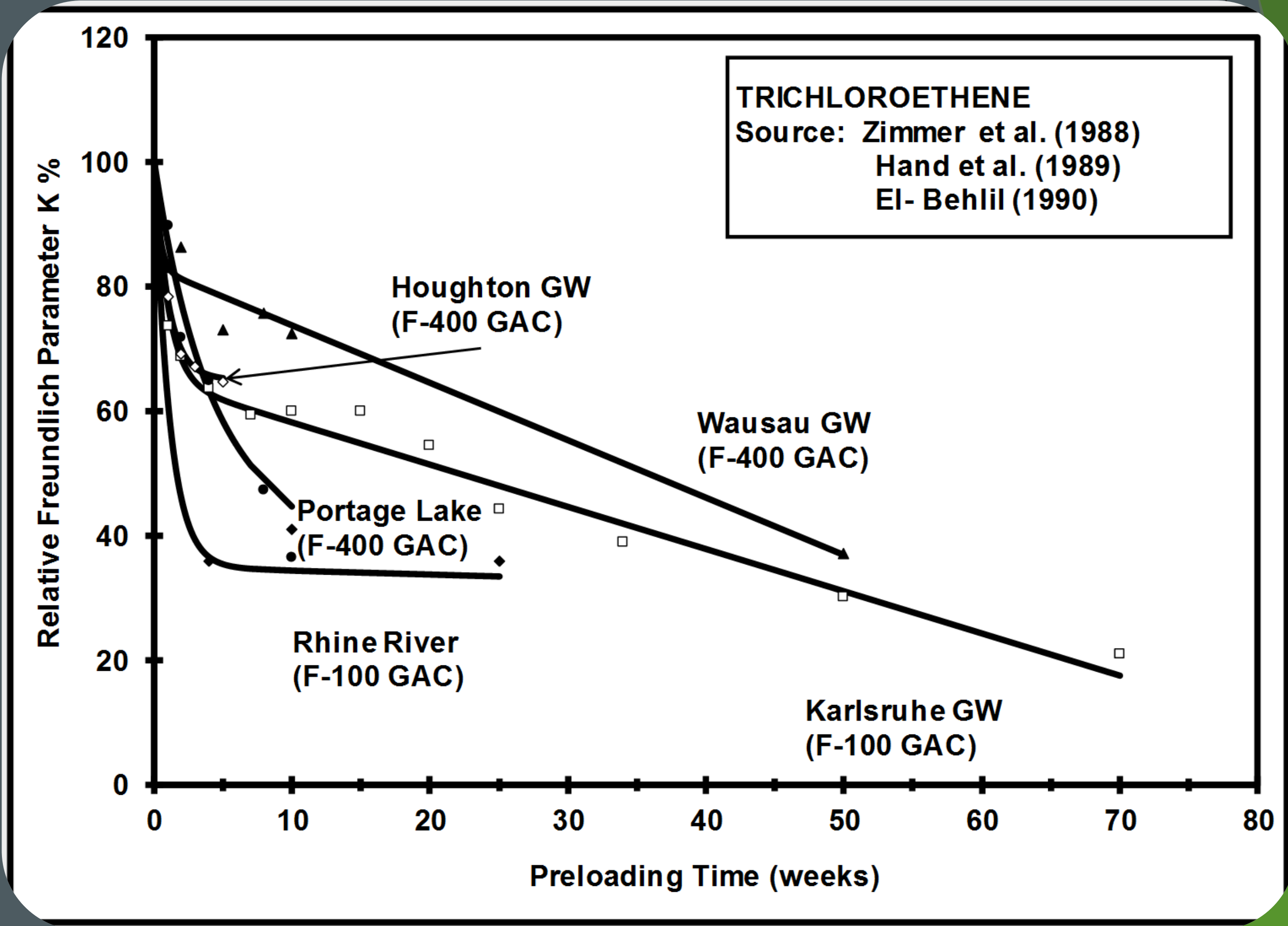
Freundlich Capacity Parameter, K

Surface Diffusion Coefficient: D_S

Pore Diffusion Coefficient: D_P

Effect of Water Type (Background Matrix) (Sontheimer et al, 1988)

$$\left\lfloor \frac{K(t)}{K} \right\rfloor_{TCE} = 0.01 * [A1 - A2 * t + A3 * \exp(-A4 * t)]$$



Effect of Compound Type (Sontheimer et al, 1988)

$$\frac{K(t)}{K} = B_1 \times \left[\frac{K(t)}{K} \right]_{TCE} + B_2$$

Correction Factors for the Reduction in Freundlich Isotherm Capacity Parameters for Different Classes of Compounds Relative to the Reference Compound of TCE				
Class	Group	Surrogate Compound	B_1	B_2
Purgeables	Halogenated Alkanes	1,1,1-Trichloroethane	1.2	-0.2
	Halogenated Alkenes	Trichloroethene	1	0
	Trihalo-methanes	Chloroform	1	0
	Aromatics	Toluene	0.9	0.1
Base Neutrals	Nitro Compounds	3,4-Dinitrotoluene	0.75	0.25
	Chlorinated Hydrocarbons	1,4-Dichlorobenzene	0.59	0.41
Acids	Phenols	2,4-Dichlorophenol	0.65	0.35
Polynuclear-Aromatics (PNAs)		Methylene Blue	0.32	0.68
Pesticides		Atrazine	0	0.05

Impact on Intraparticle Mass Transfer

- Surface Diffusion Coefficient becomes negligible

- Intraparticle Pore Diffusion Coefficient

$$D_p = \frac{D_l}{\tau_p}$$

– VOCs in the Presence of NOM:
  - $\tau_p = 1.0$ when Time < 70 days
  - $\tau_p = 0.334 + 6.61(10^{-6}) * t$ when Time > 70 days

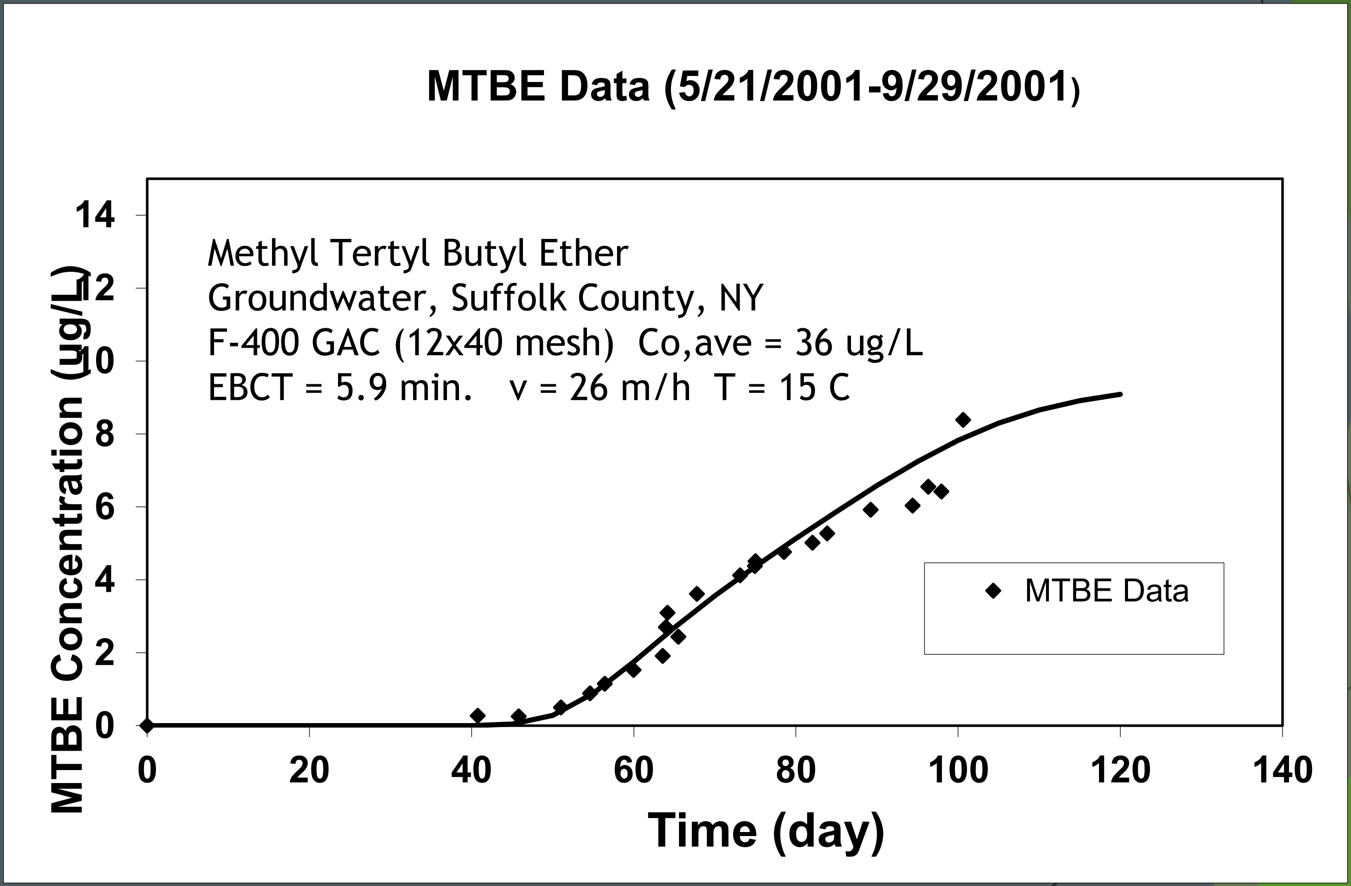
Factors Influencing VOC Adsorption in the Presence of NOM

- Preloading Time
- Adsorbent type
- Source Water
  - Solution chemistry
  - NOM molecular weight distribution
- Solute Type

MODEL VERIFICATION EFFORT

- 13 Case Studies
  - 10 Pilot Plant Experiments
  - 3 Full-Scale Plants
- 13 Water Sources
  - 10 Groundwaters
  - 3 Surface Waters
- 5 Adsorbents
- 50 Empty Bed Contact Times
- 16 Volatile & Synthetic Organic Chemicals

MTBE: PSDM PREDICTION - KARLSRUHE TAP WATER CORRELATION

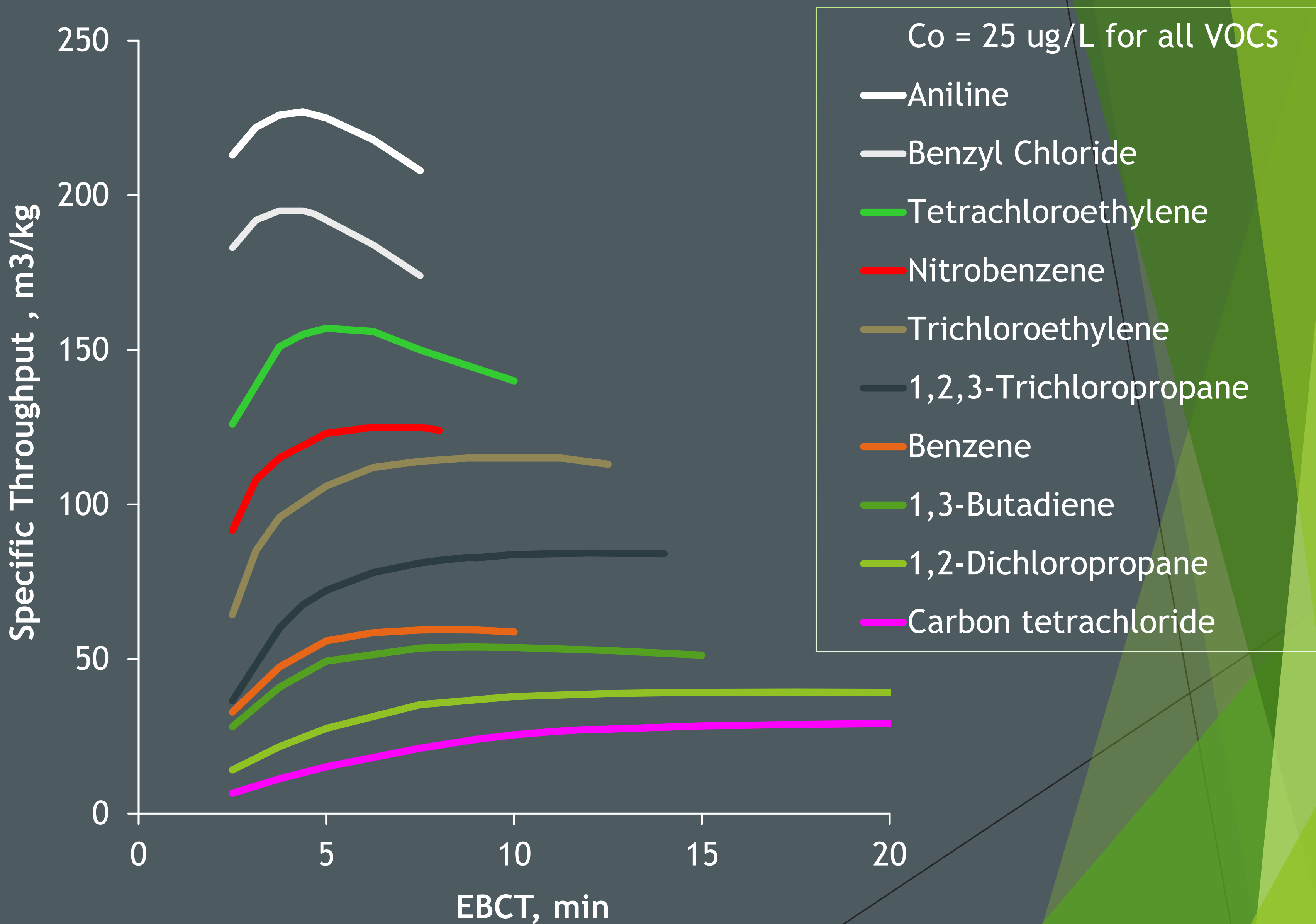


Summary Table of VOCs and their Freundlich Isotherm Parameters

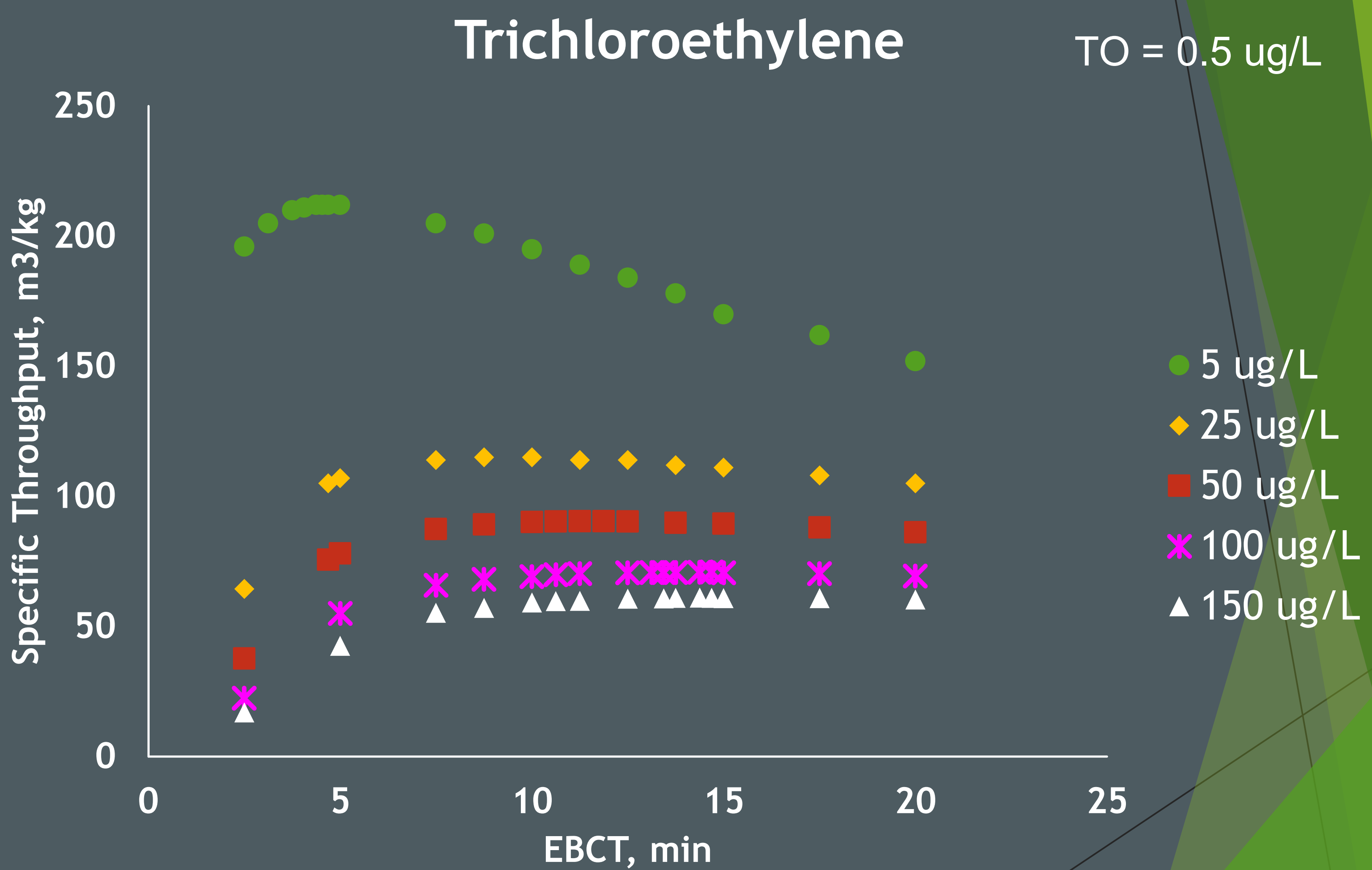
Compound	$K(mg/g*(L/mg)^{1/n})$	1/n	Source
aniline	63.4	0.2	Valderrama, 2010
benzyl chloride	144.42	0.346	Polanyi Estimation
tetrachloroethylene	245.6	0.458	Crittenden et al., 1985
nitrobenzene	61.67	0.417	Polanyi Estimation
trichloroethylene	60.1	0.416	Crittenden et al., 1987
1,2,3-trichloropropane	131.4	0.73	Speth et al., 1988
Benzene	17.8	0.398	Crittenden et al., 1987
1,3-butadiene	27	0.515	Polanyi Estimation
1,2- dichloropropane	19.3	0.597	Speth & Miltner, 1990
Carbon tetrachloride	17.4	0.63	Crittenden et al, 1987
vinyl chloride	7.77	0.683	Polanyi Estimation
1,2-dichloroethane	11.8	0.832	Crittenden 1987
dichloromethane	2.339	0.79	Khan, 2010
urethane	1.46	0.581	Polanyi Estimation
oxirane, methyl	0.063	0.869	Polanyi Estimation

Calgon F400 carbon and isotherm temperature range 16 – 20 C

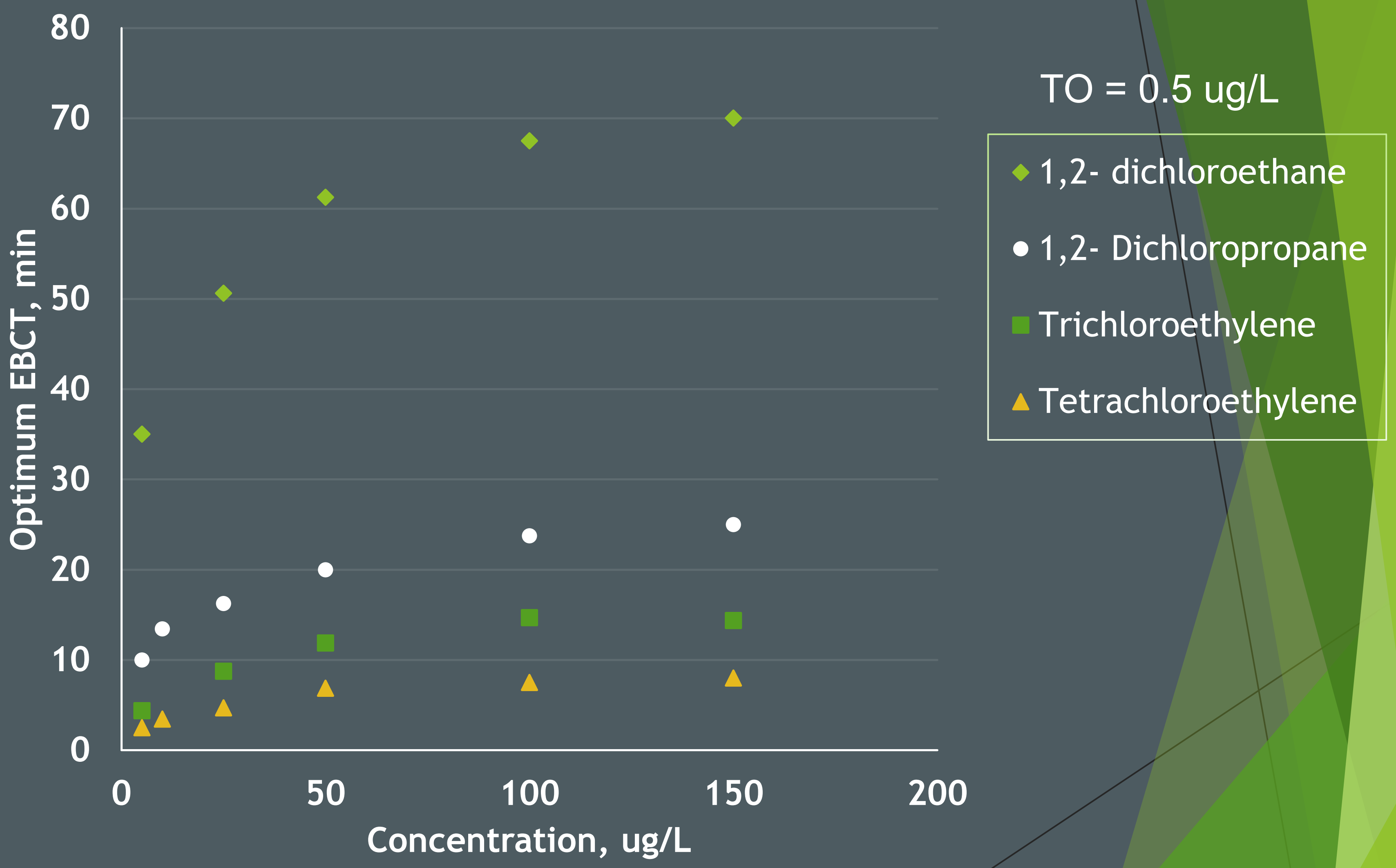
Relationship between Specific Throughput and EBCT



Impact of Initial Concentration on Specific Throughput and EBCT



Relationship between Optimum EBCT and Initial Concentration



Sensitivity of Specific Throughput to Treatment Objective

Sensitivity of Specific Throughput to Treatment Objective

Compound	Co, ug/L	% change in carbon usage rate	
		TO 5 to 1 ug/L	TO 5 to .5 ug/L
Tetrachloroethylene	25	19	25
	10	28	36
	8	29	38
1,2-Dichloropropane	25	11	14
	10	21	25
	8	26	30

TO = Treatment Objective

Summary GAC Replacement Costs

Compound	C_o µg/L	Optimum EBCT, min	GAC Cost = $/1000 gal		
			MCL = 5 µg/L	MCL = 1.0 µg/L	MCL = 0.5 µg/L
aniline	25	4.4	0.049	0.054	0.055
benzyl chloride	25	4.0	0.053	0.062	0.064
tetrachloroethylene	25	5.0	0.062	0.075	0.081
nitrobenzene	25	6.0	0.081	0.098	0.100
trichloroethylene	25	9.0	0.087	0.105	0.109
1,2,3-trichloropropane	25	12.0	0.113	0.139	0.148
Benzene	25	8.0	0.181	0.204	0.210
1,3-Butadiene	25	9.0	0.199	0.224	0.232
1,2- dichloropropane	25	18.0	0.275	0.308	0.318
Carbon tetrachloride	25	25	0.362	0.412	0.426
vinyl chloride	25	25	0.944	1.001	1.018
1,2-dichloroethane	25	50	0.957	1.078	1.117
dichloromethane	25	80	3.355	3.466	3.495

Unit GAC cost = $ 1.50 per lb

Typical GAC Capital Costs

Configuration	Single bed	Beds in series
Design Flow, gpm	511	511
Vessel Diameter, ft	12	2 x 12
Site demolition, clearing and grubbing, $	50,000	50,000
Purchase and install GAC vessel(s), $	150,000	300,000
At-grade vessel foundation, $	21,000	27,000
Site piping modifications/additions, $	62,500	125,000
Electrical, metering, and telemetry modifications, $	50,000	75,000
Backwash reclaim tank, foundation, and reclaim pump, $	41,500	50,000
Miscellaneous site work, paving, vaults, walls, landscaping, $	132,000	145,000
Mobilization @ 2 %, $	10,140	15,440
Subtotal, $	517,140	787,440
Contingencies @ 20%, $	103,430	157490
Subtotal, $	620,570	944,930
Engineering design, $	125,000	150,000
Construction management and inspection, $	59,000	65,000
Environmental/legal/ administration, $	25,000	25,000
DPH operations plan/permitting, $	15,000	15,000
Total capital costs, $	**845,000**	**1,200,000**

Typical Operation and Maintenance Assumptions

Item	Value
Power unit cost, $/KWh	0.13
Overall Pump efficiency, %	70
General labor hours, hr/wk	3
Additional inspection & maintenance hr/wk	1
Sampling labor, hr/sample	0.25
Labor unit cost, $/hr	122
Required lab & sampling, samples/2wk	2
GAC change out labor requirement, hr	8
VOC sampling cost, $/sample	150
BACT/HPC sampling costs, $/sample	35
Present worth discount rate, %	2.7
Carbon unit cost, $/lb	1.5

Summary of Present Worth Values

Co, ug/L	Compound	Configuration Type	Treatment Objective, ug/L		
			5	1	0.5
25	aniline	Single bed	1,322,000	1,335,000	1,337,000
25	benzyl chloride	Single bed	1,334,000	1,356,000	1,360,000
25	tetrachloroethylene	Single bed	1,353,000	1,386,000	1,399,000
25	tetrachloroethylene	2 beds in series	1,674,000	1,681,000	1,683,000
8	tetrachloroethylene	Single bed	1,333,000	1,386,000	1,410,000
25	nitrobenzene	Single bed	1,397,000	1,438,000	1,443,000
25	trichloroethylene	Single bed	1,409,000	1,453,000	1,462,000
25	1,2,3-trichloropropane	Single bed	1,469,000	1,532,000	1,554,000
25	Benzene	Single bed	1,636,000	1,692,000	1,706,000
25	1,3-Butadiene	Single bed	1,677,000	1,737,000	1,757,000
25	1,2- dichloropropane	Single bed	1,861,000	1,945,000	1,971,000
8	1,2- dichloropropane	Single bed	1,558,000	1,683,000	1,713,000
25	Carbon tetrachloride	Single bed	2,052,000	2,170,000	2,204,000
25	vinyl chloride	Single bed	3,420,000	3,555,000	3,595,000
25	1,2-dichloroethane	Single bed	3,441,000	3,723,000	3,815,000
25	dichloromethane	Single bed	9,036,000	9,296,000	9,364,000

Summary

- **Models** can be used to evaluate VOC fixed-bed adsorber performance.
- For a single adsorber the optimum EBCT will depend upon the VOC's adsorption potential and initial concentration.
  - VOCs with higher adsorption potentials require smaller EBCTs to maximize specific throughput.
  - Lower initial VOC concentrations require lower EBCTs to maximize specific throughput.
- Carbon usage rate is dependant upon the initial VOC concentration and treatment objective.
  - As initial VOC concentration decreases the carbon usage rate decreases for a given treatment objective.
  - As initial VOC concentration decreases the effect of lowering the treatment objective on carbon usage rate increases.

Conclusions

- For existing systems treating high initial VOC concentrations the impact of lowering the treatment objective is negligible.
- For existing systems treating low initial VOC concentrations the impact of reducing the treatment objective becomes important.
- For situations where VOC concentrations are at or just below current MCLs the capital cost is a major issue.

Questions ?