



CONTRACT NO. 92-304  
FINAL REPORT  
MAY 1995

# Biodegradation Technology for VOC Removal from Airstreams

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## Phase II: Determination of Process Design Parameters and Constraints

CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY

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AIR RESOURCES BOARD  
Research Division



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Phase II: Determination of Process Design  
Parameters and Constraints**

Final Report

Contract No. 92-304

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May 1995



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## ABSTRACT

Packed bed microbial reactors, commonly called biofilters, have been shown to be effective systems for the removal of volatile organic compounds from air streams. The objectives of the project described in this report were to (1) determine biodegradation kinetics of systems treating low concentration aromatic and aliphatic compounds, (2) determine adsorption isotherms for selected biofilter mediums and estimate the importance of adsorption as a removal mechanism, (3) determine the spatial variation in microbial activity in biofilters, (4) determine the relationships between air mass flux and organic loading rate on process performance, and (5) determine the impact of transient loadings on process performance. In addition a mathematical model was developed for biofilter performance that includes spatially variable microbial population densities. The experimental work was carried out using laboratory scale biofilters having 15 cm diameters and 120 cm depth. Two packing mediums, compost and porous ceramic pellets were used. Nutrient limitations were discovered to be important factors in process performance. Removal of toluene, hexane, and dichloromethane was determined to be reaction, rather than mass transport, limited in the concentration range of approximately 3 ppm<sub>v</sub> to 200 ppm<sub>v</sub>.

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DISCLAIMER

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## ACKNOWLEDGMENTS

Many people contributed to the completion of this project who were not members of the project team. We wish to thank Mr. Ralph Propper, our research project manager at the California Air Resources Board for his support and encouragement from the inception of the project. Mark Fuller and Der Yi Mu of the Department of Land, Air and Water Resources were exceedingly generous with their time and skills in isolating bacterial species.



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# ABBREVIATIONS AND NOMENCLATURE

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## FACILITIES OR ORGANIZATIONS

CARB	California Air Resources Board
CEWRE	Center for Environmental and Water Resources Engineering
EPA	US Environmental Protection Agency
JWPCP	Joint Water Pollution Control Plant
LACSD	Los Angeles County Sanitation Districts
POTW	publically owned treatment plant
UST	underground storage tank

## CHEMICALS

BTEX	benzene, toluene, ethylbenzene, and xylene
BTX	benzene, toluene, and xylene
DCE	dichloroethylene
DCM	dichloromethane
MMA	methylmethacrylate
PCE	tetrachloroethylene or perchloroethylene
PERC	perchloroethylene or tetrachloroethylene,
TCE	trichloroethylene
TOL	toluene
VOC	volatile organic compound
XYL	xylene
TCM	trichloromethane, chloroform

## SYMBOLS

$A_s$	surface area, $l^2$ ,
$C$	concentration of limiting nutrient, $m/l^3$ ,
$C_g$	gas phase mass concentration, $m/l^3$ ,
$C_L$	liquid phase mass concentration, $m/l^3$ ,
$D$	molecular diffusivity, $l^2/t$
$H$	dimensionless Henry's Law coefficient,
$K$	rate coefficient, units dependent upon reaction rate function,
$K_D$	solid/liquid distribution coefficient, $l^3/m$
$K_S$	saturation coefficient, $m/l^3$ ,
$L$	depth of biofilm, $l$ ,
$N_L$	liquid phase mass flux, $m/l^2 \cdot t$
$R$	reaction rate, $m/l^3 \cdot t$ ,
$v$	superficial gas velocity, $l/t$
$Y$	biomass stoichiometric yield coefficient, $m/m$ ,
$\mu_{max}$	maximum specific growth rate, $t^{-1}$ ,
$\rho_b$	mass density of microbial film, $m/l^3$ ,

EXPERIMENTAL NOMENCLATURE

COL1	laboratory biofilter 1
COL2	laboratory biofilter 2
TOL1A	<i>Pseudomonas putida</i> strain TOL 1A
DPM	disintegrations per minute
GC	gas chromatograph
MS	mass spectrometer
FID	flame ionization detector
SOL1, SOL 2	nutrient solutions used to fortify media,
PMN	potentially mineralizable nitrogen,

# ***EXECUTIVE SUMMARY***

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Packed bed microbial reactors, commonly called biofilters have been shown to be effective systems for removal of volatile organic compounds (VOCs) from contaminated air streams. In this project laboratory scale studies were conducted with the objective of establishing an improved understanding of process design parameters, operating constraints, and potential performance of microbial gas cleaning processes. A clearer understanding of these factors will encourage industry and regulatory agencies to accept this technology since it will enable designers and permit writers a more rationale basis for their actions. The principal variables to be considered in this project are: (1) factors limiting VOC removal rates, (2) the impact of loading rate variation, and (3) low feed concentration limitations on organic removal (particularly with respect to compounds removed by cometabolism).

## **SPECIFIC OBJECTIVES**

The experiments were focused on developing a theoretical framework to describe the transport and transformations of VOCs in the biofilter. Experiments were designed and conducted to test assumptions of rate limitation under carefully controlled conditions. Specific objectives were:

1. To determine the biodegradation kinetics and adsorption isotherms for the biofilter media.
2. To determine the length of time for acclimation of the microbial populations.
3. To determine the spatial variation of the microbial activity in the biofilter.
4. To determine the effect of gas loading rates on biofilter performance.
5. To determine the effect of VOC loading rates on biofilter performance.
6. To determine the effect of transient loadings on biofilter performance.

## **MATERIALS AND METHODS**

Two laboratory scale biofilters, a compost medium and a porous ceramic medium, were used in the experimental program. The experimental reactors consisted of two stainless steel columns with an inner diameter of 15 cm and an overall height of 1.52 m. The compost medium column was inoculated with material from previous experiments and the porous ceramic medium column was inoculated with an organism known to biodegrade toluene, *Pseudomonas putida* TOL1A. Both columns were supplied with a synthetic gas stream consisting of laboratory air mixed with solvents. In initial experiments a mixture of toluene (3 or 50 ppm<sub>v</sub>), trichloroethylene (3 ppm<sub>v</sub>), and dichloromethane (3 ppm<sub>v</sub>) was initially supplied to the compost medium column. After 4 months of operation, trichloroethylene was removed from the solvent mix because trichloroethylene removal had not been observed. Air containing toluene at selected concentrations was supplied to the porous ceramic medium column. In later experiments, Hexane was used as an hydrocarbon representative of aliphatics in gasoline. A compost biofilter identical to the other laboratory units was used in the hexane experiments and hexane concentrations ranged from 100 to 200 ppm<sub>v</sub>.

## RESULTS

The principal results of the project are discussed below. Of particular interest are acclimation of the microbial population to the reaction environment and the role of specific microbial species in process performance, effects of inlet concentration and air flux, response to transient loadings, spatial distribution of microorganisms in the columns, nutrient limitation effects, and potential usefulness of mathematical process models.

### Acclimation and Bioaugmentation

Acclimation, defined as the time necessary to achieve maximum removal of the contaminants, was a function of the VOC characteristics. Toluene removals were usually excellent within one week of operation. Dichloromethane removals were not measurable for three weeks after initiation of the experimental program. After six weeks the outlet DCM concentrations were near the detection limit and rates continued to improve for an additional four weeks. Later experiments using microbial cultures resulted in much more rapid acclimation. Acclimation to hexane was slow, also. However, the initial hexane experiments were conducted under nitrogen limiting conditions and the system responded nearly instantaneously when nitrogen was added.

After 3 weeks of operation, the compost medium column was inoculated with *Pseudomonas putida* strain TOL1A, an organism known to degrade toluene and to cometabolize TCE in the presence of TOL. Bioaugmentation significantly increased toluene removal rate in the bed as shown in Figure ES.1. A possible explanation for this higher rate is, that after inoculation with TOL1A there was a higher overall (TOL1A + indigenous) population density of toluene degraders in the column. However, TOL1A has been shown to have a high degradation rate for toluene and the increased biodegradation rate for toluene was sustained over several months of operations. Population density effects would not be expected to be sustained once the column reached steady state.

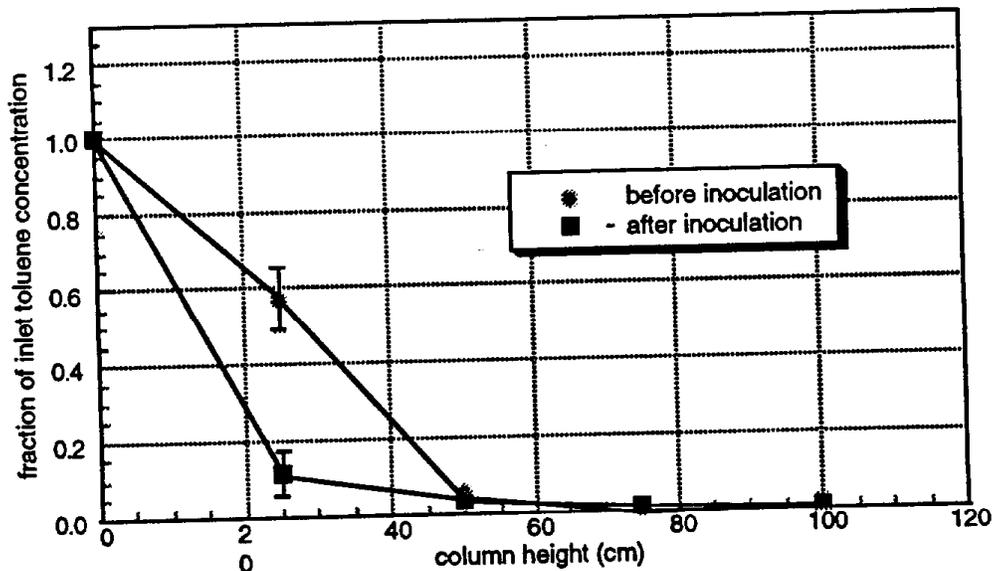


Figure ES.1  
Removal of toluene in COL1 before and after inoculation with the TOL1A organism showing significant increase in biodegradation after inoculation. Inlet toluene concentration during this period was approximately 3 ppm<sub>v</sub>.

## Effect of Compound Concentration

An increase in the inlet toluene concentration from 3 to 50 ppm<sub>v</sub> did not change the overall removal efficiency for toluene once steady state was established as shown in Figure ES.2. Toluene concentration profiles, normalized by inlet toluene concentrations did not change even with inlet concentrations sixteen times higher than in initial experiments. Independence of normalized concentration profile is consistent with the predicted concentration profile when homogeneous biomass concentration and first order biodegradation kinetics are assumed.

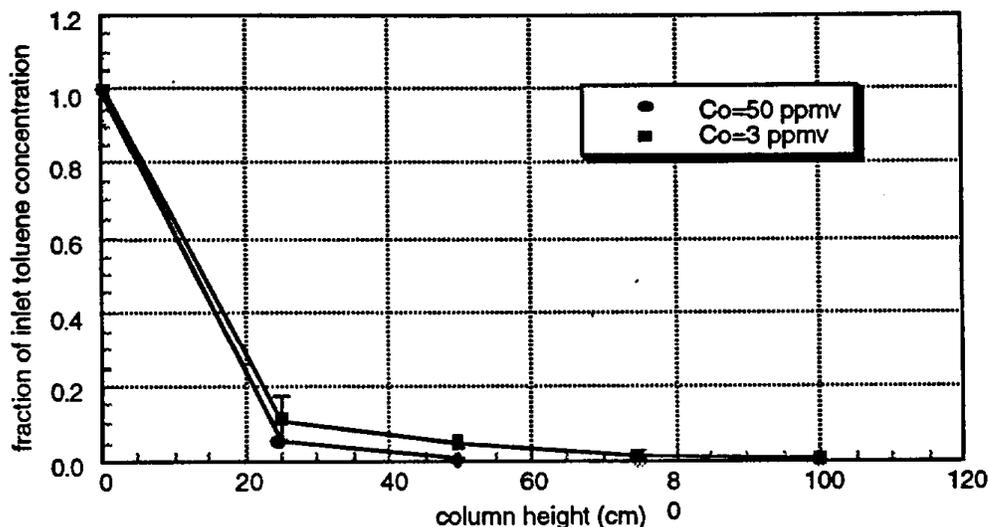


Figure ES.2  
Toluene concentration profile showing effect of increasing concentration from 3 ppm<sub>v</sub> to 50 ppm<sub>v</sub> on toluene removal efficiency.

## Effect of Gas Flux

Toluene removal efficiency at an inlet concentration of 50 ppm<sub>v</sub> was greater than 99.9 percent at superficial velocities between 1 and 2 m<sup>3</sup>/m<sup>2</sup>-min. The limited number of sampling port locations precluded accurate determination of the shape of the concentration profiles for toluene under these conditions. Instrument detection limits for toluene were 10 ppb<sub>v</sub>, 99.98% below the inlet concentration and outlet concentrations rarely exceeded this limit. Increasing the gas flux in the column resulted in more VOC degradation deeper in the bed but did not decrease overall efficiency. Limitations of tubing and flow meters prevented increasing the gas flux to the point where toluene outlet concentrations were significantly above the instrument detection limits. Dichloromethane removal efficiencies at an inlet concentration of 3 ppm<sub>v</sub> were greater than 98% and 95% at 1 and 2 m<sup>3</sup>/m<sup>2</sup>-min gas velocities, respectively.

## Effect of Transient Loadings

The effect of transient loading on biofilter performance was evaluated by stepping-up the inlet toluene concentration from 10 to 35 ppm<sub>v</sub> and determining the response of the system. The step-up was accomplished by running the system at an initial inlet toluene concentration of 10 ppm<sub>v</sub> for 14 days until steady state removal had been established. Toluene mass loading was then increased while holding the gas flux constant at 1.5 m<sup>3</sup>/m<sup>2</sup>-min. Gas samples were taken along

the length of the column four hours before and one hour after the step increase in concentration. The results are shown in Figure ES.3

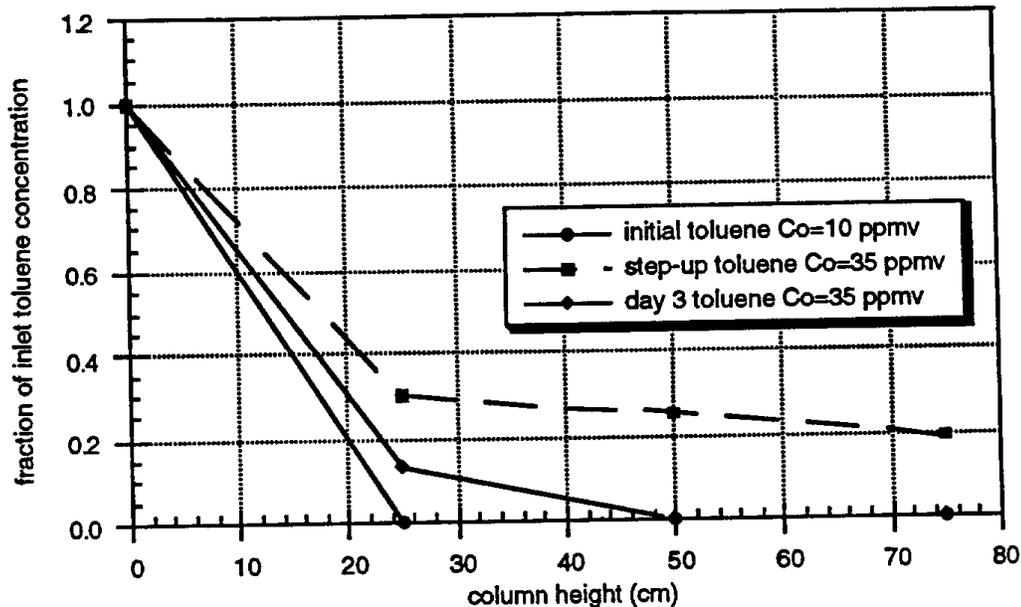


Figure ES.3.  
Toluene profiles showing the effect of a step-increase in toluene concentration on biofilter performance..

Soon after the increase in concentration, toluene removal efficiency decreased and did not fully recover after three days. This contrasts with the results shown in Figure ES.2 which indicate independence of inlet concentration of removal efficiency under steady state conditions. Mass removal of toluene more than doubled in the hour after step-up showing a good response to transient loading. This was consistent with observations made on peak loading days during the Phase I field pilot plant experiments.

One explanation for the improved response over time to changes in inlet concentration is that microbial population densities varied over the length of the column. When the inlet concentration increased, the mass flux of compounds was greater than the microbial population could utilize. After some time, growth of microbial populations resulted in the increased capacity for degradation further downstream in the column. The spatial variation of microbial populations in biofilters is discussed in more detail in below.

### Spatial Distribution of Microbial Populations

The spatial distribution of microbial populations was determined in the porous ceramic medium column using an extraction and plate counting technique. Steady state conditions could not be assessed in this system because of weekly interruptions in operations for nutrient addition as described above. Plates cultures extracted from the media revealed that the column contained a mixed microbial community which was dominated by colonies resembling the TOL1A colonies - but included several other organisms as well.

Microbial populations were found to be distributed such that higher biomass densities existed nearer the inlet to the column than the outlet. Biomass density was highly correlated with toluene mass removals in the column. The observed spatial distribution indicates that much of the

column is underutilized due to low population densities near the outlet. During peak loadings, when inlet concentrations exceed the degradation capacity of populations near the inlet, percent removals decrease, as was shown in the Phase I field trials and in the step-up experiments. Decreased removal occurs because substrates reach downstream populations too infrequently to support the biomass density necessary to degrade them. A potential solution to this problem is to increase the biomass density near the outlet by periodically switching from up-flow to down-flow operation or to supplement the upper parts of the column with appropriate substrates. Shorter columns are generally undesirable because of the necessity to accommodate surges in mass loading.

### Nitrogen Limitation

After 71 days of operation, performance of the biofilter treating hexane decreased rapidly. After 82 days of operation 1 L of a nutrient solution containing 5 g of nitrogen was added to the column. Improvement could be observed immediately as an increase in removal efficiency. On the 104th day of operation a nitrate solution containing 51 g of nitrogen was mixed into the media. As a result removal efficiencies immediately increased to values greater than 99.9 percent. Removal efficiencies greater than 99.9 percent were achieved during the following 24 days of operation.

### Comparison with Theoretical Model

A comparison between observed biofilter concentrations and those calculated from fitting first order biodegradation rate and transport equations is shown in Figure ES.4. Model profiles were calibrated against dichloromethane data because the lower degradation rates for this compound resulted in a more accurate determination of the shape of concentration profiles. The steady state toluene concentrations usually approached the detection limit at the end of the first section (i.e. at the first sampling point after the inlet) which eliminated the possibility of calibration of the equation. Future studies will allow evaluation of validity of the rate coefficient estimated here. Further indication of the validity of the model are provided by the results presented in Figure ES.2 showing toluene removal efficiency to be independent of inlet concentration.

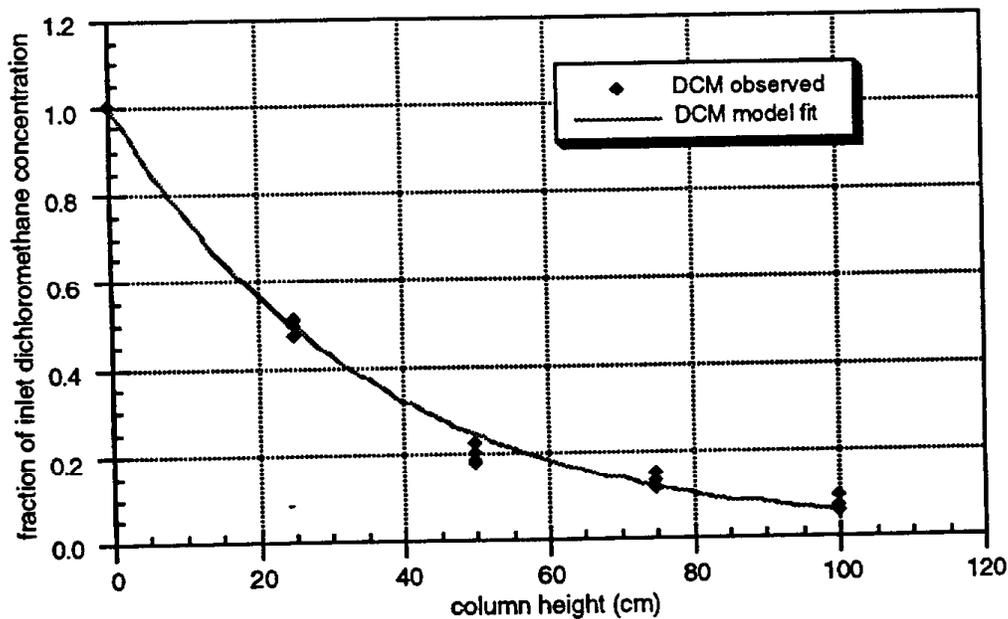


Figure ES.4  
Observed and model fit dichloromethane concentrations as a function of height in the filter bed.

## CONCLUSIONS

1. Biofilters were found to be effective in degrading low concentration emissions of aromatic , and aliphatic hydrocarbons, and biodegradable chlorinated solvents.
2. Mass transport limitations were not observed in the superficial velocity range of 1 to 3  $m^3/m^2 \cdot min$ .
3. Acclimation rate of the microbial cultures to the VOCs fed to the columns was a function of the compound characteristics.
4. The response of the experimental biofilter system to rapid changes in inlet concentrations was excellent, but not instaneous.
5. Dichloromethane degradation was found to be dependent on the presence of particular organisms capable of degrading dichloromethane.
6. A biofilm model incorporating first order biodegradation kinetics and homogeneous biomass population density accurately described dichloromethane concentration profiles in the compost column system.
7. Biomass densities were shown to vary with column height.
8. Commercial composts may be nitrogen limited media.

# **1. INTRODUCTION**

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Packed bed microbial reactors, commonly called biofilters, were shown to be effective systems for removal of volatile organic compounds (VOCs) from wastewater treatment plant off-gases in a set of experiments conducted by staff of the Center for Environmental & Water Resources Engineering (CEWRE) of the UC Davis College of Engineering during 1991 and 1992. The experiments were conducted as part of California Air Resources Board (CARB) Contract number AO -32-137 with extensive support and participation of the staff of the Joint Water Pollution Control Plant (JWPCP) of the County Sanitation Districts of Los Angeles County (LACSD) [Ergas, et al., 1992]. The experiments were designed to verify the potential of biofilters for treating the low concentration, high volume off-gas stream produced at wastewater treatment plants. A second experimental program (Phase II) was initiated in 1993 under CARB Contract No. 92304 to continue the experimental work conducted during Phase I using laboratory scale reactors with the objective of establishing an improved understanding of process design parameters, operating constraints, and potential performance of microbial gas cleaning processes. A clearer understanding of these factors will encourage industry and regulatory agencies to accept this technology since it will enable designers and permit writers a more rationale basis for their actions. The principal variables to be considered in this project are: (1) factors limiting VOC removal rates, (2) the impact of loading rate variation, and (3) low feed concentration limitations on organic removal (particularly with respect to compounds removed by cometabolism).

## **PHASE II OBJECTIVES**

The Phase II experiments were focused on developing a theoretical framework which describes the transport and transformations of VOCs in the biofilter. Experiments were designed and conducted to test assumptions of rate limitation under carefully controlled conditions. Specific objectives were:

1. To determine the biodegradation kinetics and adsorption isotherms for the biofilter media.
2. To determine the length of time for acclimation of the microbial populations.
3. To determine the spatial variation of the microbial activity in the biofilter.
4. To determine the effect of gas loading rates on biofilter performance.
5. To determine the effect of VOC loading rates on biofilter performance.
6. To determine the effect of transient loadings on biofilter performance.



## 2. BACKGROUND

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Biofilters are air pollution abatement systems which rely on microbial populations in fixed bed reactors to oxidize pollutants. Biofilters have been in use for odor control at wastewater treatment plants, composting plants, and industrial processes since the mid-1950's [Pomeroy, 1957; Carlson and Leiser, 1966]. More recent applications have demonstrated that biofiltration is an effective process for controlling volatile organic compound (VOC) emissions in some applications [Ottengraf *et al.*, 1986; Kampbell *et al.*, 1987; Togna and Folsom, 1992; Leson *et al.*, 1993; Peters *et al.*, 1993].

Emissions of VOCs are an environmental concern due to the toxicity of some of these compounds and their role in atmospheric ozone formation. Sources of VOC emissions include manufacture of chemicals, pharmaceuticals, and plastics; painting and spraying operations; oil refineries; soil and groundwater remediation operations; as well as consumer products. In addition, publicly owned treatment works (POTWs) have been identified as significant sources of VOC emissions [Chang *et al.*, 1987, Bell *et al.*, 1988, Bishop *et al.*, 1990]. Biofiltration is a promising technology for controlling VOC emissions from POTWs and has several advantages over other control alternatives, including low capital and operating costs, low energy requirements, and the absence of residual products requiring further treatment or disposal. Publicly owned treatment works emissions differ significantly from emission sources previously tested in biofiltration studies in that:

- Emissions contain toxic compounds at relatively low concentrations;
- Emissions contain mixtures of compounds, including degradable VOCs, chlorinated compounds, hydrogen sulfide, and odorous compounds; and
- Large temporal variations in compound concentrations occur.

Laboratory column experiments were conducted at the Center for Environmental and Water Resources Engineering (CEWRE) laboratories at the University of California at Davis (UC Davis). Laboratory systems consisted of two experimental columns. The first column was filled with the same compost media used in the field studies of Phase I. In the initial experiments (extending from March, 1993 to April, 1994) the column was supplied with a synthetic inlet gas stream containing toluene, dichloromethane, and trichloroethene. These three compounds had been found to be degraded, somewhat degraded, and rarely degraded, respectively, during the Phase I experiments conducted at the JWPCP. In May, 1994 a series of experiments using hexane as the model aliphatic hydrocarbon began. Compounds were supplied at controlled inlet concentrations and gas samples were taken at the inlet, outlet, and at 25 cm intervals through the bed.

The second column was filled with a synthetic filter media composed of a silica-based porous ceramic which was inoculated with a microbial culture known to degrade toluene. The column was supplied with a gas stream containing toluene. Toluene concentrations were monitored at the inlet, outlet, and throughout the bed as described above. Microbial population numbers at various heights in the column were determined by an extraction and plate-counting method.

Development of theoretical models which describe the transport and biodegradation of VOCs in biofiltration systems was fundamental to this research effort. Two theoretical models have been developed and calibrated using data developed in the project [Ergas, 1993; Morgenroth, 1994]. The first model predicts the removal of a VOC in a biofilter where the compound is degraded via first order kinetics and the microbial population is not limiting. A closed form solution was developed for this case. The second model assumes a spatial distribution of microorganisms in the biofilter and first order kinetics. A finite difference solution was developed for this case.

## REVIEW OF BIOFILTER OPERATIONS

The term biofilter is commonly used to define processes which use compost, peat, bark, soil, or mixtures of these substances as a support media for microbial cultures that degrade gaseous contaminants. The filter medium is maintained at a high moisture content, generally 50 to 70%, and individual particles are at least partially surrounded by a liquid film. Air containing gaseous pollutants is blown through the filter media bed where components partition into the liquid film. Biodegradable compounds in the liquid film are available for metabolism by microorganisms growing on the particle surface and in pores. A definition sketch of a typical biofilter system is shown in Figure 2.1 and a conceptualization of the microscale system is shown in Figure 2.2. Favorable conditions with regard to moisture, nutrients, oxygen, pH, and temperature must be provided for growth and maintenance of microbial populations. Process parameters of importance therefore are media composition, moisture content, pH buffering capacity, and gas temperature. In addition, gas loading and VOC loading rates are important to the design of these systems and to determine removal efficiencies.

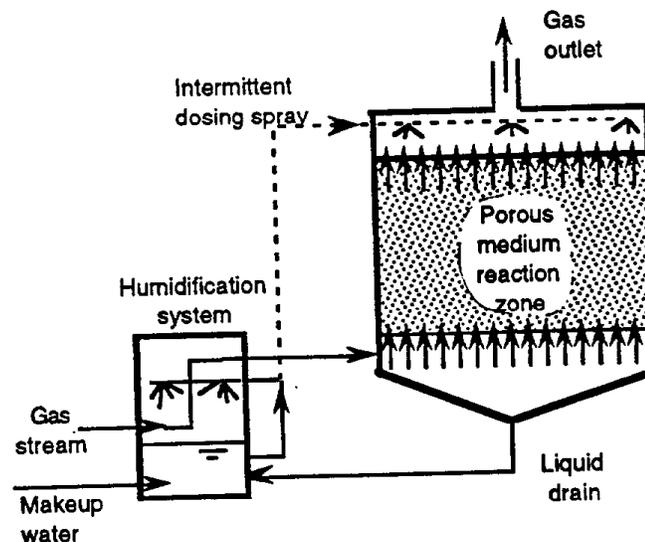


Figure 2.1. Typical biofilter schematic.

## Alternative Process Configurations

Biological treatment of contaminated gases is carried out using several, conceptually similar, configurations. The terms soil filters, soil biofilters, or soil beds are used to delineate processes where the filter medium is soil. Soil biofilters are generally less permeable to gas flow

than biofilters which use compost, peat, or bark media and a larger area is required for the same back pressure. Other processes employed for biological treatment of waste gases include biotrickling filters and bioscrubbers [Ottengraf, 1986; Brauer, 1986; Utgikar and Govind, 1990]. Biotrickling filters are packed bed scrubbers with bacteria growing as a film on the packing medium. Pollutants are absorbed into a continuously flowing liquid film and can then undergo biodegradation. Bioscrubbers separate the processes of absorption and biodegradation into two units; a packed bed absorption unit and a continuous flow stirred-tank biodegradation unit much like an activated sludge reactor. Biotrickling filters and bioscrubbers have been generally used with higher concentration inlet gas streams ( $>1000 \text{ ppm}_v$ ) than biofilters because biofilters are subject to clogging by bacterial cells at high inlet gas concentrations [Togna and Folsom, 1992]. At lower inlet gas concentrations however, biofilters are more favorable to mass transfer due to higher specific surface areas and smaller liquid film thicknesses [Ockeloen *et al.*, 1992]. Biotrickling filters have also been used where formation of acidic metabolites requires continuous addition of chemicals for pH control [Hartmans and Tramper, 1991].

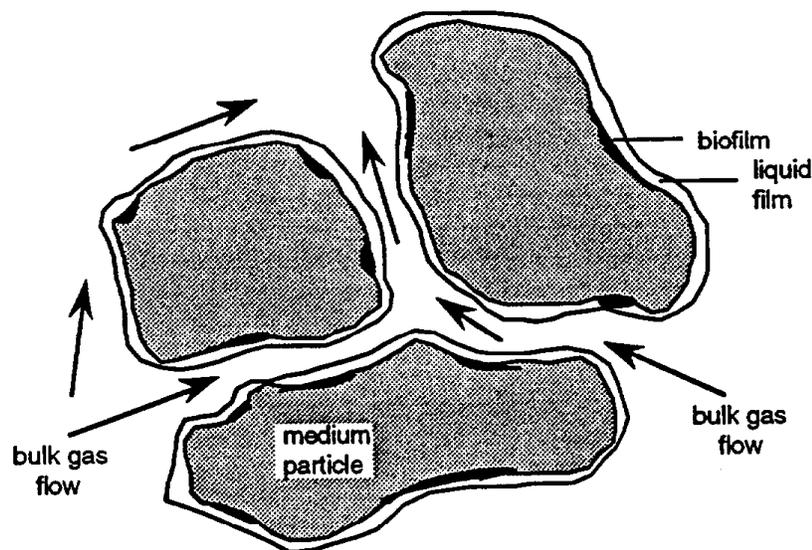


Figure 2.2 Conceptualization of microscopic section through the porous bed.

### Media Composition

Biofilter media provide sites for adsorption of pollutants and attachment of microorganisms. A high specific surface area of the filter media is favorable to the mass transfer of pollutants. High porosity reduces the energy required for distributing gases through the filter bed. In addition, the filter media can serve as sources of nutrients required for microbial growth. Nutrients required by microorganisms include nitrogen, phosphorous, potassium, magnesium, sulfur, iron, calcium, manganese, zinc, copper, and molybdenum.

The filter media may also provide an additional source of organic carbon and contain an active microbial community which may or may not need to be augmented with specific organisms. The type of organic matter in the filter media will also determine the nature of the microbial population. For example, a compost media composed of wood wastes may have a highly active population dominated by actinomycetes and fungi. Relatively non-specific enzymes enable fungi to utilize a broad range of energy and carbon sources (i.e. substrates) including sugars, organic acids, disaccharides, starch, pectin, cellulose, fats, and lignin [Alexander, 1991]. Because of the nonspecificity of their enzymes, fungi are able to degrade or partially degrade hydrocarbons of complex structure and long chain length, compounds

ordinarily resistant to biodegradation. Recently, a great deal of interest has been shown in white rot fungus (the species of greatest interest is *Phanerochaete chrysosporium*) which is able to degrade lignin under nitrogen, sulfur, or carbohydrate limiting conditions using a peroxide-dependent extracellular enzyme system. This enzyme system has been shown to degrade PCBs, DDT, and other resistant hydrocarbons [EPA, 1983; Glasser *et al.*, 1991; Bumpus *et al.*, 1985].

Several types of filter media have been used in biofiltration studies including compost, peat, bark, soil, diatomaceous earth, porous ceramics, and hydrophobic microporous membranes. Hodge *et al.* [1991] evaluated hydrocarbon fuel vapor removals in biofilter systems with four different types of media; a soil mixture, granular activated carbon (GAC), sintered diatomaceous earth, and a mix of GAC and diatomaceous earth. For the GAC and diatomaceous earth columns a nutrient source was added and the columns were inoculated with a microbial culture. Removal efficiency was highest in the GAC columns, followed by the soil columns, with the lowest rates achieved in the diatomaceous earth systems. Adsorption was determined to be an insignificant removal mechanism, although the authors suggested that greater adsorptivity of the GAC contributed to the greater degradation rate by increasing surface diffusion to microorganisms.

Allen and Yang [1991] evaluated various compost sources including yard waste compost, sewage sludge compost, wood waste compost, and mixtures of wastes for H<sub>2</sub>S removal in laboratory scale biofilters. They found that they achieved greater than 99% removal of H<sub>2</sub>S in all of the systems, although composts with larger particle sizes had lower pressure drops and better moisture holding capacity.

Joyce *et al.* [1992] evaluated loam, redwood compost, and mixtures of sewage sludge and rice hulls, mushroom compost and rice hulls, redwood compost and top soil, and mushroom compost and cocoa bean hulls for odor and VOC removal at a sewage lift station. Redwood compost and topsoil systems showed poorer results for H<sub>2</sub>S removal. Mushroom compost mixtures showed the highest removal efficiencies for H<sub>2</sub>S. Mushroom compost/rice hull mixture was further tested for VOC removal efficiency with high removal efficiencies (> 86%) for BZ, TOL, EtBZ, and XYL and lower removal efficiencies (30-45%) for chloromethane, DCM, TCM, and TCE.

Eitner [1989] compared the removal efficiencies of odorous compounds by three common biofilter media (compost, bark material, and peat-soil mixture). Parameters evaluated were pH, moisture content, organic content, flow resistance, microbial population, and respiration activity. Higher removal efficiencies were achieved with compost than with the peat-soil mixture or the bark. High microbial population and microbial activity in the compost beds may account for the improved performance. Unstable compound degradation at high concentrations was observed with the peat-soil mixture. Addition of 5% activated carbon to the filter media was found to significantly increase the removal efficiency for degradable VOCs. Prehumidification of gases provided good moisture content in all filter materials.

Hartmans *et al.* [1992], experimented with biofilter media made from a hydrophobic porous membrane material (Accurel IE-PP). A suspension of bacteria and nutrients was circulated on one side of the polypropylene membrane while air containing TOL and DCM was passed along the other side. Inlet DCM and TOL concentrations were 40 and 20 ppm<sub>v</sub> respectively. The system achieved 99% and 95% removal efficiencies for DCM and TOL respectively with a 0.16 minute residence time. Good mass transfer characteristics of the membrane material were reported to be responsible for the smaller volume requirements of the system.

Ottengraf *et al.* [1986], reported that addition of activated carbon to compost biofilter media enhanced biodegradation of acetone, ethanol, 2-propanol, and dichloroethane from pharmaceutical manufacturing emissions. A possible mechanism suggested was the provision of

storage capacity during peak loads, followed by desorption during periods of reduced loads. Further process improvement may be possible by dividing the processes of adsorption/desorption and biodegradation into two separate stages. This procedure increases the active sites of the adsorbent by putting the humidification stage after the adsorbent stage.

Gas distribution is improved and the pressure drop across the bed (and correspondingly the energy requirements) can be lowered by increasing the permeability of the filter bed. Increasing permeability is accomplished by using coarse materials or adding a coarse fraction of materials to the filter media. Bark and wood chips have been used for this although these materials tend to degrade over time. Inert materials such as styrofoam spheres [Deshusses and Hammer, 1992], perlite [Ergas *et al.*, 1992], vermiculite, and ground tires [Ottengraf, 1989] have also been used to increase filter media permeability.

### Moisture Control

Moisture content of the biofilter media can strongly influence biological activity. Water is the major component of bacterial protoplasm and an adequate supply of water is essential for microbial growth and maintenance. Furthermore, water is a necessary transfer medium because bacteria can only transfer substrates that are in aqueous solution across cell membranes [Atlas and Bartha, 1987]. Too little moisture in the media results in dry zones and loss of microbial activity. Too much moisture, however, inhibits gas transport and results in the development of anaerobic zones with the resulting elimination of aerobic metabolism and the ascendance of anaerobes or facultative anaerobes. Aeration and moisture are directly related because pore space in media not filled by water is filled with gas.

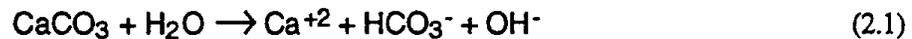
In their work with biofiltration for hydrogen sulfide oxidation, Hartenstein and Allen [1986] reported that optimal values of moisture content for compost media fall into the range between 50 to 70% by weight. Moisture may be provided either by spraying water over the surface of the bed, by humidifying the influent gases, or by using both. Humidification of the influent gases has the advantage of providing even distribution of moisture throughout the bed, however supplemental water may be needed because biological activity tends to increase filter bed temperature. Increasing the inlet temperature of the humidification system allows more moisture to be held in the inlet air and has been used successfully to prevent drying of the bed [Ergas *et al.*, 1993].

### pH Control

Emissions from municipal wastewater treatment plants and many industrial processes often contain significant concentrations of sulfides and chlorinated organic compounds. Biological metabolism of reduced sulfur compounds and chlorinated organic compounds produces acid by-products ( $H_2SO_4$  and  $HCl$ ) with a corresponding decrease in pH of the filter media. Highly acid conditions generally inhibit microbial activity and most bacteria favor neutral conditions. The sulfur oxidizing bacteria however, are well adapted to acidic conditions. An obligate aerobic chemo-autotrophic genera, they produce sulfuric acid through oxidation of  $H_2S$ , and function well at pH values as low as 1. In general, for VOC removal, the pH of the filter material should be maintained between 7 and 8.5. Where VOC and reduced sulfur emissions need to be treated in one system, as in POTW emissions, provision must be made for buffering the acidic metabolites of the sulfur oxidizing bacteria.

Ottengraf [1986], found that addition of agricultural liming agents to the filter bed controlled acidification of the filter material. Materials traditionally used for liming soils are oxides, hydroxides, carbonates, and silicates of calcium or calcium and magnesium [Tisdale and Nelson, 1975]. The reaction of all liming materials involves the neutralization of  $H^+$  ions in

solution by  $\text{OH}^-$  or  $\text{SiO}_2(\text{OH})_2^{-2}$  ions furnished by the buffer, as with the reaction of calcium carbonate:



Agricultural liming materials include slaked lime ( $\text{Ca}(\text{OH})_2$ ), unslaked lime ( $\text{CaO}$ ), limestone ( $\text{CaCO}_3$ ), crushed oyster shell ( $\text{CaCO}_3$ ), dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ), marl (earth +  $\text{CaCO}_3$ ), and slags ( $\text{CaSiO}_3$ ). Differences in the neutralizing capacity and speed of reaction of these materials depend upon molecular composition, material purity, and fineness of particles. In addition to liming, Allen and Yang [1992] found that periodically washing the biofilter bed with distilled water or a sodium bicarbonate solution was successful in removing hydrogen ions and extending the life of the bed. Bioscrubber and biotrickling filter systems have been used with continuous pH buffer addition to the nutrient medium to control high concentration DCM emissions [Hartmans and Tramper, 1991].

### Temperature Control

The rate of biochemical reactions is governed by temperature as well as other factors. In general an increase in temperature increases the rate of reaction up to some optimal temperature, above which there is a decrease in reaction rate. Each microorganism has a optimal temperature range for growth. Mesophiles can grow from about 15 to about 45°C and most have optimal growth in the range of 25 to 35°C; they comprise the bulk of soil bacteria. Psychrophiles develop best at temperatures below 20°C. Thermophiles grow best at temperatures between 45 and 65 °C. Kampbell *et al.* [1987] found that removal efficiency for biofiltration of gases containing propane, isobutane, and n-butane was unchanged by bed temperatures ranging from 12-24 °C. At temperatures below 12 °C the bed lost all ability to degrade VOCs. It was determined that removal efficiencies of greater than 85% for the three compounds could be maintained from March through December in Wisconsin without insulating or heating the biofilter. Generally, in very cold climates, biofilters are insulated and the inlet gases heated.

The combined effect of cold temperatures and shut downs on biofilter performance was investigated by Lehtomaki *et al.* [1992] who operated a pilot scale biofilter at a mineral wool production plant in Finland. Shut downs lasted up to five days and biofilter bed temperatures dropped from 30 to 1°C with outside temperatures down to -4 °C. Biofilter removal efficiencies were found to return to normal (>90%) within 5 hours of restarting the system with warm (30 °C) inlet gases.

### Operating Parameters

Volatile organic compound removal efficiency in biofiltration is dependent on several operating parameters which control the rate at which compounds are delivered to the bed. The empty bed residence time,  $t_r$ , represents the theoretical average time that a gas molecule would spend inside an empty filter bed. It is calculated as:

$$t_r = \frac{V}{Q} \quad (2.3)$$

where  $V$  is the empty bed volume ( $L^3$ ) and  $Q$  is the volumetric gas flow rate ( $L^3/T$ ). Empty bed residence times used in VOC removal studies vary between 0.3 [Ottengraf, 1986] and 12 minutes [Speitel and McLay, 1993] minutes with higher residence times necessary for less degradable compounds. The gas flux or superficial velocity,  $v$  ( $L/T$ ), is a measure of the average fluid velocity through the empty bed:

$$v = \frac{Q}{A} \quad (2.4)$$

where  $A$  is the bed cross-sectional area ( $L^2$ ). The two parameters are related by:

$$v = \frac{H}{t_r} \quad (2.5)$$

where  $H$  is the bed height of the filter bed ( $L$ ). Biofilter heights are commonly around one meter although biotowers of 1.5 meters or more have been reported [Hartenstein and Allen, 1986]. The theoretical velocity of the gas through the pores of the filter material or the Darcy velocity,  $v$ , is calculated by dividing the gas flux by the void fraction,  $f$  (dimensionless). The VOC loading rate,  $R$  ( $m/L^3-t$ ), can be determined as:

$$R = \frac{QC}{V} \quad (2.6)$$

where  $C$  is the inlet gas concentration ( $m/L^3$ ).

## Gas Distribution

Biofilters may be operated in an upflow or downflow mode. Although they are commonly operated in upflow mode, downflow operation allows periodic removal of filter media near the inlet (upper) end of the bed and eliminates the problem of liquid hold up during spray humidification. Three types of gas distribution systems are currently in use in biofiltration systems [Eitner and Gethke, 1987]: 1) perforated pipes, 2) pressure chamber systems, and 3) sinter-block systems. In perforated pipe systems, the bed is underlain with a network of perforated pipes set in a gravel bed. In pressure chamber filter systems, air supply and distribution is carried out by way of a large pressure chamber at the bottom of the bed. This type of system is limited to smaller filter beds due to instability of large pressure chambers and the weight of the filter material in large filters [Hartenstein and Allen, 1986]. In the sinter block system, air distribution is accomplished through prefabricated slotted concrete blocks which provide both aeration and drainage systems. The blocks have sufficient mechanical strength that they can be driven on to provide access to the filter material, e.g. by a front end loader.

## BIOFILTER MICROBIOLOGY

Microorganisms are the primary agents for reactions which lead to the transformations of synthetic as well as natural carbon compounds in the environment. Typically, microbial populations utilize carbon in organic molecules as a substrate for the manufacture of cell constituents. At the same time, energy is released and the population increases. Oxidation-reduction reactions leading to the release of energy are referred to as catabolism, and the synthesis of cell constituents is called anabolism. The combined processes of anabolism and catabolism are called metabolism. Two major categories of metabolism are important in biofiltration systems; chemo-heterotrophic metabolism and chemo-autotrophic metabolism.

Chemo-heterotrophic microorganisms utilize organic carbon compounds for carbon and energy sources. In biofiltration systems, organic pollutants can serve as the substrates for these organisms. Oxygen generally serves as a terminal electron acceptor in aerobic systems, however anaerobic metabolism at microsites in the media is a possible removal mechanism. Organic carbon compounds may also be obtained from the compost or other organic media. Growth of chemo-heterotrophs typically results in the conversion, or mineralization of the organic compounds into cell constituents and inorganic compounds such as carbon dioxide, water, chloride, orthophosphate, ammonium, or nitrate.

Chemo-autotrophic bacteria utilize atmospheric carbon dioxide as a carbon source and reduced inorganic compounds as electron donors. Generally oxygen is used as a terminal electron acceptor. These bacteria are the agents of hydrogen sulfide oxidation in biofiltration systems. Bacterial species of the genera *Psuedomonas*, *Thiobacillus*, and *Clostridium* carry out the oxidation of hydrogen sulfide. As mentioned above, a common feature of sulfur oxidizing bacteria is their acid tolerance. Some strains are able to grow at pH 1 to 2 and fail to grow at pH 6 [Stainer *et al.*, 1986]. Low pH is maintained through the metabolism of reduced sulfur compounds which results in acid formation.

### Cometabolism

Several of the compounds common to POTW emissions have been shown to be degraded only by a process called cometabolism. In cometabolism (also called cooxidation, incidental, or gratuitous metabolism) microbial degradation of an organic compound does not supply energy or carbon to the cells. Specific cosubstrates must be available as primary carbon and energy sources for the organism in order to induce synthesis of the necessary enzymes in the cometabolizing population. For these compounds to be degraded in a biofilter, the primary substrate must be present in the waste gases or be supplied to the microorganisms.

Cometabolism plays an important role in the biodegradation of many chlorinated and non-chlorinated molecules. Cometabolism of the chlorinated VOCs, TCM [Strand and Shippert, 1986], TCE [Wilson and Wilson, 1985], and 1,2-dichloroethane (DCA) [Speitel and Closmann, 1991] have been observed under methanotrophic conditions. Trichloroethene cometabolism by organisms which degrade the aromatic compounds, toluene and phenol [Nelson *et al.*, 1988, Fan and Scow, 1993] is discussed in more detail below.

Speitel and McLay [1993] investigated the ability of methanotrophic bacteria to cometabolize TCE and DCA in biofilters. Lab scale reactors were supplied with a gas stream containing air, methane, and a chlorinated solvent. Inlet chlorinated compound concentrations ranged from 50 - 170 ppm<sub>v</sub>, methane concentration ranged from 3 to 6 percent, and residence times ranged from 5 - 12 minutes. Removal efficiencies ranged from 20 - 80% with removal of DCA being higher than TCE. Low degradation rates observed in this study indicate possible toxicity of the chlorinated solvents to the organisms or competitive inhibition of the bacteria in the presence of methane.

Mu and Scow [1993] characterized indigenous microbial populations in soil with regard to TOL and TCE degrading ability, inhibition, and optimal co-substrate ratio. Experiments were performed in soil microcosms. Volatile organic compound concentration was determined by gas chromatography of the microcosm head-space gas. Degradation of 1.0 µl/ml of TCE at various TOL concentrations is shown in Figure 2.3. As the TOL concentration increased, the extent of TCE degradation increased but the rate of TCE degradation decreased up to a TOL concentration of 250 µg/ml. At 1000 µg/ml TOL, TCE degradation was completely inhibited. Degradation of 20 µg/ml of TOL in the presence of varying amounts of TCE is shown in Figure 2.4. Degradation of TCE was not observed in microcosms receiving 20 µg/ml or higher of TCE. The

rate of TOL degradation was found to decrease with increasing TCE concentration. At TCE concentrations of 50 and 60  $\mu\text{g/ml}$ , no TOL degradation was observed. The results indicated that significant TCE removal should be expected at low TCE and TOL concentrations when the TOL:TCE ratio was 20:1 and that TCE and TOL degradation would be inhibited at high concentrations of either compound.

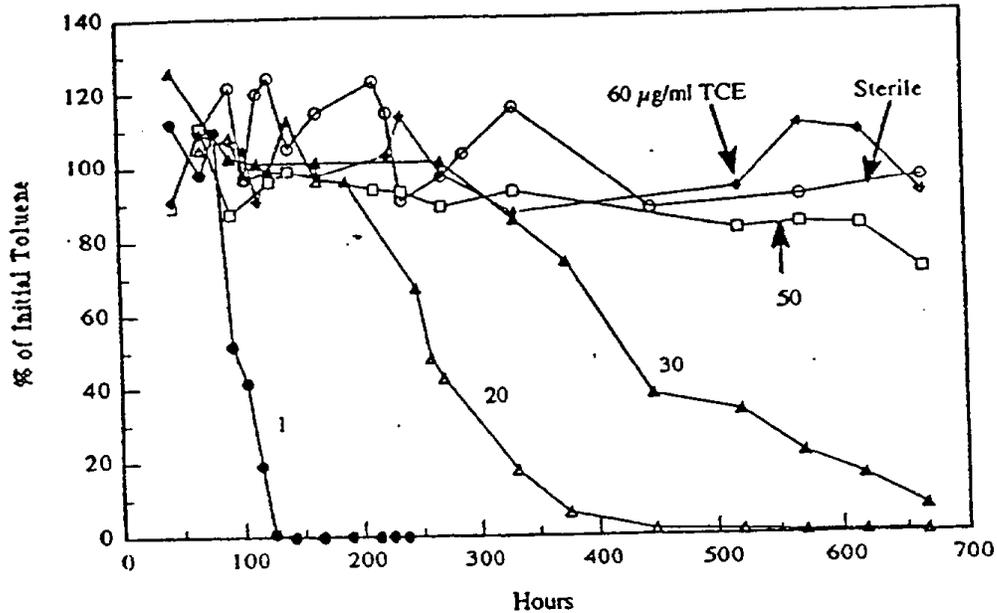


Figure 2.3. Degradation of 20  $\mu\text{g}$  toluene per ml in the presence of various TCE concentrations [from Mu and Scow, 1993].

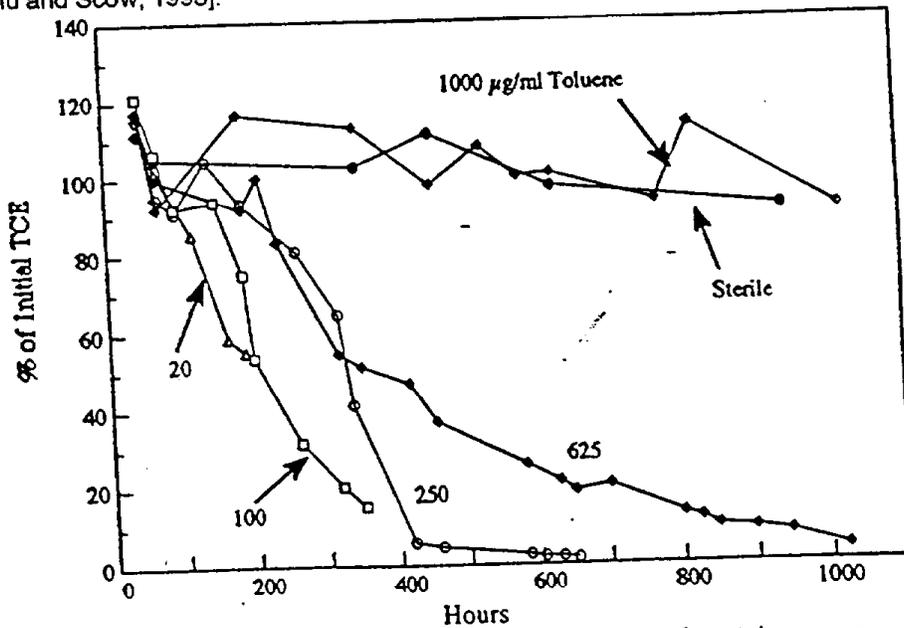


Figure 2.4. Degradation of 1  $\mu\text{g}$  TCE per ml in the presence of various toluene concentration [from Mu and Scow, 1993].

### Formation of Metabolic Intermediates

Biotransformation processes do not always result in the complete mineralization of the organic compound [Pitter and Chudoba, 1990]. Often, the compound is only minimally degraded or transformed to the minimum extent necessary to change the identity of the compound. Although the compound may no longer be detected, a similar, and sometimes more toxic compound, remains. In biofiltration there is the concern that incomplete degradation of compounds may lead to more toxic emissions from these systems. There are no reports in the literature of toxic transformation products in biofilter emissions, however very little research has been done in this area to date. In one study [Ottengraf, 1986] the formation of acetone as an intermediate in the degradation of 1-ethoxy-2-propanol was reported. The acetone that was generated was also degraded when sufficient residence time in the biofilter was provided, however.

### Inhibition

The presence of a second substrate can inhibit the degradation of a pollutant due to diauxic or toxic effects. This is especially significant to the control of POTW emissions by biofiltration because of the presence of a wide range compounds in these gases. In diauxy, metabolic control operates in such a way that enables organisms to select the substrate that allows them to grow at the highest rate. The less desirable substrate, will only be degraded when the concentration of the more readily degraded substrate is limiting [Harder and Dijkhuizen, 1982]. Biofilters, which are essentially plug flow systems, have the advantage that the more degradable compound can be degraded near the inlet of the bed while the less degradable compound can be degraded further downstream. In these cases more capacity must be provided to degrade the two compounds. The presence of a second compound or its metabolites can also be toxic to some microorganisms.

An investigation of SO<sub>2</sub> inhibition of the biofiltration of hexanal in a Picea bark biofilter was conducted by van Langenhove *et al.* [1989]. Hexanal was supplied to the biofilter at an inlet gas concentration of 10 ppm<sub>v</sub> and SO<sub>2</sub> was added to the column at gradually increasing concentrations. At SO<sub>2</sub> concentrations less than 20 ppm<sub>v</sub>, hexanal biodegradation was not inhibited and removal efficiencies were 85%. At an SO<sub>2</sub> concentration of 40 ppm<sub>v</sub> however, hexanal removal decreased to 40% and at 100 ppm<sub>v</sub> SO<sub>2</sub>, hexanal removal decreased to less than 10%. The toxicity of SO<sub>2</sub> to microorganisms is well known and is the reason that SO<sub>2</sub> used as a preservative in some foods.

Dharmavaram *et al.* [1993] evaluated a pilot scale biofilter for the removal of acetone from lithographic plate-making operations. Inlet acetone concentrations of 150-1000 ppm<sub>v</sub> were shown to be easily degraded in experimental systems. Field trials however, showed that trace concentrations of phenol (6 ppb<sub>v</sub>) inhibited acetone degradation even though phenol by itself is easily degradable. It was suggested that metabolites from the degradation of phenol were toxic to the acetone degraders.

Use of a biotrickling filter to remove DCM and methylmethacrylate (MMA) from artificial glass manufacturing off-gases was investigated by van Lith *et al.* [1993]. Removal efficiency for DCM was greater than 80% when DCM was the sole pollutant treated. When MMA was introduced into the gas stream, DCM removal efficiency for DCM dropped to less than 10% although MMA removal was high (>95%). A two-stage system featuring a biofilter for MMA removal followed by a biotrickling filter for DCM removal was effective in achieving greater than 95% removal for both compounds.

## Bioaugmentation

Organisms that metabolize air pollutants such as aromatic hydrocarbons and hydrogen sulfide are ubiquitous in the environment and are often present in compost or soil media. Some compounds, however, may be foreign to the metabolic pathways of the microorganisms naturally present in a media. For these compounds, the filter media must be augmented with microorganisms having a pathway for the pollutant for degradation to occur. Organisms for bioaugmentation are most often isolated from a site where the pollutant is present. Use of organisms derived from enrichment culture or genetic engineering is also possible.

Several authors have successfully made use of bioaugmentation to increase the removal efficiency of specific compounds in biofiltration systems. Williams and Miller [1992] found that inoculation of a peat biofilter with *Hyphomicrobium I55* increased H<sub>2</sub>S and dimethyl sulfide removal. Spitel and McLay [1993] inoculated porous ceramic media with an organism, *Methylosinus trichosporium OB3b*, able to cometabolize TCE and dichloroethane under methanotrophic conditions with some success as discussed in Section 2.3.1 above. Biotrickling filters inoculated with *Hyphomicrobium DM2* and *Methylobacterium DM4* [Hartman and Tramper, 1991] achieved DCM removal efficiencies of over 85%. The use of bioaugmentation of biofilters may be useful for removing chlorinated and other compounds which resist degradation in POTW emissions or to increase the degradation rate of degradable compounds.

## Acclimation and Transient Conditions

A lag period may occur before biodegradation is observed in microbial systems or before a microbial population responds to a change in compound concentration. The lag results from the acclimation of the microbial population and is a concern in biofilter operations because reduced removal efficiency may occur after periods of shut-down or due to variations in inlet concentration. Several explanations have been put forth to explain the acclimation period [Spain, 1990]: 1) microbial enzymes may be induced only after exposure to the chemical, 2) initially small populations of microorganisms capable of degrading the pollutant may be present and time is required to allow them to grow up to the point where significant degradation can occur, or 3) genetic mutations or genetic exchange between indigenous populations may be occurring.

Several authors have reported the phenomena of an acclimation period during start up of biofilter operations. Ottengraf and van den Oever [1983] reported that a ten day period was required before steady state conditions were observed in their systems treating lacquer thinner emissions. Peters *et al.* [1993], reported a one week acclimation period before steady state degradation of kerosene and unleaded gasoline vapors occurred.

Acclimation periods have also been reported in biofiltration systems after periods of shut down, when concentrations have been increased, or due to shock loads. Ottengraf *et al.* [1984], reported a small loss in microbial activity after a two week shut-down period. Peters *et al.* [1993], reported that after a 5-fold increase in inlet concentration the biofiltration system took 2 days to reach steady state, that 2 days were required for reacclimation after a 5-day shut-down, and that shock loading reduced biofilter performance for 5 days.

Togna and Frisch [1993], investigated biofiltration of styrene emissions from spray booth operations in a pilot-scale system. The spraying operations were discontinuous with typical operation from 7:00 A.M. to 12:00 midnight and shut-down on weekends. During Christmas vacation, operations were shut down for two weeks. During operation the biofilter was subject to rapid changes in inlet concentrations ranging from 13 to 130 ppm<sub>v</sub> styrene. Initially, a two day acclimation period was observed during which average styrene removal efficiency was 75%.

After that start-up period, removal efficiency averaged greater than 95%. The unit was found to recover from weekend and vacation shutdowns after 5 to 6 hours of operation.

### Microbial Ecology

Ecological factors may also influence removal efficiencies in biofiltration systems. Many species of microorganisms make up the microbial community in the filter media. In the natural environment compounds are often not acted on by a single species but a consortia of microorganisms works in concert. One species may initiate a transformation of the parent compound and secondary utilizers use intermediates derived from incomplete catabolism by the primary utilizers. Secondary utilizers may also grow on metabolic by-products of the primary utilizers which are not derived directly from the compound. These secondary utilizers can play a role in supporting the primary utilizers, e.g., by providing certain co-factors or nutrients, or by removing toxic by-products [Atlas and Bartha, 1987].

### REVIEW OF BIODEGRADATION OF SELECTED VOCs

A discussion of aerobic biodegradation pathways of the VOCs investigated in this study is presented in this section. The compounds were selected to be representative of common VOCs found in POTW emissions. In addition three of the compounds are readily biodegradable (BZ, TOL, XYL), one is a chlorinated compound which can be used as a carbon and energy source for microbial metabolism by specific populations (DCM), two are known to be aerobically degraded only by cometabolism (TCM and TCE), and one compound is not known to be degraded aerobically (PERC). For the purpose of this review, the compounds have been grouped as aromatic hydrocarbons, aliphatic, and chlorinated aliphatic compounds.

Biodegradation rates and pathways for biotransformation determined in laboratory cultures do not necessarily reflect biodegradation in biofiltration systems. In addition, the study of metabolic pathways generally identifies only those compounds which are excreted outside the cell and accumulate long enough for the intermediate to be above the detection limit of the analytical technique [Alexander, 1981].

### Biodegradation of Aromatic Compounds

The ability of bacteria to oxidize aromatic hydrocarbons is well known. Ubiquitousness of these organisms in soil was demonstrated by Gray and Thornton [1928]. Of 245 soil samples examined, 60% were found to contain organisms capable of oxidizing naphthalene, cresol, or phenol. Although these compounds are degradable, aromatic compounds are more chemically stable, and therefore more resistant to enzymatic attack, than other cyclic hydrocarbons due to the sharing of delocalized electrons by the pi bonds. The presence of substituents on the benzene ring decreases this resonance-enhanced stability, however not all substituents increase degradability.

Bacteria generally oxidize aromatic hydrocarbons to trans-dihydrodiols using either two monooxygenase or one dioxygenase enzyme, incorporating two oxygen atoms into the molecule as shown in Figure 2.5 [Rochkind *et al.*, 1986]. Dihydrodiol is further oxidized to dihydroxylated derivatives (catechols). These dioxygenase reactions have been shown to occur for benzene, halogenated benzenes, toluene, p-chlorotoluene, xylenes, biphenyl, naphthalene, anthracene, phenanthrene, benzo[a]-pyrene, and 3-methylcholanthrene [Gibson, 1988]. The aromatic ring is then degraded via either the ortho-cleavage pathway (a) to yield cis-cis-muconic acid or the meta-cleavage pathway (b) to yield 2-hydroxymuconic semialdehyde [Pitter and Chudoba, 1990]. Fungi and other eukaryotes oxidize aromatic compounds using a monooxygenase enzyme to form an epoxide which can then undergo hydration to yield trans-dihydrodiols [Cerniglia, 1984; Rochkind *et al.*, 1986].

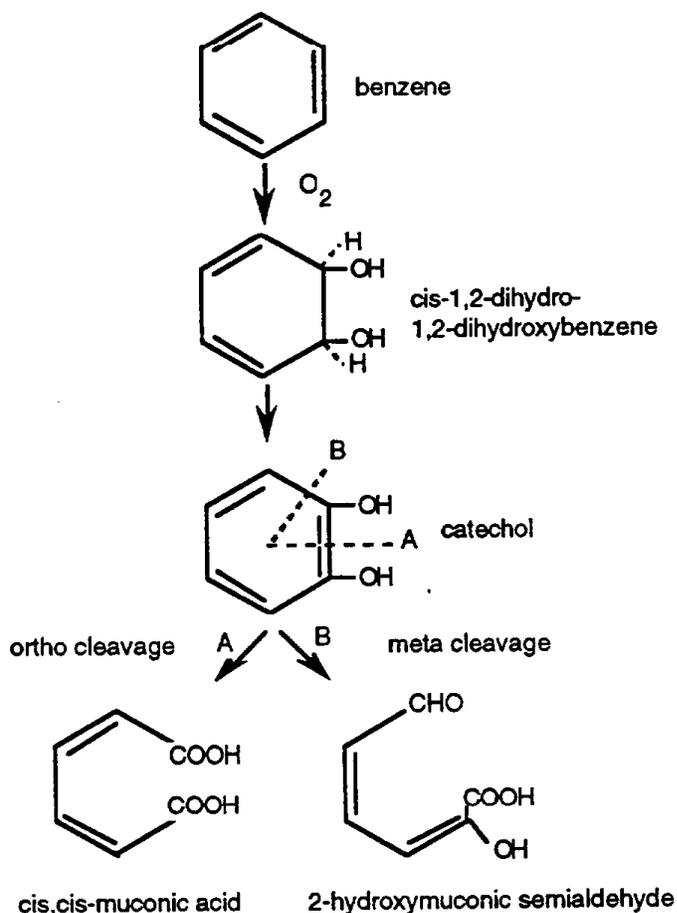


Figure 2.5. Initial steps in the degradation of benzene.

### Biodegradation of Aliphatic Hydrocarbons

Aliphatic hydrocarbons are generally more hydrophobic and have higher Henry's law coefficients than BTX compounds or chlorinated hydrocarbons (Table 2.2). Given equal gas phase concentrations, the compound concentration in the biofilm will be more than two orders of magnitude smaller for hexane than for BTX compounds. In the biofilm the rates of diffusion and biological degradation decrease with decreasing compound concentration in the liquid phase. Thus, because of their hydrophobic properties aliphatic hydrocarbons may be difficult to remove in a biofilter.

If the concentration in liquid culture is high enough, hexane is considered to be easily biodegradable [Atlas, 1981; Brock and Madigan, 1991]. Numerous organisms can use hexane as an energy source and the metabolic pathway for aliphatic hydrocarbons is well studied. Normally, the degradation of n-alkanes proceeds by a monoterminial attack. Usually a primary alcohol is formed followed by an aldehyde and a monocarboxylic acid. Further degradation of the carboxylic acid proceeds by  $\alpha$ -oxidation with the subsequent formation of two-carbon unit shorter fatty acids and acetyl coenzyme A, with eventual liberation of  $CO_2$  [Atlas, 1981; Britton, 1984; Hutzinger and Veerkamp, 1981].

Table 2.1  
Properties of hexane, BTX, and dichloromethane<sup>a</sup>

	Hexane	BTX	Dichloromethane
Solubility, mg/L	11	160 - 1800	19500
Henry's Law Constant <sup>b</sup>	56.45	0.21 - 0.28	0.11
Vapor pressure, atm	0.201	0.009 - 0.125	0.59

<sup>a</sup>Sources: CRC [1992] and Schwarzenbach et al. [1993].

<sup>b</sup>dimensionless: (=C<sub>gas</sub>/C<sub>liquid</sub>)

A favorable application for a biofilter is the treatment of effluent from soil vapor extraction units. Soil vapor extraction is often used to remediate soils contaminated by leaking underground storage tanks (UST). In the USA, the EPA has identified 85,000 leaking USTs with a predicted cleanup cost of 32 billion dollars [Baumann, 1992]. Thus finding an efficient technology to treat gaseous effluents is essential. Soils contaminated with gasoline contain mostly C6 to C12 organic compounds [Baumann, 1992]. Of the organic C6 compounds, hexane is the most volatile [CRC, 1992]. Soil remediation techniques must meet air quality standards concerning the following target compounds: (1) toxic air contaminants (e.g. benzene) and (2) volatile organic compounds leading to the formation of ozone and subsequently smog in the atmosphere, e.g. reactive hydrocarbons as part of the total petroleum hydrocarbons (TPH). In California, the Bay Area Air Quality Management District requires for TPH minimum removal efficiencies of 90 %, 97 %, or 98.5 % depending on the concentration.

For BTX compounds high removal efficiencies ( 90 %) have been reported for various influent concentrations and retention times [Ergas et al., 1993; Ottengraf, 1983; Peters, 1993; Tahraoui and Rho, 1994; Joyce et al., 1992]. The efficiencies reported for removal of non-chlorinated short chain aliphatic hydrocarbons are in many cases lower and vary from 0 to 99 %, as shown in Table 2.2. Thus further research is required to meet effluent standards.

### Biodegradation of Chlorinated Aliphatic Compounds

Chlorinated organic compounds tend to be resistant to microbial attack and so they persist in the environment. Chlorinated aliphatic compounds, including DCM, TCE, TCM, and PERC are common soil and groundwater contaminants. Organic compounds generally act as electron donors, however because of the electronegativity of the chlorine substituents, polychlorinated compounds can act as electron acceptors in reducing environments. In general, the greater the number of chlorines in the molecule, the less biodegradable the compound will be in aerobic systems and the greater potential there is for degradation in anaerobic systems [Vogel et al., 1987].

Cometabolism plays an important role in the biotransformations of TCE and TCM. In the case of TCE, degradation occurs as a result of cometabolism by either methanotrophs [Alvarez-Cohn and McCarty, 1991], aromatic degraders [Folsom et al., 1990], or ammonium oxidizers [Vannelli et al., 1989] through the action of monooxygenase or dioxygenase enzymes. An example of the oxidation of TCE by an organism degrading TOL is shown in Figure 2.6. Epoxidation of TCE is thought to occur through the action of the toluene dioxygenase enzyme. The epoxide is then further hydrolyzed and oxidized to carbon dioxide and HCl.

Table 2.2  
Removal of aliphatic hydrocarbons in biofilters

Compound	Filter Material	Inlet Concentration g/m <sup>3</sup> (ppmv)	Residence Time min	Efficiency %	Reference
Methane	artificial	1.65 - 6.60 (2500 - 10000)	5 - 20 min	20 - 90 %	Sly et al., 1993
Propane	soil	0.0001 (0.075)	96 hr.	0 %	Frye et al., 1991
Propane	soil	10.9 - 18.1 (6000 - 10000)	40 hr.	92 - 98 %	Ebinger et al., 1987
Butane	yard waste	0.060 - 0.478 (25 - 200)	1 - 2 min	075 - 90 %	Kardono and Allen., 1994
Pentane	peat moss	0.046 - 10.1 (15 - 3400)	3 min	40 %	Togna and Singh, 1994
TPH	soil	(2000)	15 min	90 - 99 %	Kampbell et al., 1987
hexane	compost	0.354 - 0.709 (100 - 200)	1 - 3 min	40 - 99.9 %	this study

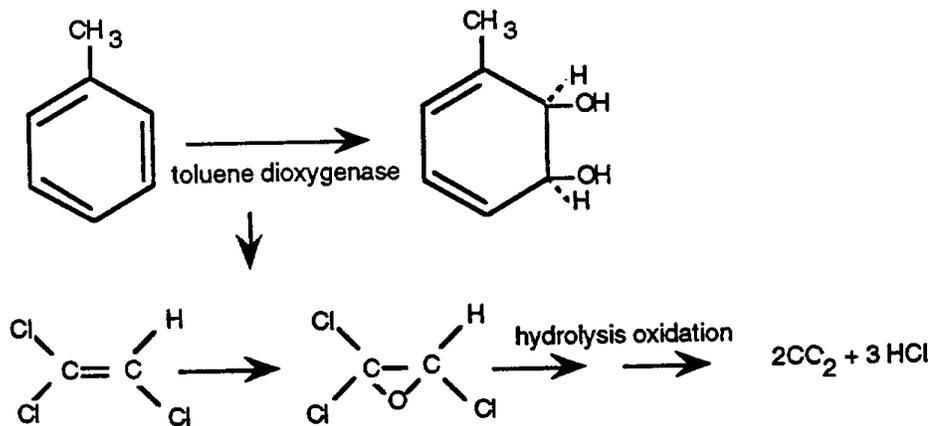


Figure 2.6. Cometabolism of TCE by an organism degrading toluene.

Utilization of DCM by aerobic bacteria as a sole carbon and energy source has been investigated. Brunner *et al.* [1980] isolated an organism, denoted *Pseudomonas DM1*, which dechlorinated DCM by substituting a hydroxyl group for one chlorine substituent as shown in Figure 2.7. Formaldehyde which forms as an intermediate product of the hydrolysis of DCM is further degraded to carbon dioxide [Pitter and Chudoba, 1990].

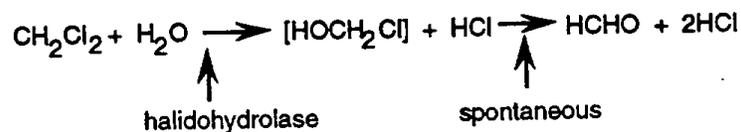


Figure 2.7. Hydrolysis of DCM by *Pseudomonas DM1*.

Stucki *et al.* [1981] described the degradation of DCM by *Hyphomicrobium DM2* through the action of the tripeptide, glutathione (GSH) as shown in Figure 2.8. Formation of the glutathione compound permits further hydrolysis and decomposition to formaldehyde which is readily degradable.

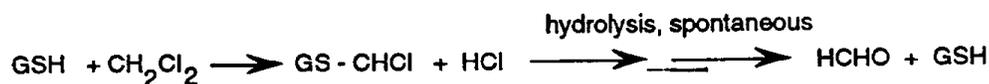


Figure 2.8. Hydrolysis of DCM by *Hyphomicrobium DM2* through the action of GSH.

Rittman and McCarty [1980a] isolated a DCM degrading organism from primary wastewater effluent exposed to DCM over a period of a year. Their findings support the possibility that the ability to degrade DCM is induced in natural populations exposed to the compound over extended periods.

## SUMMARY

Although a large amount of research has been reported in the last few years on biofiltration of VOCs, previous investigators have focused on systems treating continuous emissions of relatively high concentration VOCs with few components. However, in many field applications of biofiltration, including control of VOC emissions from POTWs, off-gasses are characterized by low concentration emissions of a number of compounds with temporal variations in compound concentrations. Microbiological research has shown that compound concentration, the presence or absence of additional substrates, and transient conditions significantly influence the rate and extent of microbial transformations of VOCs. Microbiological research, however, has been primarily focused on biological treatment of soil and groundwater. In this study, experiments were performed to investigate biofiltration of low concentration, variable, multi-component VOC emissions. Experimental design drew from previous microbiological and biofiltration experience. The following factors effecting biofilter performance were investigated:

- Role of compound concentration on the rate and extent of biodegradation of low concentration VOC emissions in biofilters;
- Effect of the presence of multiple and potentially inhibiting or complementary compounds on the biodegradation of VOCs in biofilters;
- The range of superficial velocities for optimal control of POTW emissions;
- Effect of acclimation during start-up and adjustment of microbial populations to shut-down events, transient conditions, and shock loadings;
- Capability of degrading chlorinated compounds and compounds known to be degraded only by cometabolism in biofilters; and
- Use of bioaugmentation to increase removal efficiency of biofilters for some compounds.

# 3. THEORETICAL DEVELOPMENT

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A theoretical model was developed to aid in understanding mass transport and biodegradation for the control of VOC emissions in biofilters. The model builds on the approach used in earlier models of transport and biodegradation in biofilms [Jennings *et al.*, 1976; Harremoes, 1978; Rittman and McCarty, 1980b; Baveye, 1989]. The approach of both biofilter and biofilm models is to solve the one-dimensional mass balance equations over a microscopic cross section of a biofilm assuming simplified reaction kinetics. By using simplifying assumptions of biodegradation kinetics, three different solutions can be obtained: 1) zero order reaction/ reaction limitation, 2) zero order reaction/ diffusion limitation, and 3) first order reaction. Both zero order reaction solutions (cases 1 & 2) have been used by other researchers [Ottengraf and van den Oever, 1983; Togna and Folsom, 1992; van Lith, 1989] to describe biofilm phase reaction in compost biofilters treating industrial VOC emissions. The first order reaction kinetics solution (case 3), was developed for this study to describe biofiltration of compounds at concentrations typical of POTW emissions. Closed form solutions for the macroscopic gas phase mass balance for a given VOC are obtained by volume averaging the biofilm equations over biofilter media. Solutions for each of the three cases are developed and compared in the remainder of this chapter.

Although these simple models are useful as tools for the design of biofiltration systems and for understanding the mechanisms of biofiltration, they do not completely account for the complexities of mass transport in a heterogeneous porous media and biodegradation kinetics of multicomponent substrates. Furthermore, in the lab scale reactor microbial population densities violate the key assumption of homogeneous density in the simple model equations. Therefore, due to its relevance to this study, another case is presented which represents a more complex solution to the above equations, a variable biofilm density model. Because a closed form solution could not be obtained for the variable biofilm density case, a numerical solution was developed.

## BIOFILM MASS BALANCE

A representation of a microscopic section of biofilter media is shown above in Figure 2.2. Air containing VOCs follows a tortuous path through the media which are surrounded by a liquid film containing microorganisms. Soluble compounds in the gases partition into this biologically active film, or biofilm, where they are available for biodegradation. An idealized model incorporating flat biofilm geometry is shown in Figure 3.1. While the porous media are not perfectly flat, the biofilm surface can be assumed to be flat if the thickness of the biofilm is less than 1% of the radius of curvature of the support medium [Rittman and McCarty, 1978]. Bulk transport in the gas phase is generally assumed to be of the plug flow type. Each substrate (electron donors and electron acceptors) and each nutrient required for microbial metabolism must be transported from either the bulk gas phase or the solid phase to the biofilm where the reaction takes place. All products (e.g. CO<sub>2</sub>, metabolites), except biomass, must be transported out of the biofilm. The phenomena involved are bulk gas phase advection, gas film diffusion, liquid film diffusion, biofilm diffusion, adsorption, and reaction.

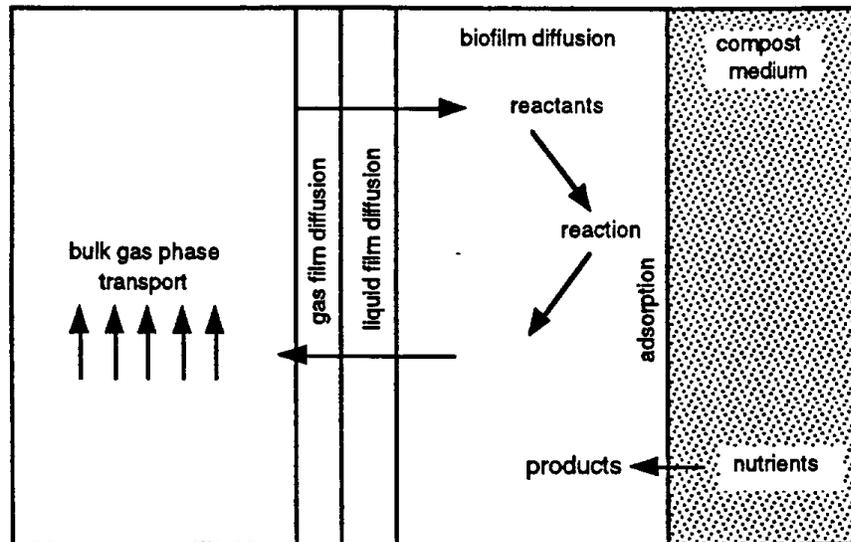


Figure 3.1. Conceptual model of phases and transport processes in biofilter media.

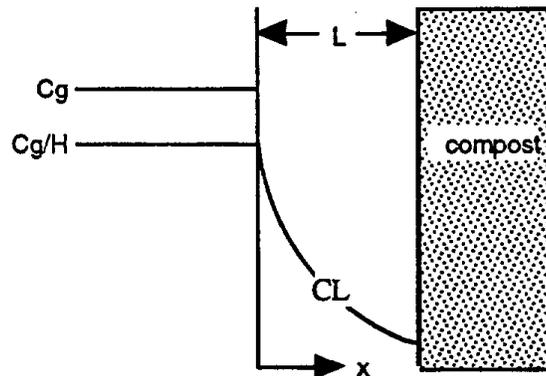


Figure 3.2. Schematic representation of the phases in a biofilter.

A simplified representation of the phases in a biofilter, with coordinate axes, is shown in Figure 3.2. In this model, only one substrate, the pollutant, is assumed to be rate-limiting. In their modeling and experimental studies, Baltzis and Shareefdeen [1993] found that oxygen availability may be a rate-limiting factor in biofiltration systems. Numerical simulations showed that at high methanol concentration (4800 ppm<sub>v</sub>) increased removal was possible by increasing the inlet oxygen concentration above atmospheric levels. Their results indicated that at the low VOC concentrations considered in this study (< 50 ppm<sub>v</sub>) oxygen transfer was not rate-limiting. The model did not take into account, however, the effect of media biodegradation on oxygen utilization which may be more significant in compost based media than in the peat media that was used in the experimental investigation by Baltzis and Shareefdeen [1993].

The model formulation assumes that interfacial resistance between bulk gas and liquid phases is neglected, in effect the liquid layer concentration at the interface is assumed to be in equilibrium with the gas phase concentration. The biomass density is assumed to be homogeneous in the  $x$ -dimension. With the above assumptions, the differential equation describing the mass balance for a compound,  $C_L$ , in the liquid layer of the biofilter is:

homogeneous in the  $x$ -dimension. With the above assumptions, the differential equation describing the mass balance for a compound,  $C_L$ , in the liquid layer of the biofilter is:

$$\frac{\partial C_L}{\partial t} + \frac{\partial N_L}{\partial x} + R = 0 \quad (3.1)$$

where  $C_L$  is the liquid phase compound concentration ( $M/L^3$ ),  $N_L$  is the liquid phase compound flux ( $M/L^2-T$ ),  $R$  is the reaction rate due to biodegradation ( $M/L^3-T$ ), and  $x$  and  $t$  are spatial and temporal coordinates. The liquid phase flux,  $N_L$ , is described by Fick's first law of diffusion for the transport of a compound in a quiescent fluid:

$$N_L = -D \frac{\partial C_L}{\partial x} \quad (3.2)$$

where  $D$  is the liquid phase diffusion coefficient ( $M^2/L$ ). The resulting differential equation becomes:

$$\frac{\partial C_L}{\partial t} - D \frac{\partial^2 C_L}{\partial x^2} + R = 0 \quad (3.3)$$

The biodegradation rate is commonly described by the Monod substrate utilization expression:

$$R = \mu_{\max} \rho_b \frac{C_L}{K_s + C_L} \quad (3.4)$$

where  $\mu_{\max}$  is the maximum specific growth rate of the biomass ( $M/L^3-T$ ),  $K_s$  is the substrate saturation constant ( $M/L^3$ ), and  $\rho_b$  is the biomass density ( $M/M$ ). The Monod expression is empirically derived and has been used extensively to describe the rate of biodegradation of a compound in liquid culture (e.g. batch culture or chemostat experiments). Use of the Monod expression in porous media assumes that the relatively large fluctuations in substrate concentrations and microbial reactions which exist in porous media on the microscopic scale are smoothed out by volume averaging the process to obtain the macroscopic equations [Baveye, 1989]. This volume averaging process is described in section 3.2 below. The net growth rate of the biomass can be assumed to follow the following expression:

$$\frac{\partial \rho_b}{\partial t} = RY - b\rho_b \quad (3.5)$$

where  $Y$  is the biomass yield per unit of substrate utilized ( $M/M$ ) and  $b$  is the biomass specific decay coefficient ( $T^{-1}$ ). An assumption can be made that a quasi-steady state condition exists whereby the total amount of biomass is just equal to that which can be supported by the substrate flux [Rittman and McCarty, 1980b] i.e., the rate of cell growth is equal to the rate of energy expended for cell maintenance:

$$RY = b\rho_b \quad (3.6)$$

and the net growth rate,  $\partial \rho_b / \partial t$ , is equal to zero. A second justification for this steady state assumption even during periods of biofilm growth is that biological growth processes are slow

relative to system residence times. By making the assumption that a steady state condition exists in the biofilm, and that mass does not accumulate in the system after some initial period, Equation 3.3 reduces to the steady state total differential equation:

$$D \frac{d^2 C_L}{dx^2} - \mu_{\max} \rho_b \frac{C_L}{K_s + C_L} = 0 \quad (3.7)$$

Analytical solutions to equation 3.7 using zero and first order simplifications of the Monod expression are discussed in the following sections.

### Zero Order Reaction

At liquid phase substrate concentrations much greater than the half saturation constant,  $C_L \gg K_s$ , the following zero order rate expression results:

$$D \frac{d^2 C_L}{dx^2} - K = 0 \quad (3.8)$$

where  $K$ , the zero order reaction rate ( $M/L^3-T$ ) is equal to  $\mu_{\max} \rho_b / K_s$ . Zero order reaction kinetics are used when the substrate is assumed to not be rate-limiting either due to high inlet pollutant concentrations or because another compound is serving as a primary substrate. Two cases are commonly described. In the first case, the compound fully penetrates the biofilm which is of thickness  $L$ , and this is referred to as the reaction limiting case. In the second case, gas phase compound concentration is lower and the compound penetrates the biofilm to some distance  $\lambda$  which is less than  $L$ , where the rest of the biolayer is assumed to be inactive. The latter case is referred to as the diffusion limiting case. Solutions for these two cases are given below.

**Reaction Limiting Case:** For the case where the compound fully penetrates the biofilm, or reaction limiting case, Equation 3.8 can be solved with the right hand boundary condition:

$$\text{at } x = L \quad \frac{dC_L}{dx} = 0 \quad (3.9)$$

which assumes that the flux into the solid phase is zero. This assumption has the interpretation that the flux into the solid phase due to adsorption is equal to the flux out of the solid phase due to desorption. The left hand boundary condition given as:

$$\text{at } x = 0 \quad C_L = \frac{C_g}{H} \quad (3.10)$$

where  $H$  is the Henry's law coefficient (dimensionless) and  $C_g$  is the bulk gas phase concentration ( $M/L^3$ ). Use of the right hand boundary condition assumes that the gas and liquid phases at the interface are at equilibrium, a condition that can be described by Henry's law as discussed above. The solution to the reaction limiting case is:

$$C_L = \frac{K}{D} x - \frac{KL}{2D} x^2 + \frac{C_g}{H} \quad (3.11)$$

or dimensionless form

$$C^* = 1 + \frac{\phi^2}{2} (\sigma^2 - 2\sigma) \quad \text{where: } \begin{cases} C^* = \frac{C_L H}{C_g} \\ \sigma = x/L \\ \phi = \sqrt{\frac{K_H L^2}{C_g D}} \end{cases} \quad (3.12)$$

The parameter,  $\phi$ , referred to as the Thiele number, is used to describe the ratio between the reaction rate and the diffusion rate.

**Diffusion Limiting Case:** For the case where the penetration thickness is less than the biofilm thickness, the diffusion-limiting case, the right hand boundary condition changes to:

$$\text{at } x = \lambda \quad \frac{dC_L}{dx} \rightarrow 0 \quad (3.13)$$

Note that as  $x \rightarrow \lambda$ ,  $C_L \leq K_s$  and the assumption of zero order kinetics is violated. The solution to Equation 3.8 in dimensionless form becomes:

$$C^* = 1 + \frac{\phi^2}{2} \left( \sigma^2 - 2\sigma \frac{\lambda}{L} \right) \quad (3.14)$$

The penetration thickness,  $\lambda$ , can be calculated by setting  $C^*$  equal to zero at  $\sigma = \lambda/L$  yielding the result:

$$\lambda = \sqrt{\frac{2C_g D}{K_H}} \quad (3.15)$$

### First order Reaction

At liquid phase substrate concentrations much less than the half saturation constant,  $C_L \ll K_s$ , the Monod expression reduces to a first order rate expression. Values of  $K_s$  reported in the literature for most organic compounds are greater than one mg/l [Stanier *et al.*, 1986]. In this study, biofilm phase equilibrium VOC concentrations did not exceed 0.5 mg/l and would not be expected to exceed that value for any single compound in most POTW applications. Equation 3.7 with the first order rate expression becomes:

$$D \frac{d^2 C_L}{dx^2} - k C_L = 0 \quad (3.16)$$

where  $k$  is the first order rate coefficient,  $k = \mu_{\max} \rho_b / K_s$ . With the boundary conditions 3.9 and 3.10, the solution in dimensionless form is:

$$C^* = \cosh \phi' \operatorname{sech} (\phi' \sigma + \phi') \quad \text{where } \phi' = \sqrt{\frac{k L^2}{D}} \quad (3.17)$$

$\phi'$  is also referred to as the Thiele number although the terms are somewhat different from those in Equation 3.12.

### GAS PHASE MASS BALANCE

A representation of a biofilter bed and coordinate axis are shown in Figure 3.3. The differential equation which describes the steady state mass balance for the gas phase compound at a position  $z$  in the filter bed is given by Equation 3.18.

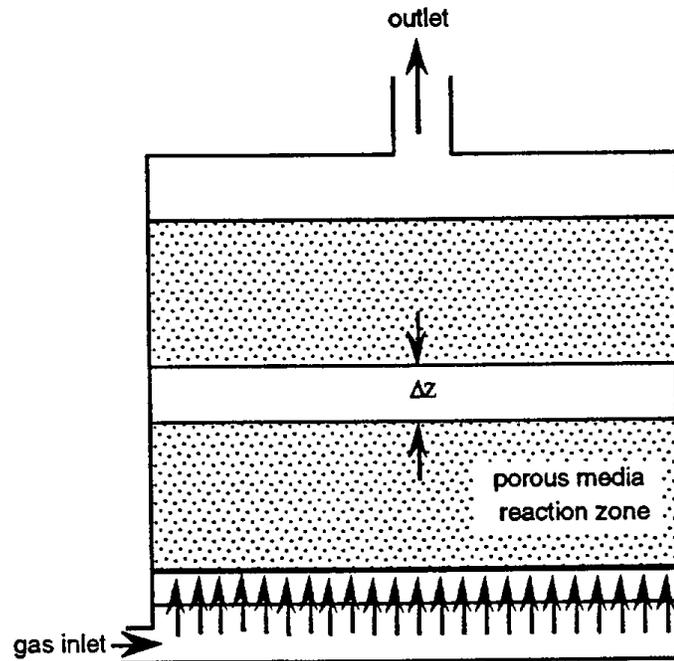


Figure 3.3. Schematic representation of a biofilter bed.

$$v \frac{dC_g}{dz} + N_g A_s = 0 \quad (3.18)$$

where  $v$  is the gas velocity ( $L/T$ ) through the porous media, or Darcy velocity, which is obtained by dividing the superficial gas velocity by the media void fraction,  $A_s$  is the surface area per unit volume of the porous media ( $L^2/L^3$ ), and  $N_g$  is the constituent flux from the gas phase into the biofilm layer ( $M/L^2-T$ ). Equation 3.18 assumes that gas flow through the biofilter bed is of the plug flow type and that transport in the  $x$ -direction does not occur in the liquid or the biofilm. By volume averaging the microscopic equations derived in Section 3.1, the flux into the biolayer,  $N_g$ , can be determined from Equations 3.12, 3.14, and 3.17 for zero order/ reaction limitation, zero order/ diffusion limitation, and first order biodegradation kinetics respectively. For the zero order/ reaction limitation case the flux is determined from 3.12 as:

$$N_g = -D \left( \frac{dC_L}{dx} \right)_{x=0} = KL \quad (3.19)$$

For the case of zero order biodegradation kinetics with diffusion limitation the flux is determined from Equation 3.14 as:

$$N_g = -D \left( \frac{dC_L}{dx} \right)_{x=0} = K\lambda \quad (3.20)$$

For the case of first order biodegradation kinetics the flux is determined from Equation 3.17 as:

$$N_g = -D \left( \frac{dC_L}{dx} \right)_{x=0} = \frac{kC_g L \tanh \phi'}{H} \quad (3.21)$$

With the assumption that the substrate half-saturation constant, maximum specific growth rate, and biomass density are not functions of position in the reactor, Equation 3.18 may be solved analytically for the three cases with the boundary condition,  $C_g = C_0$  at  $z=0$ , where  $C_0$  is the influent concentration, to yield the following solutions:

zero order, reaction limitation:

$$\frac{C_g}{C_0} = 1 - \frac{KzA_s L}{vC_0} \quad (3.22)$$

zero order diffusion limitation:

$$\frac{C_g}{C_0} = 1 - \frac{zA_s}{v} \sqrt{\frac{KD}{2C_0 H}} \quad (3.23)$$

first order:

$$\ln \left( \frac{C_g}{C_0} \right) = - \frac{kzA_s L \tanh \phi'}{Hv} \quad (3.24)$$

The assumption of homogeneous biodegradation kinetics implies that the biomass density does not change with position in the reactor. This assumption may be violated in systems with an inert biofilm support medium because higher substrate concentrations at the inlet to the filter bed allow higher population densities in this region. Where a compost medium is used and inlet organic compound concentrations are low, substrate provided by the pollutant is small compared to that provided by the media and the assumption of homogeneous population density may hold true. The case of a non-homogeneous population growing on an inert media will be discussed in Section 3.3 below.

Equation 3.22, the zero order/ reaction limitation solution, indicates that the curve of concentration versus height in a biofilter would be a straight line and that higher inlet gas phase concentrations, would require a deeper bed for the same removal efficiency. Figure 3.4 presents the results of an investigation by Leson *et al.* [1991] of the control of ethanol emissions using a compost biofilter and illustrates zero order reaction behavior. Note the inlet concentration, given as 1000  $\mu\text{g/l}$ , is approximately 500  $\text{ppm}_v$  ethanol.

At a lower inlet concentration, the results of toluene removal experiments conducted by Ottengraf [1983] in a laboratory scale biofilter were shown to agree with model predictions (Figure 3.5) when the assumption of zero order kinetics with diffusion limitation was made, as in Equation 3.23. Note the inlet concentration, given as 0.84  $\text{g/m}^3$  is approximately 200  $\text{ppm}_v$ .

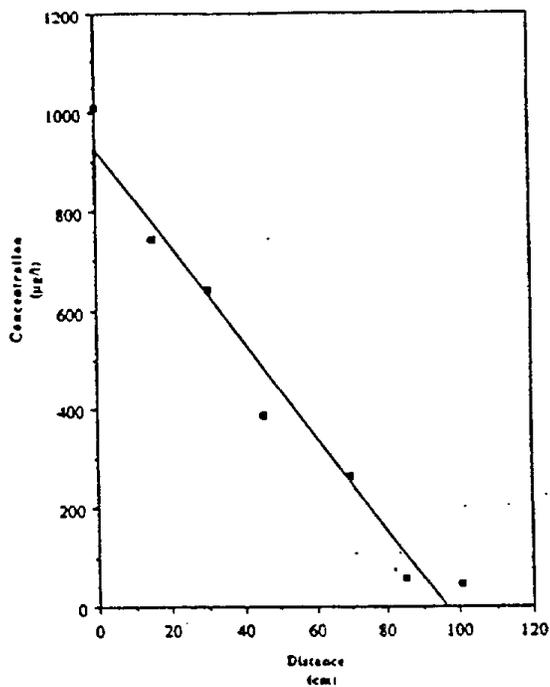


Figure 3.4. Linear concentration profile for ethanol in a laboratory-scale biofilter [from Leson *et al.*, 1991].

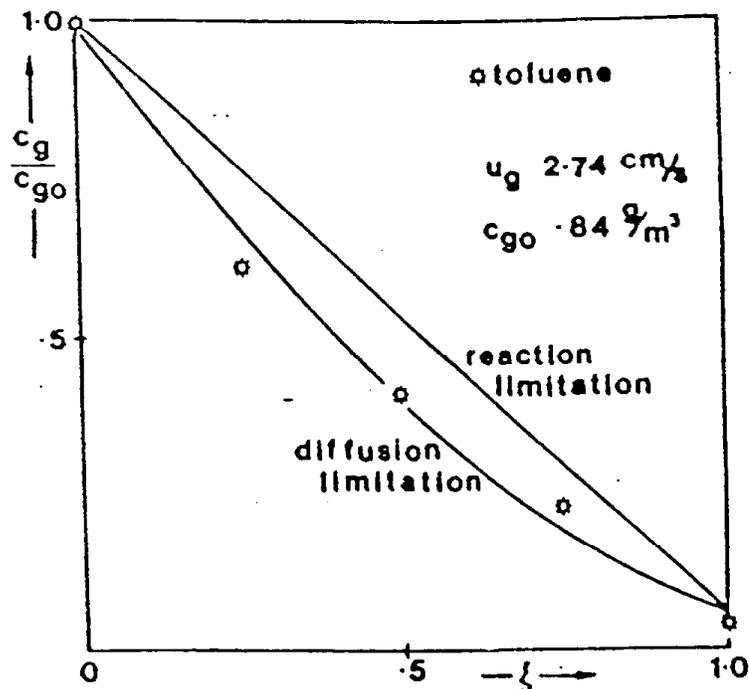


Figure 3.5. Concentration profile for toluene in a laboratory-scale compost biofilter showing diffusion limitation in the biofilm [from Ottengraf, 1983]. Note that  $z$  is a dimensionless length coefficient equal to  $z$  divided by the height of the biofilter bed.

As shown in Figures 3.5 and 3.6, Equations 3.22 and 3.23 provide an adequate model of compound removal at high inlet concentrations relative to POTW emissions. However, the first order rate expression was expected to more adequately model the conditions expected in field and laboratory experiments of this study and therefore Equation 3.24 was derived to model transport and degradation in laboratory scale biofilters. The model predicts that the curve of concentration vs. position in a biofilter column is exponential and that removal efficiency is independent of inlet concentration. Comparisons of observed biofilter performance and model predictions are presented in Chapter 5.

### VARIABLE BIOFILM DENSITY MODEL

As discussed above, the assumption of homogeneous biofilm density can not be made for inert biofilter support media because substrate comes only from the pollutant and the mass flux and therefore microbial population density will be higher nearer to the inlet of the biofilter bed. To model the situation where biofilm density varies in the vertical direction, a numerical model based on a finite difference solution to the transport equations was developed for use in this study. The mass balance equation for the gas phase transport is:

$$\frac{\partial C_g}{\partial t} = D' \frac{\partial^2 C_g}{\partial z^2} - v \frac{\partial C_g}{\partial z} - N_g A_s \quad (3.25)$$

where  $D'$ , the dispersion coefficient, and the second order derivative term are added for numerical stability. This changes the assumption of plug flow gas phase transport to one which allows gas phase dispersion in the axial direction. The parameter  $D'$  can be made sufficiently small so that the solution is not significantly affected however. The flux from the gas phase into the biofilm is calculated from Equation 3.17, the first order biodegradation rate biofilm compound expression, as:

$$N_g = -D \left( \frac{dC_L}{dx} \right)_{x=0} = \frac{k' \rho_b(z) C_g L \tanh \phi}{\phi} \quad (3.26)$$

$$\text{where } k' = \frac{\mu_{\max}}{K_s} \text{ and } \phi = \sqrt{\frac{k' \rho_b(z) L^2}{D}} \quad (3.27)$$

where the biomass density,  $\rho_b(z)$ , is assumed to be homogeneous in the  $x$  direction but variable in the  $z$  direction. With the biofilm flux term of Equation 3.26, Equation 3.25 becomes:

$$\frac{\partial C_g}{\partial t} = D' \frac{\partial^2 C_g}{\partial z^2} - v \frac{\partial C_g}{\partial z} - K' C_g \quad (3.28)$$

$$\text{where: } K' = \frac{k' \rho_b(z) L A_s \tanh \phi'}{\phi'} \quad (3.29)$$

A numerical solution for Equation 3.28 was developed and used to predict the transport and transformation of a pollutant in a biofilter for this study. A central difference approximation was made based on a Taylor series representation of the time and spatial derivatives. The column

was discretized into a finite number of nodes (n) of length  $\Delta z$ . The mass concentration,  $C_g$ , at the nodes  $z+\Delta z$  and  $z-\Delta z$  were expressed as:

$$C_g(z+\Delta z) = C_g(z) + \Delta z \frac{\partial C_g}{\partial z} \Big|_z + \frac{\Delta z^2}{2!} \frac{\partial^2 C_g}{\partial z^2} \Big|_z + \frac{\Delta z^3}{3!} \frac{\partial^3 C_g}{\partial z^3} \Big|_z + \dots \quad (3.30)$$

and

$$C_g(z-\Delta z) = C_g(z) - \Delta z \frac{\partial C_g}{\partial z} \Big|_z - \frac{\Delta z^2}{2!} \frac{\partial^2 C_g}{\partial z^2} \Big|_z - \frac{\Delta z^3}{3!} \frac{\partial^3 C_g}{\partial z^3} \Big|_z - \dots \quad (3.31)$$

The only restrictions on the Taylor series expansions are that the functions of  $C_g$  are single valued and continuous. Finite difference approximations of the first and second order derivatives are developed from the Taylor series approximations by rearranging and truncating the above equations. The central difference approximation for the first and second order derivative terms, and the forward difference approximation for the first order temporal derivative term are:

$$\frac{\partial C_g}{\partial z} \Big|_z = \frac{C_g(z+\Delta z) - C_g(z-\Delta z)}{2\Delta z} \quad (3.32)$$

$$\frac{\partial^2 C_g}{\partial z^2} \Big|_z = \frac{C_g(z+\Delta z) - 2C_g(z) + C_g(z-\Delta z)}{\Delta z^2} \quad (3.33)$$

and

$$\frac{\partial C_g}{\partial t} \Big|_z = \frac{C_g(t+\Delta t) - C_g(t)}{\Delta t} \quad (3.34)$$

substitution of 3.32 through 3.34 into Equation 3.28 yields:

$$\begin{aligned} \frac{C_g^{j+1} - C_g^j}{\Delta t} = & \alpha \left( D \frac{C_g^j(z+\Delta z) - 2C_g^j(z) + C_g^j(z-\Delta z)}{\Delta z^2} - v \frac{C_g^j(z+\Delta z) - C_g^j(z-\Delta z)}{2\Delta z} - K' C_g^j \right) \\ & + (1-\alpha) \left( D \frac{C_g^{j+1}(z+\Delta z) - 2C_g^{j+1}(z) + C_g^{j+1}(z-\Delta z)}{\Delta z^2} - v \frac{C_g^{j+1}(z+\Delta z) - C_g^{j+1}(z-\Delta z)}{2\Delta z} - K' C_g^{j+1} \right) \end{aligned} \quad (3.35)$$

where the superscripts j and j+1 indicate that  $C_g$  was taken at the time steps t or t+ $\Delta t$  respectively and  $\alpha$  is an averaging parameter such that  $0 < \alpha < 1$ . For  $\alpha = 0.5$  the solution is numerically stable, and is termed the Crank-Nicholson solution. By rearranging and combining like terms in Equation 3.35 a set of n simultaneous linear equations is obtained. The  $i^{\text{th}}$  equation of the solution vector for the Crank-Nicholson solution can be written as:

$$\begin{aligned} & \left[ \frac{D'}{2\Delta z^2} - \frac{v}{4\Delta z} \right] C_g^{j+1}(z-\Delta z) + \left[ \frac{D'}{\Delta z^2} - \frac{1}{\Delta t} + \frac{K'}{2} \right] C_g^{j+1}(z) + \left[ \frac{D'}{2\Delta z^2} + \frac{v}{4\Delta z} \right] C_g^{j+1}(z+\Delta z) \\ & = \left[ \frac{D'}{2\Delta z^2} + \frac{v}{4\Delta z} \right] C_g^j(z-\Delta z) + \left[ \frac{D'}{\Delta z^2} + \frac{1}{\Delta t} - \frac{K'}{2} \right] C_g^j(z) + \left[ \frac{D'}{2\Delta z^2} - \frac{v}{4\Delta z} \right] C_g^j(z+\Delta z) \end{aligned} \quad (3.36)$$

The algorithm proceeds by solving for the set of  $C_g$ s for the  $j+1^{\text{st}}$  iteration from a set of known values which were the results of the  $j^{\text{th}}$  iteration. The solution for the first iteration is obtained from the initial conditions, which are given. By writing the equations in the order of the nodes the coefficient matrix is tridiagonal and can be solved using Thomas' algorithm. The quasi-first order biodegradation rate,  $K'$ , is calculated for each node from Equation 3.29. The inlet boundary condition used assumes a known flux and uses a finite difference approximation of the following at the inlet node:

$$v C_o = -D' \frac{\partial C_g}{\partial z} - v C_g \quad (3.37)$$

The outlet boundary condition assumes a zero flux at the outlet node:

$$\frac{\partial C_g}{\partial z} = 0 \quad (3.38)$$

The initial conditions,  $C_g = 0$  for all  $z > 0$ , assumes that the column has no pollutant present at the beginning of the simulation. Steady state conditions are achieved by running the model until the sum of the absolute values of the difference of  $C_g$  at the  $j+1^{\text{st}}$  iteration and  $C_g$  at the  $j^{\text{th}}$  iteration is less than some tolerance value. Computational solutions were coded in FORTRAN 77.

A comparison of the analytical solution given by Equation 3.24 and the numerical solution developed in this section for the case of  $\rho_b$  constant is shown in Figure 3.6. The modeled compound was assumed to have the properties of dichloromethane ( $D=1.3 \times 10^{-9} \text{ m}^2/\text{s}$ ,  $H=0.09$ ). Both the analytical and numerical models use a gas velocity of 0.05 m/s, a first order biodegradation rate of  $2.6 \text{ min}^{-1}$ , a biofilm thickness of  $0.2 \text{ } \mu\text{m}$ , and an inlet dichloromethane concentration of  $1 \text{ ppm}_v$ . Additionally, the numerical solution uses a dispersion coefficient of  $0.0001 \text{ m}^2/\text{s}$ , a spatial discretization of  $0.01 \text{ m}$  ( $\Delta x$ ), and a time step of  $0.1 \text{ second}$  ( $\Delta t$ ). The numerical solution compares well with the analytical solution except for a slight over prediction of the compound concentration near the inlet of the column. Comparisons with experimentally determined concentration profiles are presented in Chapter 5. The source code is included in Appendix C.

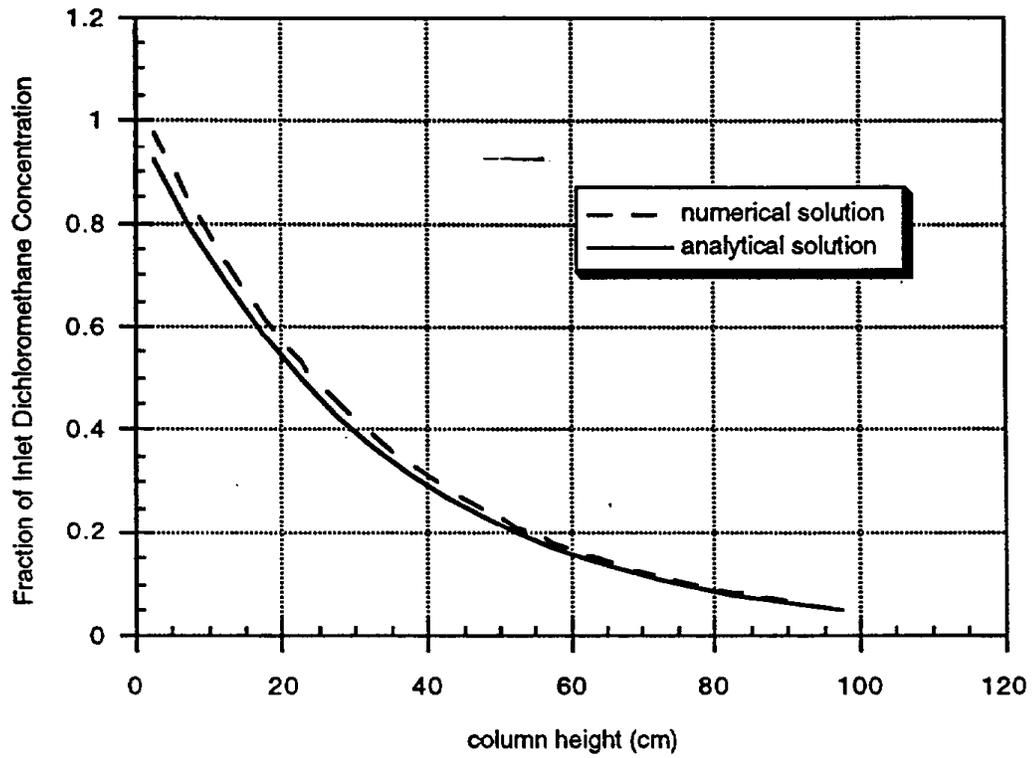


Figure 3.6. Comparison of numerical and analytical solutions to the biofilter transport equations.

# 4. MATERIALS AND METHODS

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Two laboratory scale columns were used in the experimental program. The first column (COL 1), was filled with a compost mixture and inoculum similar to that used in the pilot scale biofilter experiments of the Phase I experiments (Ergas et al., 1992b). The second column (COL 2), was filled with a porous ceramic media and inoculated with the TOL1A organism. Both columns were supplied with a synthetic gas stream consisting of laboratory air mixed with solvents. A mixture of TOL (3 or 50 ppm<sub>v</sub>), TCE (3 ppm<sub>v</sub>), and DCM (3 ppm<sub>v</sub>) was initially supplied to COL 1. After 4 months of operation, TCE was removed from the solvent mix because TCE removal had not been observed. Air containing TOL at various concentrations was supplied to COL 2.

## REACTOR DESCRIPTION

The experimental reactors consisted of two stainless steel columns with an inner diameter of 15 cm and an overall height of 1.52 m, as shown in Figure 4.1. The lower section of each column consisted of a 3.5 liter liquid reservoir which served as a humidification chamber. A glass window allowed inspection of the liquid level in the reservoir which was maintained by a constant flow of de-ionized water using a fluid metering pump (Fluid Metering Incorporated, RPG-6). The upper part of each column was divided into four 30 cm sections. Each section was filled with 25 cm of filter media supported by a perforated stainless steel plate. Above each section was a plenum for taking gas samples.

Compressed air from the laboratory was filtered through two microfiber filter-regulators (Beckman, AFR-920-60) which removed particulate matter from the air and reduced the gas pressure from 120 to 10 psig. The flow was then split between two rotameters (Aalborg, 044.40) which measured and regulated gas flow to each column. Pressure gauges measured the gas pressure at the outlet of each rotameter. Air coming from each rotameter was split again with approximately two thirds of the flow being bubbled through the water reservoir using fritted-glass gas dispersion tubes. A solvent mixture was added to the remaining air for each column using two syringe pumps (Sage, model 341B) and glass gas-tight syringes (Hamilton, 1000 series). Mixing of the two flows occurred in a plenum above the liquid reservoir. Sample ports fitted with Teflon™ lined septa were located above the media in each section, above the reservoir, and at the inlet. Media access ports were located in the middle of each media section. An additional port at the top of COL 2 allowed a nutrient solution to be pumped out of an additional reservoir using a positive displacement pump (Masterflex, model 7017-20). All materials which contacted the VOCs were glass, Teflon™, or stainless steel.

The reactors were located in a constant temperature room which was maintained at 23 °C at the CEWRE laboratory. Liquid reservoir sections were wrapped with heat tape controlled by a temperature controller and thermocouple and kept slightly warmer (approximately 2 °C) than the inlet gas. Increasing the inlet temperature allowed more moisture to be held in the inlet air to prevent drying of the media.

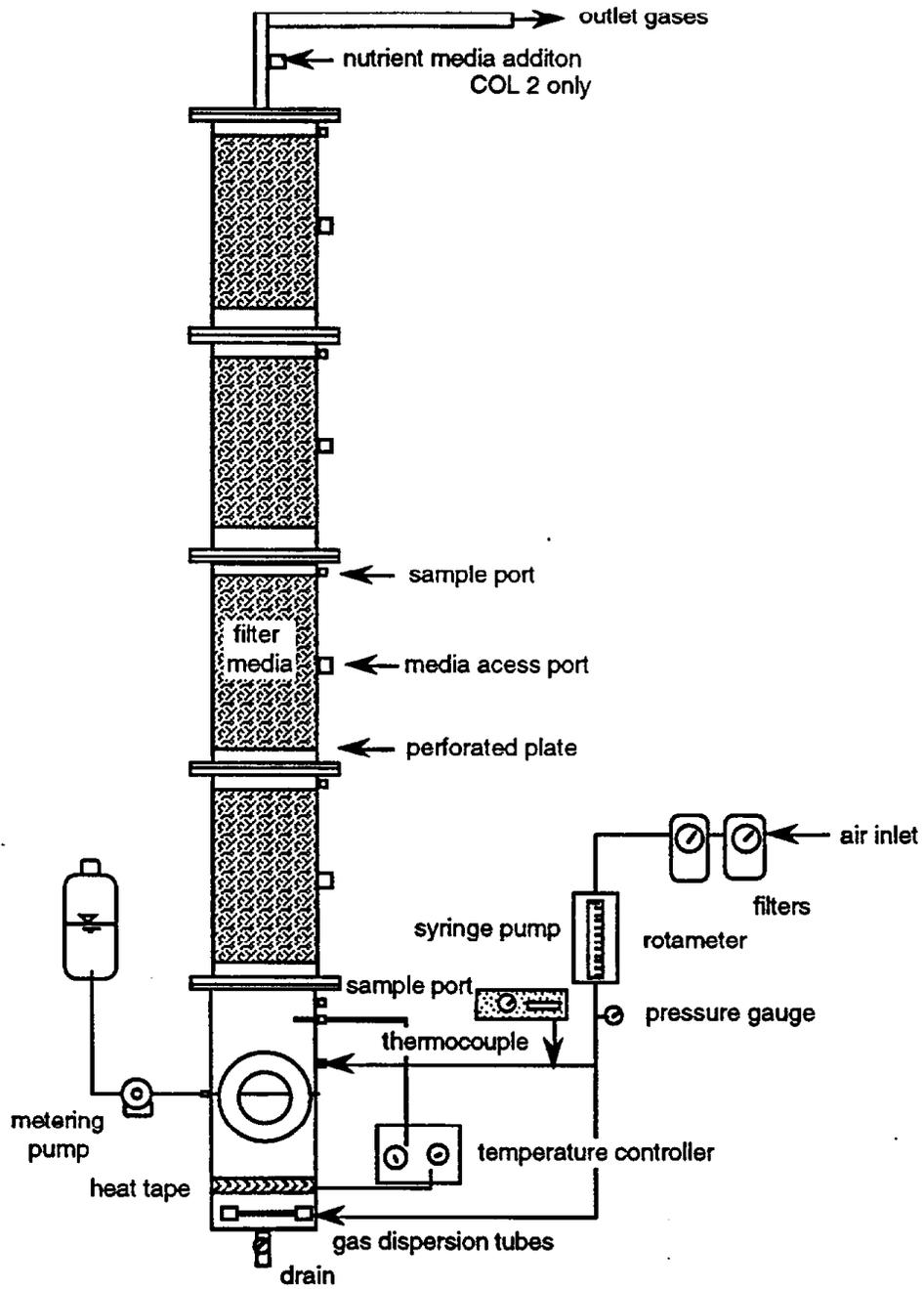


Figure 4.1. Experimental set-up of the bench scale biofiltration system.

## FILTER MEDIA

Two filter media, compost and porous ceramic beads, were used in the Phase II experiments.

### Compost Medium

Compost (Kellogg's brand Nitrohumus, Carson, CA) used in the medium contained 50% digested sewage sludge from the JWPCP and 50% forest products and contributed approximately half of the medium mixture by volume. The compost was determined to have an average size of 0.8 mm by sieve analysis as shown in Figure 4.2. Chemical analysis by the LACSD laboratory of a bag of similar compost was done on January 9, 1991. The compost was shown to be low in total nitrogen (1.3% as N) and have significant concentrations of pesticides (91  $\mu\text{g}/\text{kg}$  as total detected pesticides) and heavy metals including: arsenic (10 mg/kg), cadmium (12 mg/kg), lead (72 mg/kg), mercury (0.7 mg/kg), nickel (75 mg/kg), and selenium (12 mg/kg). Microbial cultures and water to bring the mixture to a moisture content of 55 percent, were added.

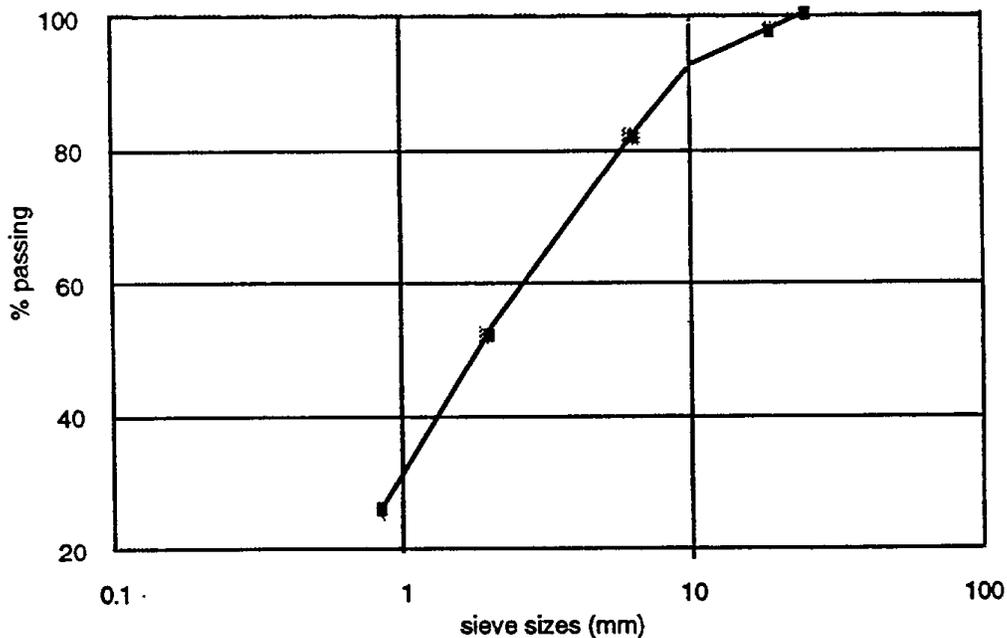


Figure 4.2. Sieve analysis of compost used in biofiltration studies. Percentages indicate the percent of the compost by weight passing the indicated sieve sizes which are given in mm.

Perlite (Nor-Cal Perlite Co., Richmond, CA) is an expanded volcanic material which is ordinarily used for increasing the porosity of potting soil. Addition of approximately 50% perlite, by volume, to the biofilter media decreased the pressure drop across the filter bed. Determination of pressure drop across a filter bed vs. percent perlite in the filter media was made using a column filled with mixtures of compost and perlite at a 50% moisture content. The 5 cm diameter by 0.92 m PVC column was configured as shown in Figure 4.3. Pressure drop across the column was determined with a water manometer. Gas flow rate, maintained at  $1.0 \text{ m}^3/\text{m}^2\text{-min}$ , was determined with a bubble flow meter (SKC West) and stop watch. Pressure drop generally increased with increasing perlite addition up to a perlite concentration of 30% (Figure 4.4). Thereafter, head losses across the column decreased to a minimum of 0.76 cm of water at 100% perlite.

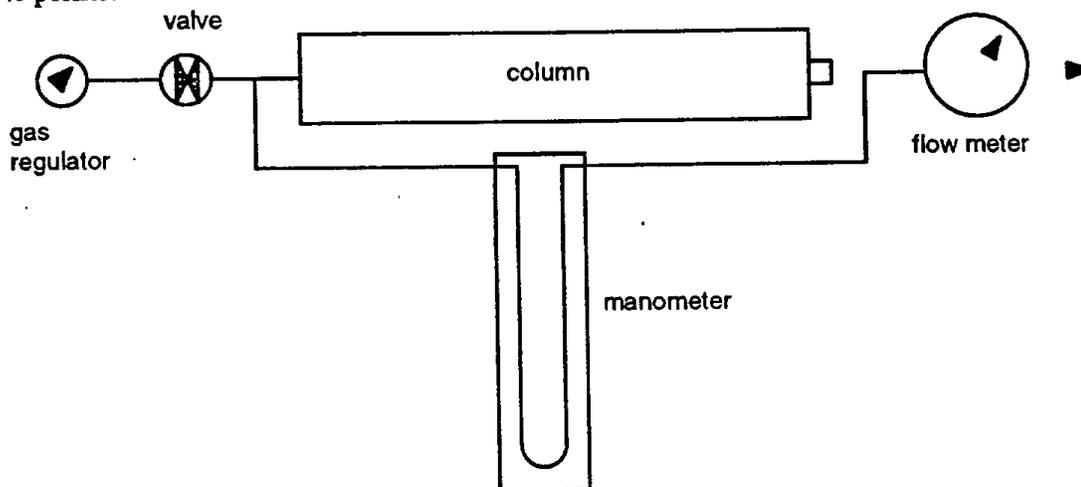


Figure 4.3.  
Apparatus used for determining pressure drop across the filter media.

### Microcosm Experiments

Batch microcosm experiments were conducted to determine whether microorganisms present in the compost media had the ability to mineralize TOL. Four ten gram samples of filter media, two of the air-dried compost and two of the compost mixed with an equal volume of perlite, were put into acid-washed and sterilized microcosm assemblies as shown in Figure 4.5. Sterile, de-ionized water was added to bring the moisture content of the compost to 50%. Ten  $\mu\text{g}$  of unlabelled TOL were added to each microcosm and ring labeled  $\text{C}^{14}$  TOL (Sigma Chemical Company, St. Louis, MO) was added to bring the activity of each flask to 67,000 disintegrations per minute (DPM). The mass of labeled TOL was not enough to significantly increase the concentration of TOL in the microcosms. Each microcosm was equipped with a small vial of base (3 ml of 0.1 N NaOH) which served as a  $\text{CO}_2$  trap. Flasks were stoppered with Teflon™ covered silicone stoppers. A stainless steel canula, inserted through holes drilled into the stoppers, allowed access to the base for sampling. A syringe needle, inserted through the stoppers, allowed gases to enter when a sample was withdrawn. Canulas and needles were stoppered with Teflon seals when sampling was not in progress. At regular intervals, base was removed from the vials, mixed with scintillation fluid, counted using a Beckman LS 6000 IC liquid scintillation counter, and replaced with fresh base.

As shown in Figure 4.6, organisms capable of degrading TOL were present in the compost media. The slightly higher degradation rate in the compost compared with the compost/perlite mixture is most likely due to higher population densities in the former system.

These results are comparable to those of a parallel experiment performed by Fuller [1991] with a rindge soil known to contain organisms that degrade TOL. A sterilized control in that experiment did not show significant evolution of  $C^{14}O_2$ . Recovery of labeled TOL was low; less than 15% of the  $C^{14}$  added. Subsequent destruction of the samples and use of a methanol extraction technique to recover TOL left in the media showed that volatilization and leakage out of the microcosm may have been a factor in the low recoveries.

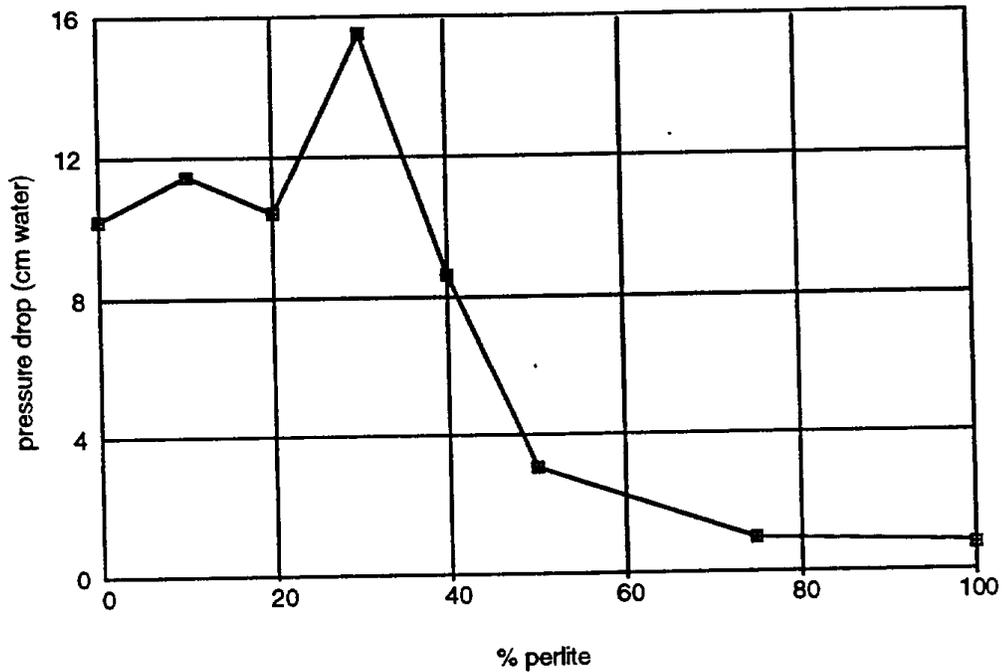


Figure 4.4. Head loss across a 0.92 m column at various perlite percentages gas flux was fixed at  $1.0 \text{ m}^3/\text{m}^2\text{-min}$ .

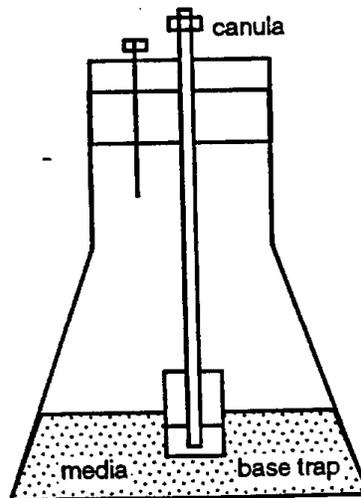


Figure 4.5. Sketch of apparatus used in microcosm experiments.

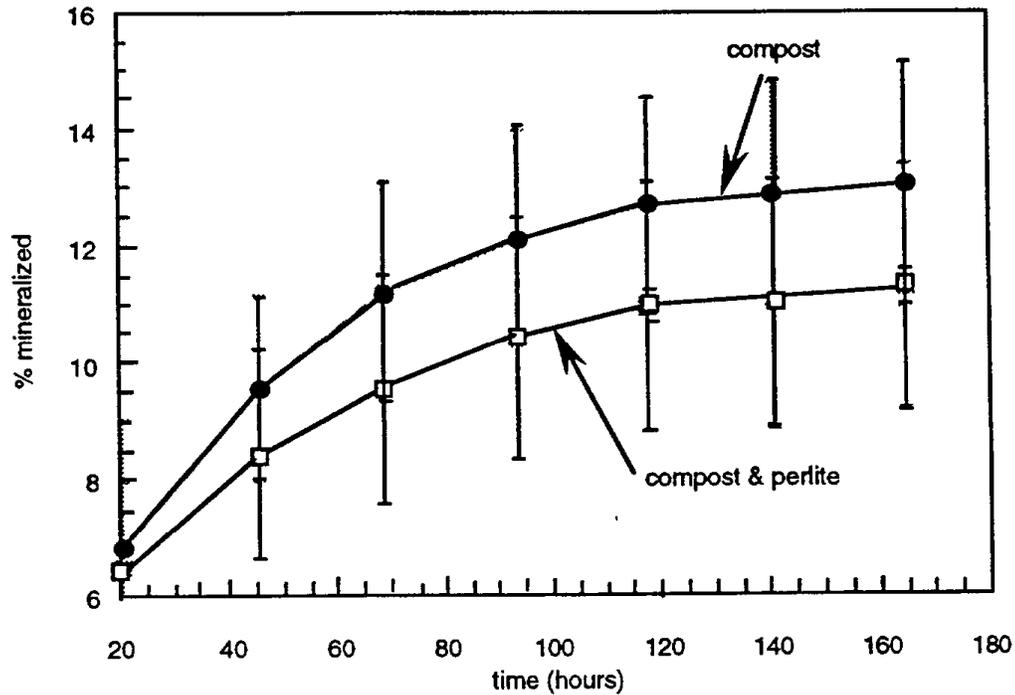


Figure 4.6. Results of microcosm experiments showing the percent of C[14] labeled toluene initially in the sample that was mineralized to C[14]O<sub>2</sub>.

### Ceramic Medium

Filter medium used in COL 2 was a silica-based porous ceramic typically used for enhancing soil porosity and moisture content. The product (Isolite CG-6, Innova Corp. Denver, CO), was composed of diatomaceous earth and natural binders and was extruded into uniform pellets of approximately 6 mm diameter and rotary kiln fired at 1000 °C. Physical properties of the media, provided by the manufacturer, are given in Table 4.1. Porous ceramic media were determined to have a field capacity moisture content of 40%.

Table 4.1. Physical properties of porous ceramic media used in COL 2.

bulk density (g/cm <sup>3</sup> )	chemical composition compound	chemical composition (%)	pH	gas permeability (cm/s)
0.48 - 0.55	SiO <sub>2</sub>	78	6-7	0.12
	Al <sub>2</sub> O <sub>3</sub>	12		
	Fe <sub>2</sub> O <sub>3</sub>	5		

### Microbial Culture For Ceramic Medium

The filter media in COL 1 was mixed with mixed liquor suspended solids from the University of California, Davis wastewater treatment plant at 0.1 ml per gram of dry media. During the fifth week of operation TOL1A, was added at approximately  $10^6$  cells per gram of dry media. The TOL1A culture was prepared as detailed above.

Porous ceramic media used in COL 2 was inoculated with the TOL1A organism by introducing the pellets into acid-washed mason jars half-filled with phosphate-buffered mineral media (Table 4.2). The jars, nutrient solution, and porous ceramic were sterilized by autoclaving (20 minutes at 110 °C and 120 psig) and allowed to cool to room temperature. Five ml of a TOL1A culture, prepared as described above, was introduced into each jar along with enough toluene to bring the solution phase toluene concentration to 200 mg/L. The jars were quickly sealed and incubated for 4 days at 30 °C without shaking.

The jars containing the inoculated media were emptied into the cleaned biofilter sections and allowed to out-gas under the hood for several hours before the column was reassembled. Although the porous ceramic media was inoculated under sterile conditions, no attempt was made to exclude other organisms from entering the column after operations had begun. After three weeks of operation and weekly thereafter, a nutrient solution was added to COL 2 (Table 4.2) by completely filling the column using the nutrient solution addition port, allowing the porous ceramic media and microorganisms to soak for 16 hours, and then draining the nutrient solution from the column.

Table 4.2.  
Composition of nutrient solution used in COL 2 experiments.

compound	concentration (mg/L)
NaNO <sub>3</sub>	3000 <sup>a</sup>
KH <sub>2</sub> PO <sub>4</sub>	3500
K <sub>2</sub> HPO <sub>4</sub>	4300
MgSO <sub>4</sub> ·7H <sub>2</sub> O	480

a. 500 mg/L as Nitrogen

### SAMPLING AND ANALYTICAL METHODS

In the phase two experiments, volatile organic compound analysis was normally accomplished using a model GC-14A Shimadzu gas chromatograph equipped with a flame ionization detector (GC/FID). Occasional samples were run on the laboratory GC/MS system<sup>1</sup>. Filter media moisture content was determined using method 2540D in *Standard Methods for the Examination of Water and Wastewater* [American Public Health Association, 1989]. Additionally, COL 2 media were analyzed for ammonia concentration and microbial population density. Volatile organic compound adsorption isotherms were determined for the COL 1 media, and surface area measurement were determined for both media.

### Volatile Organic Compound Analysis

Five ml grab samples were taken from the columns using glass gas-tight syringes (Hamilton, 1000 series) equipped with Teflon™ syringe valves (Mininert). Samples were taken through septa at each sample port in the columns. Two syringes were dedicated for each sample.

port. Syringes were flushed with sample gases three times, filled, and then the syringe valves were closed. Samples were stored in a dark container and analyzed within eight hours of collection.

A Shimadzu 14A gas chromatograph equipped with a 0.5 ml sample loop and FID was used for volatile organic compound analysis. A 30 meter J & W Scientific DB-624 megabore column was used for compound separation at a carrier gas (He) flow rate of 20 ml/min. The column was cooled to 40 °C then heated at a rate of 12 °C/min to a temperature of 88 °C. Make up gas (N<sub>2</sub>, 30 ml/min), hydrogen (50 ml/min), and air (450 ml/min) were provided to the FID which was maintained at a temperature of 200 °C. A Shimadzu CR501 Chromatopac™ integrator was used for data acquisition, storage, and analysis.

The integrator was equipped with a calibration procedure which was utilized each sampling period. A calibration standard was drawn into a 5 ml gas-tight syringe as described above from a tank of gas standard (Scott Marin, Riverside, Ca) containing TCM, DCM, BZ, TOL, TCE, PERC, and o-XYL at nominal concentrations of 1 ppm<sub>v</sub>. A typical chromatogram of the gas standard is shown in Figure 4.7. The standard was injected onto the sample loop, analyzed, and a single point calibration was made. All samples were analyzed in duplicate. Two standards and a blank were run during each sampling period. Detection limits for the TOL, TCE, and DCM were 10, 25, and 50 ppb<sub>v</sub> respectively.

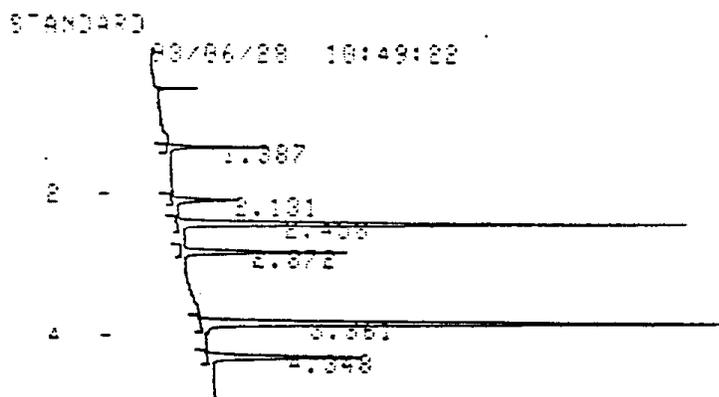


Figure 4.7.  
Example GC/FID gas standard chromatogram.

### Ammonia Analysis

Ammonia concentration of the COL 2 media was determined using a conductimetric ammonia analyzer (Wescan, model 360). The sample was prepared by soaking 5 grams of filter media in 70 ml of distilled water for several hours. Ammonium ion in the sample was first converted to ammonia gas by mixing it with a caustic solution (256 g/L KOH, 10 g/L diethylenetriaminepentaacetic acid). The solution was then passed through a gas permeable membrane where the ammonia gas was absorbed into a solution of ammonium-hydroxide (0.02 M NH<sub>4</sub>OH, 1% boric acid). A change in conductivity was proportional to ammonia

concentration in the original sample. The ammonia analyzer was calibrated by constructing a calibration curve with 0, 10, 25, 50, 75, and 100 ppm as N standards made from ammonium chloride.

### Surface Area Measurements

Determination of media surface area was accomplished by multipoint Brunauer, Emmett, Teller (B.E.T.) analysis [Brunauer *et al.*, 1938, Carter *et al.*, 1986] using a Quantisorb sorption system (Quantichrom corp., Greenvale, NY) with nitrogen gas. The method builds on multimolecular adsorption theory for calculating the number of adsorbate molecules in a monolayer. The B.E.T. equation is:

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{(C - 1)P}{V_m C P_0} \quad (4.1)$$

where:  $V$  is the gas volume adsorbed at pressure  $P$ ,  $V_m$  is volume of gas required for a single molecular layer over the entire adsorbent surface,  $P_0$  is the gas pressure required for saturation at the temperature of the experiment, and  $C = \exp[(E_1 + E_2)/RT]$  where  $E_2$  is the heat of liquefaction of the gas,  $E_1$  is the heat of adsorption of the first layer of adsorbate,  $R$  is the gas constant, and  $T$  is the temperature. In the system used, nitrogen gas was adsorbed to the surface of each media at several partial pressures. By plotting  $P/N(P_0 - P)$  vs.  $P/P_0$ ,  $V_m$  can be calculated from the slope and intercept of the curve. The surface area is calculated by multiplying  $V_m$  by the molecular cross sectional area of nitrogen ( $16.2 \times 10^{-20} \text{ m}^2$ ).

Compost and porous ceramic media were determined to have specific surface areas of 8.5 and 1.4  $\text{m}^2/\text{g}$  respectively ( $1.6 \times 10^6$  and  $7.3 \times 10^5 \text{ m}^2/\text{m}^3$  by volume). Curves obtained for both media are shown in Figures 4.8 and 4.9. As a check of the method, single point B.E.T. analysis was used to determine the surface area of an activated carbon sample (Calgon Filtrasorb 400). The calculated surface area for the GAC of  $1018 \text{ m}^2/\text{g}$  was only slightly lower than the manufacturers reported surface area of 1050 to  $1200 \text{ m}^2/\text{g}$ .

### Adsorption Isotherms

Adsorption isotherms for TOL, TCE, and DCM were performed on the compost media. A known mass of the three solvents was added to adsorption isotherm chambers along with compost and water. A three compartment model was used to calculate a linear adsorption coefficient,  $K_D$  ( $\frac{\text{g/g}}{\text{g/L}}$ ), for each compound. The model equation used is:

$$M_T = C_g V_g + H V_w C_g + S K_D H C_g \quad (4.2)$$

where  $M_T$  is the total number of moles of each solvent,  $C_g$  is the gas phase concentration in moles/L,  $V_g$  and  $V_w$  are the gas and water volumes respectively (L),  $H$  is the Henry's law constant (dimensionless), and  $S$  is the mass of the compost media (g). The first term on the right hand side represents the mass partitioned into the gas phase, the second term represents the mass in the liquid phase, and the third term represents the mass of solvent adsorbed to the media. Adsorption coefficients are determined by equating the total mass in a chamber containing solid media with the total mass of a bottle at the same concentration level not containing solid media and solving for  $K_D$ :

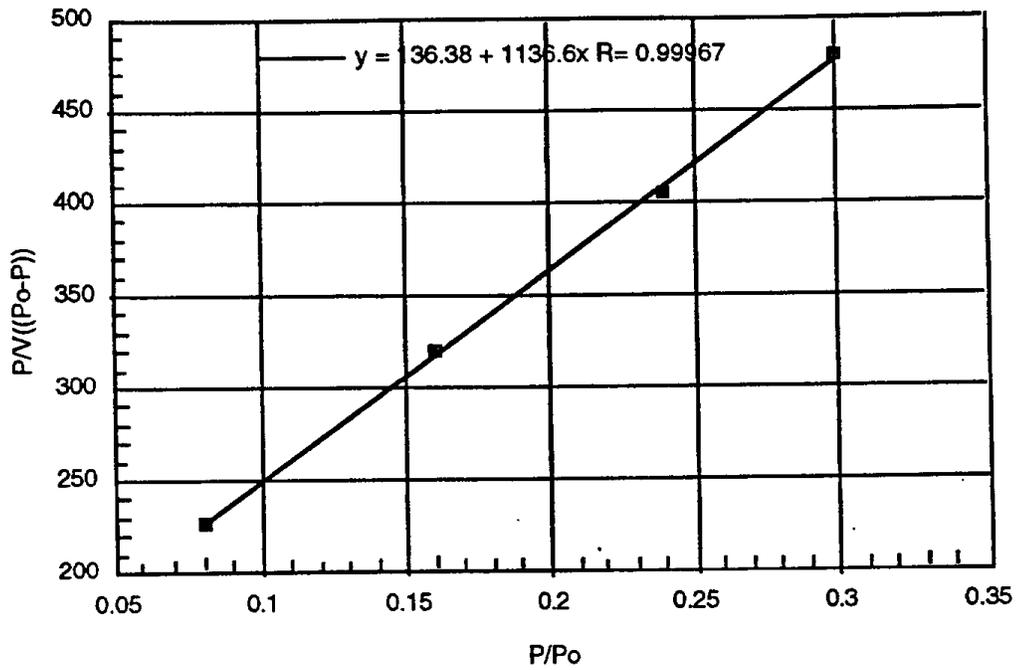


Figure 4.8.  
Multipoint B.E.T. analysis curves and best fit linear regression equations for compost media used in COL1.

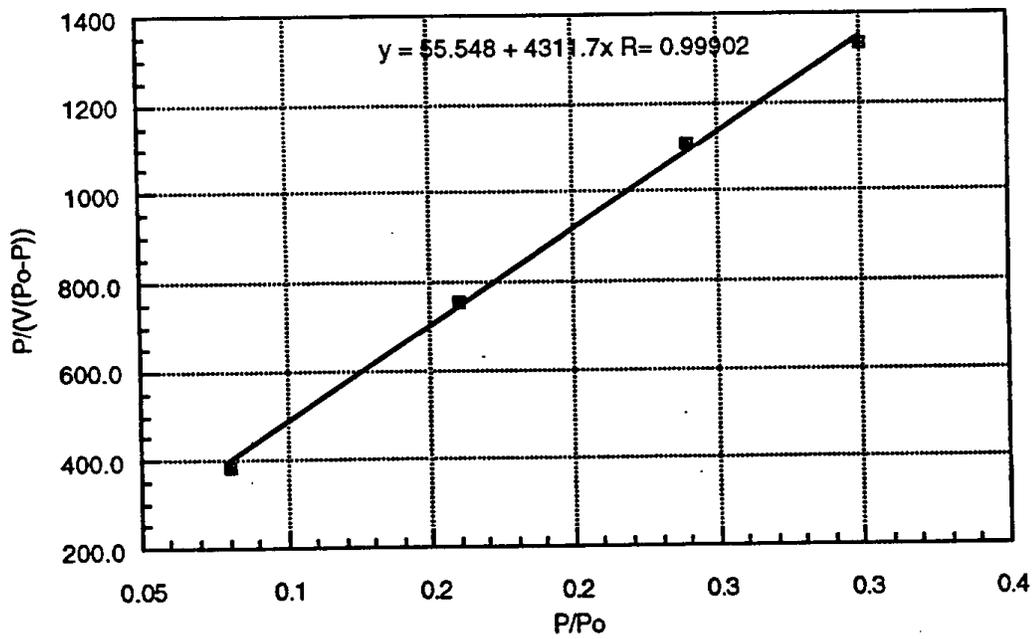


Figure 4.9.  
Multipoint B.E.T. analysis curves and best fit linear regression equations for porous ceramic media used in COL 2.

$$C_{g1}V_g + HV_{w1} C_{g1} + SK_D HC_{g1} = C_{g2}V_g + HV_{w2} C_{g2} \quad (4.3)$$

where the subscripts 1 and two refer to the chambers with and without the compost media respectively.

The 250 ml glass bottles used for the isotherm chambers were acid-washed and fitted with Teflon™ valve caps (Mininert) which had been cleaned by sonication for 20 minutes. Duplicate compost media bottles, one bottle without media, and one blank was used at each concentration level which were 0.2, 2, 20, and 200 ppm<sub>v</sub> of each component. Approximately 5 g of compost media was added to each of the compost media bottles and all of the bottles were sterilized by autoclaving. Toluene, TCE, and DCM were added to the bottles to bring the gas head space concentration to the target concentration level. Sterile de-ionized water was added to bring the moisture content to 50%. The chambers were allowed to equilibrate for 24 hours and gas head space analysis by GC/FID was performed on all of the bottles. The bottles containing compost were then destructively sampled and moisture content analysis was performed. Adsorption isotherm data along with calculated  $K_D$  values and standard deviations are given in Table 4.3. Average percentages of compound calculated to be in each phase of the systems is shown in Table 4.4.

### Bacterial Enumeration

Bacterial cell enumeration was done on the porous ceramic media using an extraction and plating technique. Approximately 1 g of media was collected from the media sampling port in each section of COL 2 and placed in a sterilized 20 ml vial containing 10 ml of the extraction media described in Table 4.5. The samples were sonicated for 20 seconds. Serial dilutions were made of the extracted bacteria using a phosphate buffered saline solution (Table 4.6) and the dilutions were plated out onto TSA plates (3.0 g/L tryptic soy broth, 15 g/L agar) using a spread-plating technique. One replicate was done at each dilution level, two blanks were done for each set of dilutions. Plates were incubated at 28 °C for 3 days. Colony numbers between 20 and 200 per plate were reported.

### Available Nitrogen

Nitrogen available to the organisms was measured using the ammonium nitrogen production under waterlogged conditions [Soil Science Society of America, 1982, Part 2, Method 35-5]. Two 5 gram moist media samples were added to two 50 mL polypropylene centrifuge tubes with screw caps. One tube contained 15 mL water and the other 50 mL of 2 M KCl. Tubes containing water + media were shaken briefly to mix and were incubated at 40°C for 10 days. Samples in 2 M KCl were shaken for 30 min, centrifuged, and filter through Whatman # 2 filter paper. At the end of the incubation period, tubes were amended with 35 mL of 2.85 M KCl to make a total 50 mL of 2 M KCl, and were extracted similarly as the nonincubated samples. Extracts were analyzed for NH<sub>4</sub>-N and samples were stored at -20°C until analysis.

### Toluene Degradation Kinetics in Liquid Culture

Solvent degradation kinetics in liquid culture were determined by reconfiguring the reactors as shown in Figure 4.10. Air containing solvents bubbled through a nutrient solution (Table 4.2) that replaced the water in the liquid reservoir. An active microbial population existed in the humidification section composed of organisms that had dripped down from the biofilter column which was located above the liquid reservoir. Inlet and outlet gas samples were analyzed for VOCs by GC/FID to determine the amount of degradation which was occurring in

the liquid culture. For the COL 2 system, the reservoir was drained into a sterile container subsequent to gas analysis. The reactor was then disassembled and the sides and bottom were scraped with a sterilized rubber scraper to remove attached cells. The drained solution and cells were then serially diluted and plated onto TSA plates as described above.

Table 4.3.  
Adsorption isotherm data for compost medium

Target head space concentration, ppmv	C <sub>g2</sub> (ppm <sub>v</sub> )	C <sub>g1</sub> (ppm <sub>v</sub> )	V <sub>w2</sub> (L)	V <sub>w1</sub> (L)	S (g)	K <sub>D</sub> (L/g)
<b>Dichloromethane</b>						
0.2 ppm <sub>v</sub> -1	0.20	0.15	1.00E-06	1.95E-03	3.99	0.21
0.2 ppm <sub>v</sub> -2	0.20	0.09	1.00E-06	1.85E-03	3.77	0.90
2 ppm <sub>v</sub> -1	1.53	1.03	1.00E-05	1.85E-03	3.78	0.36
2 ppm <sub>v</sub> -2	1.53	1.17	1.00E-05	1.63E-03	3.32	0.26
20 ppm <sub>v</sub> -1	13.38	13.15	1.00E-04	2.07E-03	4.15	0.01
20 ppm <sub>v</sub> -2	13.38	8.81	1.00E-04	2.10E-03	4.21	0.34
200 ppm <sub>v</sub> -2	136.20	88.53	1.00E-03	2.73E-03	5.05	0.30
					means K <sub>D</sub>	0.34
					Std Dev K <sub>D</sub>	0.27
<b>Trichloroethene</b>						
0.2 ppm <sub>v</sub> -1	0.12	0.11	1.00E-06	1.95E-03	3.99	0.01
0.2 ppm <sub>v</sub> -2	0.12	0.11	1.00E-06	1.85E-03	3.77	0.01
2 ppm <sub>v</sub> -1	1.63	0.82	1.00E-05	1.85E-03	3.78	0.17
2 ppm <sub>v</sub> -2	1.63	0.90	1.00E-05	1.63E-03	3.32	0.16
20 ppm <sub>v</sub> -1	14.95	11.24	1.00E-04	2.07E-03	4.15	0.05
20 ppm <sub>v</sub> -2	14.95	7.88	1.00E-04	2.10E-03	4.21	0.14
200 ppm <sub>v</sub> -2	163.39	76.84	1.00E-03	2.73E-03	5.05	0.14
					means K <sub>D</sub>	0.10
					Std Dev K <sub>D</sub>	0.07
<b>Toluene</b>						
0.2 ppm <sub>v</sub> -1	0.19	0.08	1.00E-06	1.95E-03	3.99	0.37
0.2 ppm <sub>v</sub> -2	0.19	0.06	1.00E-06	1.85E-03	3.77	0.54
2 ppm <sub>v</sub> -1	2.50	0.80	1.00E-05	1.85E-03	3.78	0.59
2 ppm <sub>v</sub> -2	2.50	0.87	1.00E-05	1.63E-03	3.32	0.59
20 ppm <sub>v</sub> -1	23.22	11.94	1.00E-04	2.07E-03	4.15	0.24
20 ppm <sub>v</sub> -2	23.22	8.33	1.00E-04	2.10E-03	4.21	0.44
200 ppm <sub>v</sub> -2	245.45	83.37	1.00E-03	2.73E-03	5.05	0.40
					means K <sub>D</sub>	0.45
					Std Dev K <sub>D</sub>	0.13

Table 4.4.  
Percent of compound in each compartment of batch adsorption systems.

compound	% in gas phase	% in liquid phase	% in solid phase
Dichloromethane	71	0.05	29
Trichloroethene	88	0.06	12
Toluene	61	0.04	40

Table 4.5.  
Bacteria extraction media.

compound	concentration (g/L)
Trizma™ HCl	6.35
Trizma™ Base	1.18
NaCl	9.0

Table 4.6.  
Phosphate buffered saline.

compound	concentration (g/L)
$\text{KH}_2\text{PO}_4$	3.5
$\text{K}_2\text{HPO}_4$	4.3
NaCl	8.5

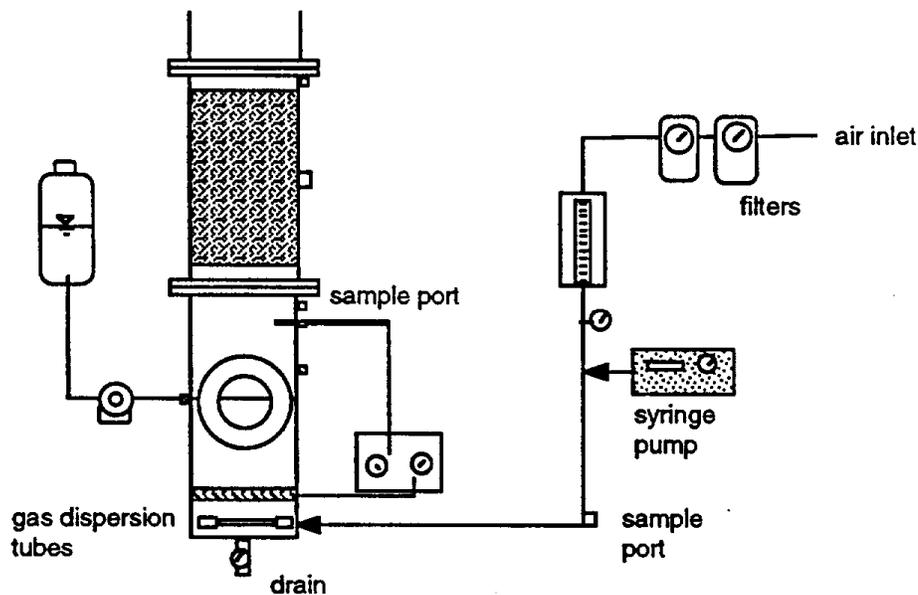


Figure 4.10.  
Schematic of biofilter columns configured for liquid culture biodegradation determination.

## HEXANE DEGRADATION EXPERIMENTS

General operating conditions for the hexane experiments are summarized in Table 4.7. In the hexane experiments, the biofilter was operated at a constant hexane loading rate (grams hexane/minute), three air flux rates (1.3 ft/min, 2.0 ft/min, and 2.6 ft/min) and influent concentration was varied with the air flowrate. Particular operating conditions for the three loading rates used are summarized in Table 4.8. During the course of the experiment, the order of the column sections was interchanged and media was mixed as summarized in Table 4.9.

Table 4.7  
Operating conditions: General

Volume of Media (V <sub>f</sub> ), m <sup>3</sup>	0.0155
Cross sectional area (A <sub>f</sub> ), m <sup>2</sup>	0.0189
Moisture Content, %	45 - 65
pH	7.4
Ambient room temperature, °C	23
Apparent density of wet media, g/cm <sup>3</sup>	0.62

Erratic performance of the laboratory hexane biofilter occurred during the first four months of operation and it was determined that a nutrient limitation existed. Nutrients were added by soaking the compost medium in a nutrient solution. Two nutrient solutions were used (Table 4.9). The lower concentrated nutrient solution, SOL #1, was calculated to achieve a nitrogen concentration in the biofilm equal to a standard culture medium [Brock and Madigan, 1991]. The higher concentrated nutrient solution, SOL #2, was 10 times as concentrated as SOL #1. SOL #2 was calculated to supply enough nitrogen for 4 weeks assuming a stoichiometric utilization of nitrogen. One liter of nutrient solution SOL #1 and SOL #2 was mixed into the media after 82 and 104 days of operation, respectively.

Table 4.8  
Operating conditions: Flow rate and concentration

	High Flow, Low Concentration	Medium Flow, Medium Concentration	Low Flow, High Concentration
Days operating with the specified operating condition	1-29 and 119 - 127	56-68	30-55 and 69 - 118
v: gas flux, m/h	47.7	35.8	23.8
superficial residence time, min	1.0	1.4	2.0
C <sub>g,0</sub> : inlet hexane concentration, g/m <sup>3</sup> or (ppmV)	0.360 (102)	0.480 (135)	0.720 (203)
LR: loading rate, g/(m <sup>3</sup> h)	21.0	21.0	21.0
Liquid hexane from syringe, mL/h	0.49	0.49	0.49

Table 4.9  
Changing the position of the media in the column

column section #	days of operation				
	startup	47	91	98	104
1	A <sup>1</sup>	D	C	MIX <sup>2</sup>	MIX
2	B	C	D	MIX	MIX
3	C	B	A	MIX	MIX
4	D	A	B	MIX	MIX

<sup>1</sup>letters give relative position of media within the column

<sup>2</sup> all the media was taken out of the column and media from all sections was mixed.

Table 4.10  
Composition of the concentrated nutrient solution

	Compound	Concentration in solution added, g/L	Target concentration in the biofilm <sup>1</sup> , g/L
SOL # 1	KNO <sub>3</sub>	13.1	1.9 <sup>2</sup>
	KH <sub>2</sub> PO <sub>4</sub>	13.8	2.0
SOL #2	KNO <sub>3</sub>	131.1 <sup>3</sup>	19.0

<sup>1</sup>Target concentrations in the biofilm were calculated assuming ideal mixing of added nutrient solution and water in the biofilm and a total water content of 5.9 L in the column.

<sup>2</sup> 0.7 g/L as Nitrogen

<sup>3</sup> Nitrogen approximated to last for a 4 week period assuming metabolism of 6.5 g carbon/day and a substrate C/N ratio of 10.

<sup>1</sup>Hewlett Packard 5980A gas chromatograph utilizing a Hewlett Packard 59970 mass spectrometer. A 0.32 mm ID by 30 m J&W Scientific DB624 capillary column was used at a carrier gas flow (He) of 1 ml/min. The column was cooled to 40 °C (4 mins.) then heated at a rate of 10 °C/min to a final temperature of 250 °C. A Hewlett Packard 5890 data acquisition system with requisite software was used for data acquisition, storage, and analysis. Quantification of abundance was done by selective ion integration of the primary ion for each compound.



# 5. RESULTS OF PHASE II: LABORATORY SCALE BIOFILTER EXPERIMENTS

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During the Phase I field studies, questions arose regarding optimal operating parameters and effective ranges of operation, acclimation of microbial populations, bioaugmentation effects, ability to control chlorinated compound emissions, and the effects of shock loading on biofilter performance. These questions prompted the design of the Phase II laboratory scale biofilter experiments which included:

- Experiments designed to test theoretical models developed in Chapter 3 which describe biofilter performance for specific gas flux and compound loading rates.
- An investigation of the spatial distribution of microbial activity in biofilters as measured by compound removal and microbial population counts along the length of laboratory-scale biofilter columns.
- An investigation of the factors governing the control of chlorinated organics using the representative compounds dichloromethane [DCM] and trichloroethene [TCE].
- Quantification of the effects of bioaugmentation of biofilter media on TOL and TCE removal.
- An investigation of removal of volatile aliphatic compounds found in gasoline, as represented by hexane.
- Testing the effect of shock loading on compound removal.
- Study of nutrient limitations in compost biofilters.

## **ACCLIMATION OF MICROBIAL POPULATIONS**

Profiles of TOL concentration through the biofilter bed in COL1 for the first three weeks of operation are shown in Figure 5.1. During the first 3 days of column operation at an inlet TOL concentration of 3 ppmv, no TOL removal was observed. Acclimation of the microbial population to TOL was fairly rapid thereafter, and at one week of operation, 85 percent removal efficiency for TOL was observed. After 3 weeks of operation, the system appeared to reach steady state and outlet concentrations were consistently below the TOL detection limits of 10 ppbv. Toluene degradation in the biofilter column by indigenous compost bacteria was consistent with TOL degradation microcosm experiments described Chapter 4. These

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experiments demonstrated that organisms capable of degrading TOL were initially present in the compost used in media formulation.

Acclimation of the microbial population to DCM took place much less rapidly than TOL acclimation. For the first three weeks of operation, no degradation of DCM was observed. During the fourth week, a drop off in DCM concentration was observed, but only in the last section of the reactor. During subsequent weeks, DCM degradation appeared to move progressively toward the inlet end of the biofilter bed. The data indicated that a DCM degrading population became established in the upper section of the biofilter and spread to the lower sections of the bed over a period of several weeks as shown in Figure 5.2.

Several researchers have investigated the utilization of DCM by aerobic bacteria as a sole carbon and energy source [Brunner *et al.*, 1980; Stucki *et al.*, 1981; Rittman and McCarty, 1980a]. The development of populations capable of degrading DCM was consistent with the work of Rittman and McCarty [1980a], who isolated a DCM degrading organism from primary wastewater effluent exposed to DCM over a period of a year. Their findings support the possibility that the ability to degrade DCM arises in natural populations exposed to the compound over extended periods.

Fuller [1993] of the Department of Land Air and Water Resources (LAWR) at UCD further investigated the community of DCM degraders that developed in COL1 during this period. Samples were taken of the COL1 media after DCM degradation was well established. Successive enrichments of the inoculum resulted in the isolation of a 12 member consortia of bacteria capable of utilizing DCM as a sole carbon and energy source. Although the consortia was able to degrade DCM, individual isolates were not able to degrade DCM under the same conditions. Experiments to further isolate and characterize these organisms are continuing.

In a related set of experiments, Kinney [1993] reinoculated COL1 with the consortia which had been grown on DCM. Dichloromethane degradation was apparent 6 days after inoculation and removal of DCM continued to improve for 13 days after inoculation. The relatively rapid establishment of DCM degradation contrasts with the lengthy acclimation period for DCM observed during the first occurrence of DCM degradation. The lengthy acclimation period observed in the initial column may have been due to the presence of initially small populations of microorganisms capable of degrading DCM in the biofilter media. Although populations may have been present, time was required for them to grow up to the point where significant degradation could be observed [Spain, 1990]. Another possible explanation for this phenomena is that genetic mutations in indigenous populations were occurring which brought about the ability to degrade DCM or its by-products.

### EFFECT OF BIOAUGMENTATION

After 3 weeks of operation, COL1 media were inoculated with an organism, *Pseudomonas putida* strain TOL1A, known to degrade TOL and to cometabolize TCE in the presence of TOL. Inoculation was performed by injecting 12 ml of a TOL1A culture, which had been grown in mineral media with 300 mg/L of TOL and 3 mg/L of TCE as the only carbon sources, into each of the four sample ports and four media access ports in the reactor. This represented approximately at  $10^6$  cells per gram of filter media. Bioaugmentation significantly increased TOL removal rate in the bed as shown in Figure 5.3. A possible explanation for this higher rate is, that after inoculation with TOL1A there was a higher overall (TOL1A + indigenous) population density of toluene degraders in the column. However, TOL1A has been shown [Fuller, 1991] to have a high degradation rate for TOL and the increased biodegradation rate for TOL in COL1 was sustained over several months of operations. Population density effects would not be expected to be sustained once the column reached steady state.

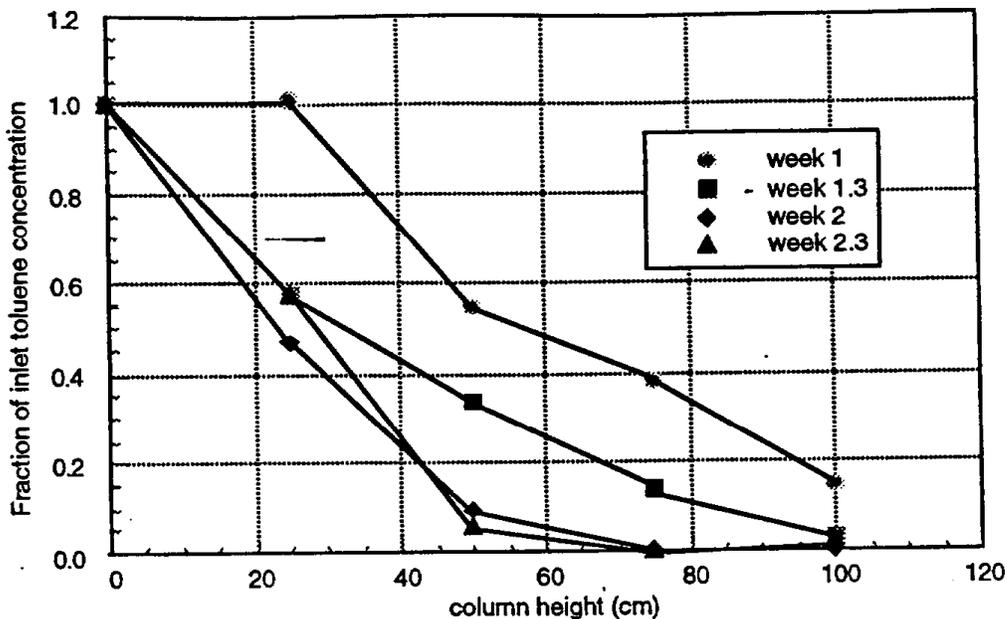


Figure 5.1. Toluene concentration profiles in COL1 during the first 3 weeks of operation showing acclimation of microbial populations to toluene. Inlet toluene concentration during this period was approximately 3 ppm<sub>v</sub>.

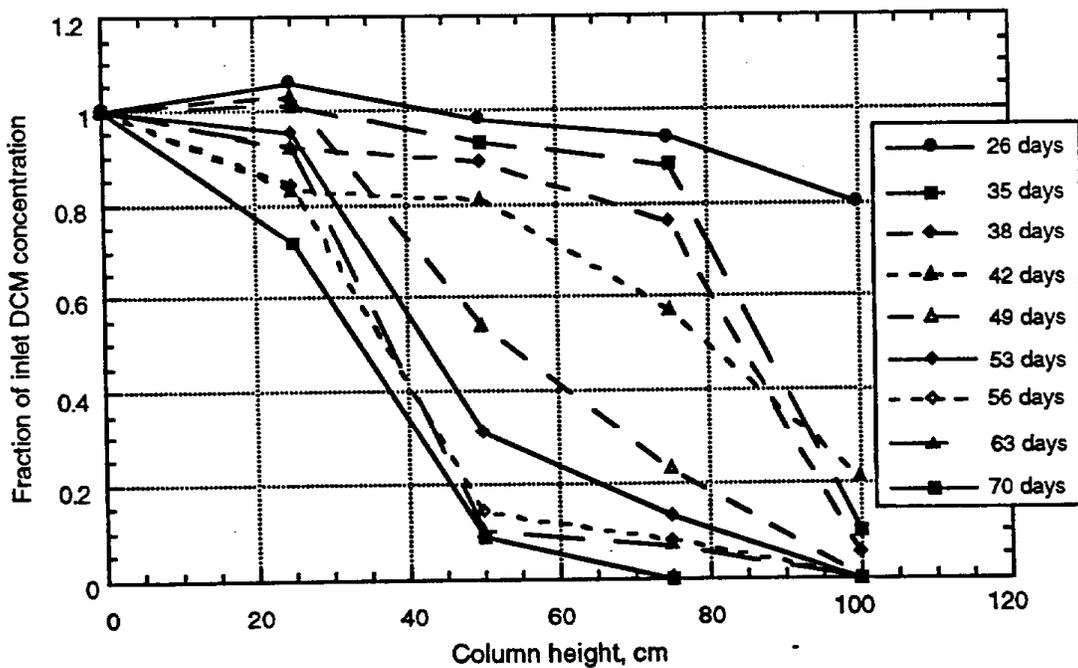


Figure 5.2. Dichloromethane profiles in the filter bed during weeks three through nine of operation showing acclimation of microbial populations to dichloromethane. Inlet dichloromethane concentration during this period was approximately 3 ppm<sub>v</sub>.

Although inoculation with TOL1A increased the rate of TOL degradation, the organisms did not initiate TCE degradation in the biofilter media as shown in Figure 5.4. In order to determine whether TCE cometabolism could be induced at a higher primary substrate to cometabolite ratio, inlet TOL concentration was increased to 50 ppm<sub>v</sub> twenty days after inoculation while maintaining the TCE concentration at 3 ppm<sub>v</sub>. The increase in TOL concentration was not found to enhance TCE degradation in the column.

Degradation of TCE was observed, however, in the liquid reservoir which served as a humidification chamber for the column. During this period, the compounds were added to the air which was bubbled through the humidification chamber as discussed in Section 4.2.8. An active microbial population existed in the humidification section composed of organisms that had dripped down from the biofilter column which was located above the liquid reservoir. An additional port was added to sample inlet gases to the humidification chamber. The results for the three compounds are shown in Table 5.1. First order biodegradation rate coefficients were determined by modeling the humidification chamber as a continuous-flow stirred-tank reactor (CFSTR) at steady state according to the equation:

$$Q(C_i - C) - \frac{kCV}{H} = \frac{dC}{dt} = 0 \quad (5.1)$$

where  $C_i$  is the inlet concentration (ppm<sub>v</sub>),  $C$  is the outlet concentration (ppm<sub>v</sub>),  $Q$  is the gas flow rate (16.7 L/min),  $V$  is liquid volume in the reactor (3.6 L),  $k$  is the first order biodegradation rate coefficient (min), and  $H$  is the Henry's law coefficient (Table 2.3 dimensionless). An assumption made in development of Equation 5.1 was that the liquid concentration in the reservoir was at equilibrium with the gas phase concentration of the outlet gases. Therefore, solubility of the compound has a large effect on the calculated first order rate coefficient as indicated in the large differences in rates calculated for DCM and TCE.

Trichloroethene concentration was shown to decrease by 33 percent after treatment in the liquid reservoir. The degradation rate for TCE was even higher than was observed for TOL or DCM which was unexpected given that TCE was not degraded in the column. Apparently, conditions in the humidification chamber such as biomass density, co-substrate ratio, or aeration, were favorable to TCE cometabolism. The high degradability of TOL resulted in most of the primary substrate being removed in the first 25 cm of the biofilter column. The TOL/TCE ratio required for TCE cometabolism could not be maintained throughout the column length. One strategy that may be applied to remedy this problem is to add TOL at several points over the length of the column to keep the TOL/TCE ratio at optimum for TCE degradation. Another strategy would be to continuously reinoculate the column with organisms (TOL1A or another organism) which have been induced with TOL or another co-substrate such as phenol or methane.

### EFFECT OF COMPOUND CONCENTRATION

An increase in the inlet TOL concentration from 3 to 50 ppm<sub>v</sub> did not change the overall removal efficiency for TOL once steady state was established as shown in Figure 5.5. Toluene concentration profiles, normalized by inlet TOL concentrations did not change even with inlet concentrations sixteen times higher than in initial experiments. Independence of normalized concentration profile is consistent with the predicted concentration profile when the assumptions of homogeneous biomass concentration and first order biodegradation kinetics are made as discussed in Chapter 3. The resulting equation for the concentration profile in the column is:

$$\ln \left( \frac{C_g}{C_o} \right) = - \frac{kzA_sL}{Hv} \frac{\tanh \phi'}{\phi'} \quad (5.2)$$

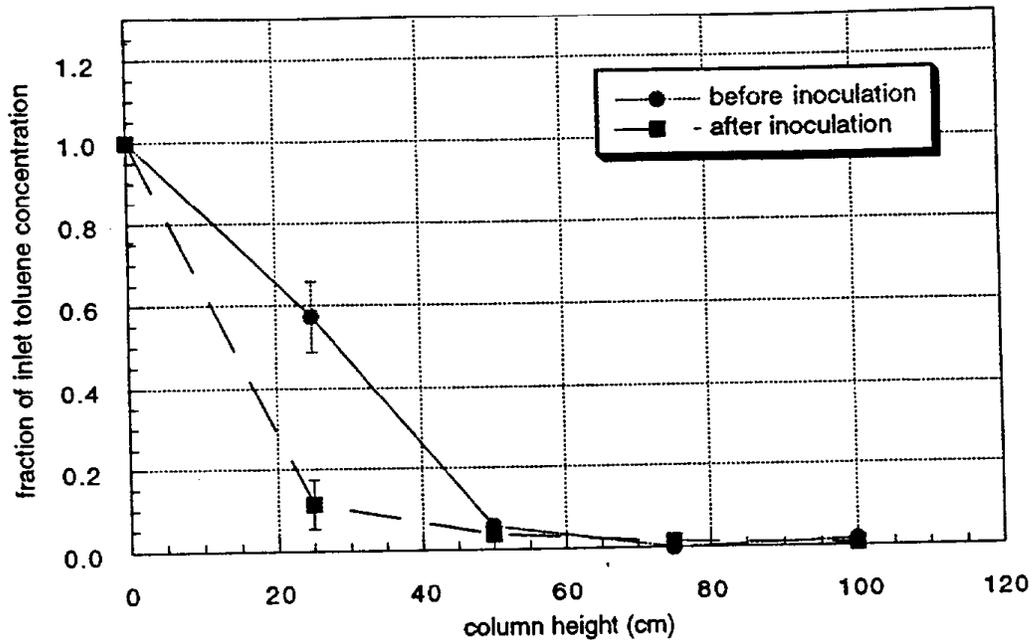


Figure 5.3. Removal of toluene in COL1 before and after inoculation with the TOL1A organism showing significant increase in biodegradation after inoculation. Inlet toluene concentration during this period was approximately 3 ppm<sub>v</sub>.

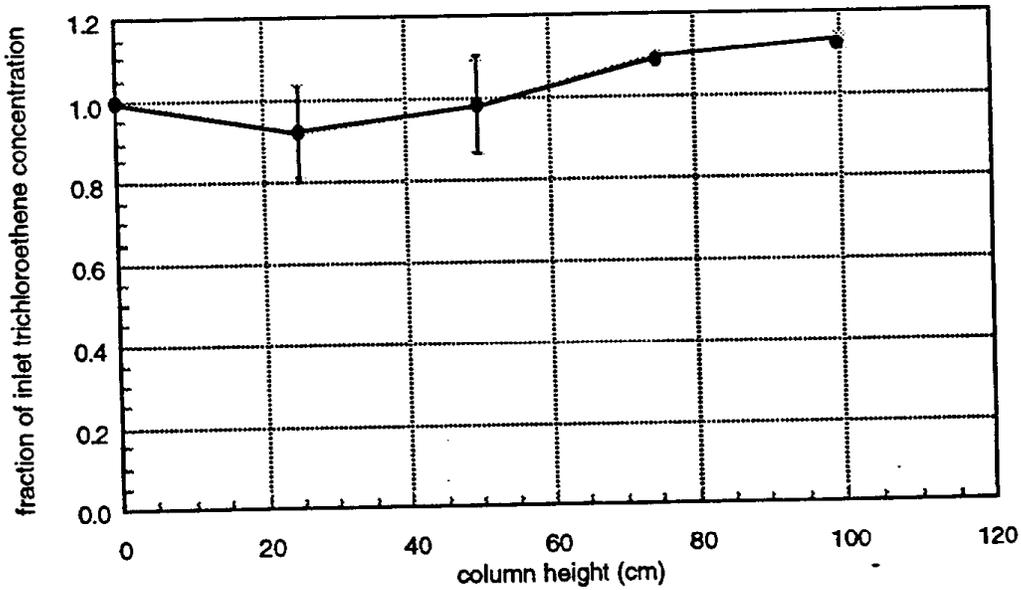


Figure 5.4. Typical profile for TCE in COL1 showing insignificant TCE degradation in the biofilter column even after inoculation with the TCE cometabolizing organism and increasing the TOL concentration.

## 5. RESULTS OF PHASE II: LABORATORY SCALE BIOFILTER EXPERIMENTS

Table 5.1.  
Degradation of TOL, TCE, and DCM in liquid culture

compound	inlet to reservoir ppm <sub>v</sub>	outlet of reservoir ppm <sub>v</sub>	first order degradation rate constant min <sup>-1</sup>
Toluene	60	50	0.22
Trichloroethene	3.0	2.0	0.90
Dichloromethane	4.0	2.5	0.24

where  $C_g$  ( $M/L^3$ ) is the concentration at height  $z$  ( $L$ ) in the column,  $C_0$  is the inlet concentration ( $M/L^3$ ),  $k$  is the first order biodegradation rate ( $T^{-1}$ ),  $A_s$  is the media specific surface area ( $L^2/L^3$ ),  $H$  is the Henry's law coefficient (dimensionless),  $L$  is the biofilm thickness ( $L$ ),  $v$  is the gas velocity ( $L/T$ ), and  $\phi'$  is the Thiele number (dimensionless). For constant media properties and biodegradation rate, the removal efficiency,  $\eta$ , is exponential with bed height:

$$\eta = 1 - \frac{C_g}{C_0} = 1 - e^{-Kz} \quad \text{where: } K = \frac{kA_s L \tanh \phi'}{Hv \phi'} \quad (5.3)$$

This exponential behavior was empirically derived by Bohn [1992] in work with soil biofilters for VOC and odor control. At higher gas phase VOC concentrations, other researchers [Ottengraf and van den Oever, 1983; Togna and Folsom, 1992; van Lith, 1989] have shown a dependence of removal efficiency on inlet concentration. The results here suggest, that for compounds which support growth at concentrations in the range of 50 ppm<sub>v</sub> and below, an increase in bed depth is not required to obtain the same removal efficiency at higher concentrations. This implies that mass transfer and biodegradation rate capacities are not exceeded in this concentration range. In the experiment reported here, concentrations of TOL in the column were determined after steady state conditions were established. Hence, they do not address the response of the biofilter column to transient conditions which will be discussed below.

Equation 5.2 was developed without regard to biofilter scale and should be applicable to full scale processes as long as the conditions are such that a first order reaction rate model adequately describes the reaction environment. The laboratory columns were the same depth as most prototype biofilters and the particle size of the medium was small enough to eliminate significant wall effects.

### EFFECT OF GAS FLUX

Toluene removal efficiency at an inlet concentration of 50 ppm<sub>v</sub> was greater than 99.9 percent at superficial velocities between 1 and 2 m<sup>3</sup>/m<sup>2</sup>-min as shown in Figure 5.6. The limited number of sampling port locations precluded accurate determination of the shape of the concentration profiles for TOL under these conditions. Instrument detection limits for TOL were 10 ppb<sub>v</sub>, 99.98% below the inlet concentration and outlet concentrations rarely exceeded this limit. Increasing the gas flux in the column resulted in more VOC degradation deeper in the bed but did not decrease overall efficiency. Limitations of tubing and flow meters prevented increasing the gas flux to the point where TOL outlet concentrations were significantly above the instrument detection limits. Dichloromethane removal efficiencies at an inlet concentration of 3 ppm<sub>v</sub> were greater than 98% and 95% at 1 and 2 m<sup>3</sup>/m<sup>2</sup>-min gas velocities, respectively.

## 5. RESULTS OF PHASE II: LABORATORY SCALE BIOFILTER EXPERIMENTS

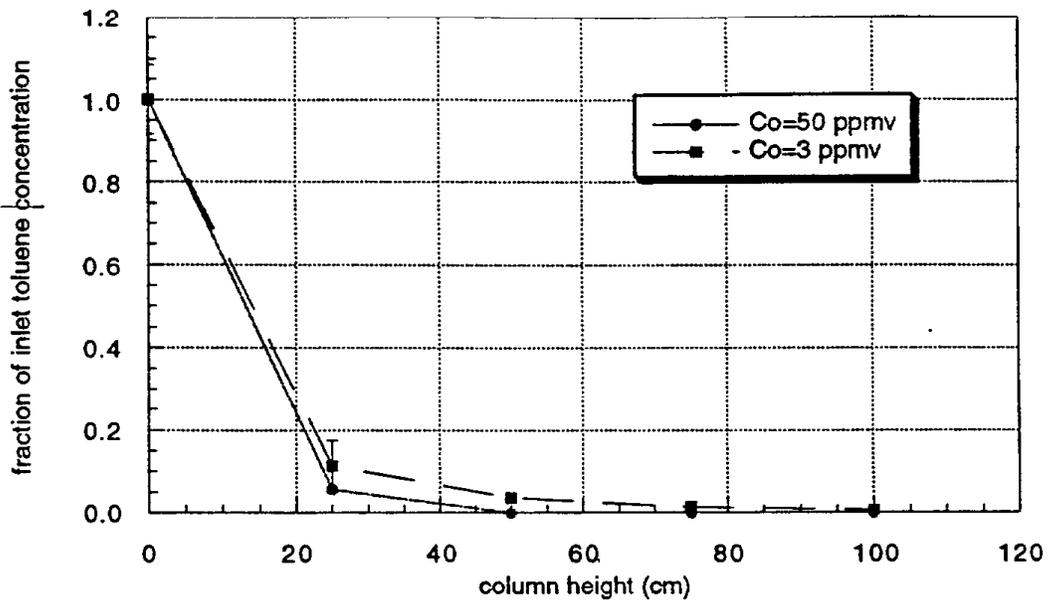


Figure 5.5. Toluene concentration profile showing effect of increasing concentration from 3 ppm<sub>v</sub> to 50 ppm<sub>v</sub> on toluene removal efficiency.

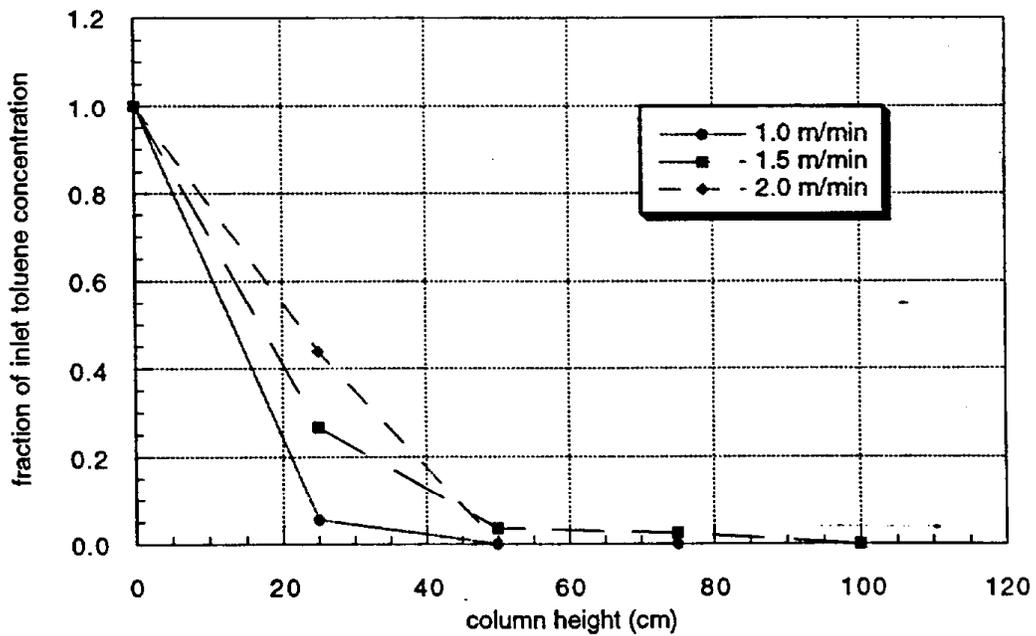


Figure 5.6. Toluene concentration profile showing effect of changes in gas flux on toluene removal efficiency.

### EFFECT OF TRANSIENT LOADING

The effect of transient loading on biofilter performance was evaluated by stepping-up the inlet TOL concentration from 10 to 35 ppm<sub>v</sub> and determining the response of the system. The step-up was accomplished by running the system at an initial inlet TOL concentration of 10 ppm<sub>v</sub> for 14 days until steady state removal had been established. Toluene mass loading was then increased while holding the gas flux constant at 1.5 m<sup>3</sup>/m<sup>2</sup>-min. Gas samples were taken along the length of the column four hours before and one hour after the step increase in concentration. The results are shown in Figures 5.7 and 5.8.

Soon after the increase in concentration, TOL removal efficiency decreased and did not fully recover after three days. This contrasts with the results, of Figure 5.5, which indicate independence of inlet concentration of removal efficiency under steady state conditions. Mass removal of TOL more than doubled in the hour after step-up showing a good response to transient loading. This was consistent with observations made on peak loading days during the Phase I field pilot plant experiments.

One explanation for the improved response over time to changes in inlet concentration is that microbial population densities varied over the length of the column. When the inlet concentration increased, the mass flux of compounds was greater than the microbial population could utilize. After some time, growth of microbial populations resulted in the maximum degradation further downstream in the column. The spatial variation of microbial populations in biofilters is discussed in more detail in below.

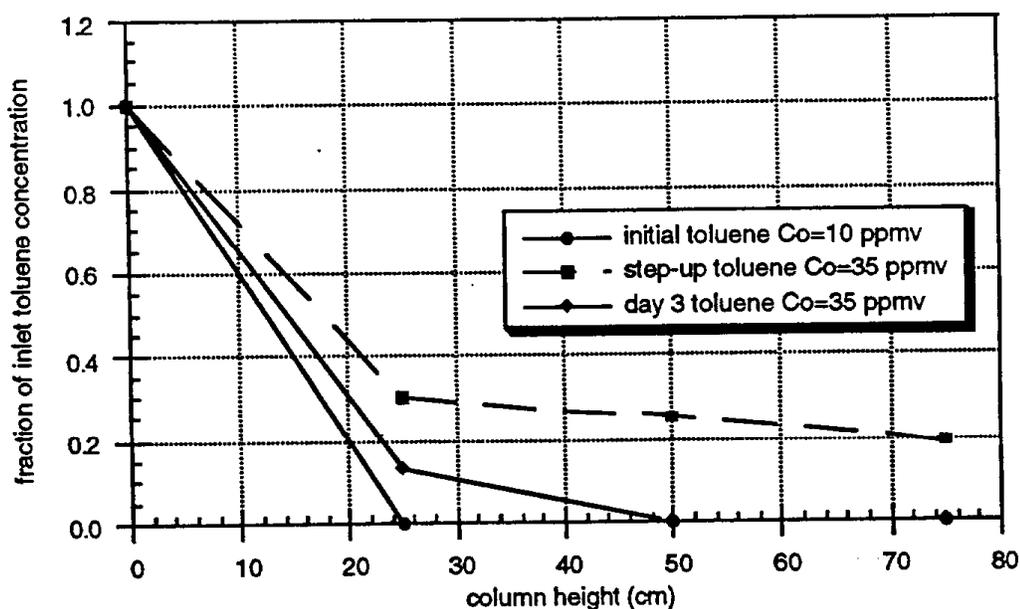


Figure 5.7. Toluene profiles showing the effect of a step-increase in toluene concentration on biofilter performance.

Togna and Frisch [1993] found similar initial results in their study of populations of styrene degraders in a compost biofilter treating spraying operation off-gases. Initially the system responded slowly to transient mass loading of the system as measured by bed removal efficiency. After several months of operation under transient conditions however, the system

was able respond quickly to changes in inlet VOC concentrations. This may have been due to selection for organisms which could shift quickly from degrading low to high concentrations of styrene or to the growth of microbial populations deeper in the bed. There is some evidence that metabolic control in some organisms allows shifting from oligotrophic to eutrophic metabolism [Koch, 1976]. This study, however, only evaluated the response of a population at steady state to a single shift in compound concentration and further research is necessary to fully understand the effects of transient conditions.

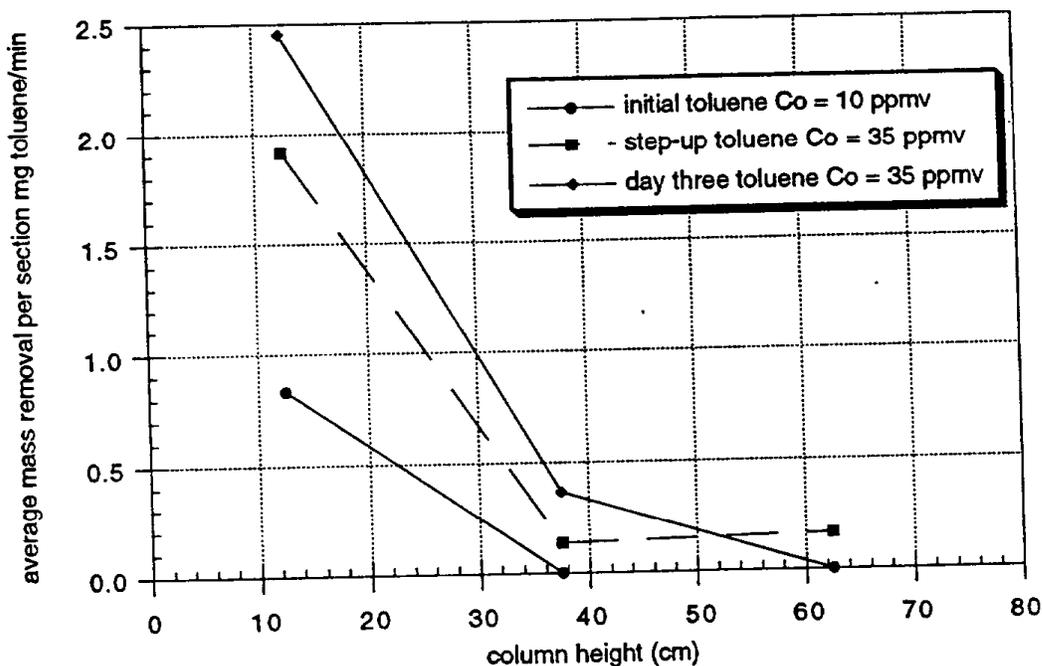


Figure 5.8. Mass removal of toluene in biofilter before and after step-increase in toluene concentration. Toluene removal immediately increased to more than twice the initial removal and increased more after three days of acclimation.

### EFFECT OF SHOCK LOADING

Accidental release of several milliliters of a pure solvent mixture, containing TOL, TCE, and DCM into the humidification reservoir of COL1 resulted in shock loading of the column. The solvent mix consisted of a TOL/TCE/DCM molar ratio of 50/3/3. Stripping of the VOCs from the humidification chamber resulted in saturation concentrations of the three compounds for several minutes. Toluene removal efficiency decreased somewhat in the first day after shock loading but then deteriorated to the point where almost no removal was occurring in the upper 75 cm of the bed as shown in Figure 5.9.

On the ninth day after shock loading the system, TCE was removed from the inlet gas mix to determine whether the decrease in TOL removal efficiency was a result of a toxic effect of TCE on the TOL degrading populations. Toluene removal efficiency did not recover however, even after TCE was taken out of the mix and an extended period of time elapsed. Reinoculation of the column with a fresh TOL1A culture 47 days after shock loading partially restored the TOL degrading ability of the system.

During this same period of time, DCM removal appeared to be unaffected by shock loading of the system as shown in Figure 5.10. The continued removal of DCM while TOL removal was inhibited indicates that separate microbial populations were degrading the two compounds and that the DCM degraders were more resistant to shock loading of TCE and TOL.

After the shock loading experiments, COL1 was taken apart and refilled with fresh media which was inoculated with a fresh TOL1A culture. A portion of the media from the upper sections of the old column was also mixed with the fresh compost to introduce the DCM degraders into the new system. The old media, which was removed from COL1 at this time, appeared very black and densely packed, indicating anaerobic activity had been occurring. Head losses in the system had increased from 0.75 to 2.8 cm of water and moisture content of the media had increased from 50 to 66 percent. Possible explanations for this change in media characteristics are the ascendance of populations of anaerobic organisms after shock loading, an increase in moisture content leading to development of anaerobic zones, or compaction of the media due to aging and decomposition of the compost. Reduction in TOL degrading ability was not observed in Phase I system during pilot scale operations, so media aging and decomposition seems an unlikely explanation for the TOL inhibition observed after shock loading. It is more likely that increased moisture content led to development of channeling and anaerobic zones.

### COMPARISON WITH THEORETICAL MODEL

A comparison between observed biofilter concentrations and those calculated from fitting the first order biodegradation rate transport equations developed in Chapter 3 (Equations 3.24 and 5.2) is shown in Figure 5.11. Model profiles were calibrated against DCM data because the lower degradation rates for this compound resulted in a more accurate determination of the shape of concentration profiles. The steady state TOL concentrations usually approached the detection limit at the end of the first section (i.e. at the first sampling point after the inlet) which eliminated the possibility of calibration of the equation. Parameter values used in the model and their method of determination are given in Table 5.2. Two of the model parameter values might be termed weaker than the others, L and k. Liquid film depth, L, was estimated as the total water volume in the column divided by the total measured surface area. Such an estimate implies uniform coverage of the medium surface, which is unlikely. The first order reaction rate coefficient, k, was then determined by regression of the data. Because only one parameter was determined by regression the model may prove to be a useful tool for predicting performance of compost biofilters treating low concentration VOC emissions. Future studies will allow evaluation of validity of the rate coefficient estimated here. Further indication of the validity of the model are the results, presented above, showing TOL removal efficiency to be independent of inlet concentration.

Table 5.2.  
Model parameters used in first order model.

parameter	value	method of determination
$A_s$	$1.6 \times 10^6 \text{ m}^2/\text{m}^3$	B.E.T. analysis
v	3 m/min	gas flux/void ratio
H	0.09	reference a
D	$1.3 \times 10^{-9} \text{ m}^2/\text{s}$	Wilke-Chang method <sup>b</sup>
L	0.2 $\mu\text{m}$	water content/surface area
k	2.6 $\text{min}^{-1}$	regression of model

a - Certified Rubber Company, 1978; b - Reid and Prausnitz, 1977

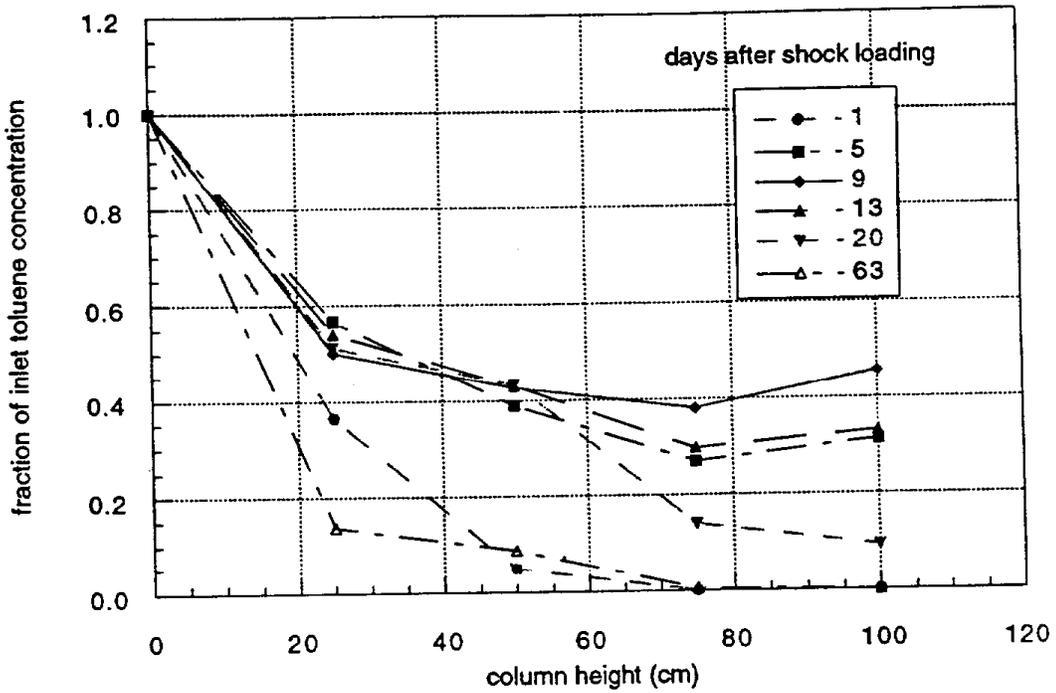


Figure 5.9. Effect of shock loading on toluene removal efficiency. Trichloroethene was removed from the solvent mix 9 days after shock load. Column was reinoculated with the TOL1A organism 47 days after shock load.

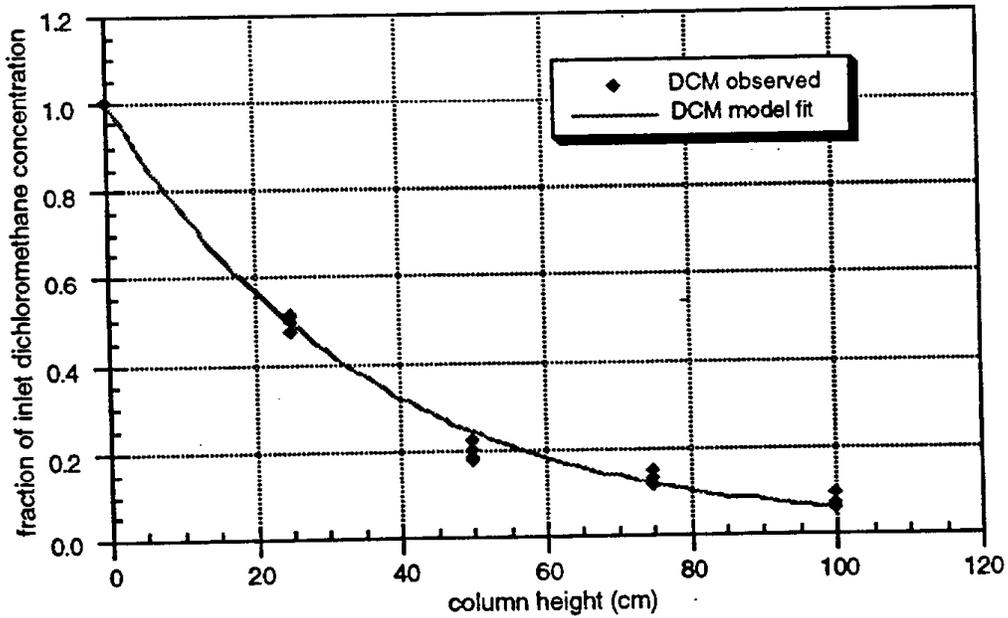


Figure 5.11. Observed and model fit dichloromethane concentrations as a function of height in the filter bed.

## NITROGEN UTILIZATION AND TOLUENE DEGRADATION

The second column (COL 2), which utilized porous ceramic media as discussed in Chapter 4, was used to determine nitrogen utilization and spatial distribution of microbial populations. Unlike the compost media, the porous ceramic media did not contain the necessary nutrients for microbial growth and hence was amended with a nutrient solution. Nutrients were added to COL2 by soaking the media in a nutrient solution as described in Chapter 4 (Table 4.2). Initially, the nutrient solution contained 500 mg/L of nitrogen as ammonium. At a 40 percent moisture content, this represented approximately 7.4 grams of available nitrogen in the column. The available nitrogen was estimated based on an assumption that the liquid retained in the column after draining had the same chemical makeup as the nutrient solution. For an inlet TOL concentration of 50 ppm<sub>v</sub>, a carbon to nitrogen ratio of 10, and a cell yield of 0.4, a 40 day nitrogen supply was provided.

An initial acclimation period of several days, during which no TOL removal was observed was followed by a period during which TOL was degraded as shown in Figure 5.12. The acclimation period observed was somewhat unexpected since media had been inoculated with a TOL1A culture which was actively degrading TOL prior to start-up of column operations. Apparently, an acclimation period was required before removal of TOL could be observed in the biofilter column. The acclimation may be due to attachment of the film to the media or growth and distribution of organisms through the bed.

Two weeks after start-up of COL 2, TOL concentration profiles showed that TOL degradation had ceased. Ammonia analysis of the porous ceramic media indicated that nitrogen concentration had dropped to below instrument detection limits, in retrospect as a result of volatilization of ammonia from the column. Addition of a nutrient solution to the column containing nitrogen in the nitrate form resulted in a resumption of microbial activity shown in Figure 5.12. Utilization of nitrate over time resulted in decreased microbial activity near the inlet to the column where TOL mass removal was highest. During subsequent experiments COL2 was amended with mineral media containing nitrate-nitrogen on a weekly basis.

## SPATIAL DISTRIBUTION OF MICROBIAL POPULATIONS

The spatial distribution of microbial populations was determined in COL2 using the extraction and plate counting technique described in Chapter 4. The results are shown in Figures 5.13 through 5.16. Steady state conditions could not be assessed in this system because of weekly interruptions in operations for nutrient addition as described above. Plates cultures extracted from the media revealed that the column contained a mixed microbial community which was dominated by colonies resembling the TOL1A colonies but included several other organisms as well.

Microbial populations were found to be distributed such that higher biomass densities existed nearer the inlet to the column than the outlet. Biomass density was highly correlated with TOL mass removals in the column. The observed spatial distribution indicates that much of the column is underutilized due to low population densities near the outlet. During peak loadings, when inlet concentrations exceed the degradation capacity of populations near the inlet, percent removals decrease, as was shown in the Phase I field trials and in the step-up experiments. Decreased removal occurs because substrates reach downstream populations too infrequently to support the biomass density necessary to degrade them. A potential solution to this problem is to increase the biomass density near the outlet by periodically switching from up-flow to down-flow operation or to supplement the upper parts of the column with appropriate substrates. Shorter columns are generally undesirable because of the necessity to accommodate surges in mass loading.

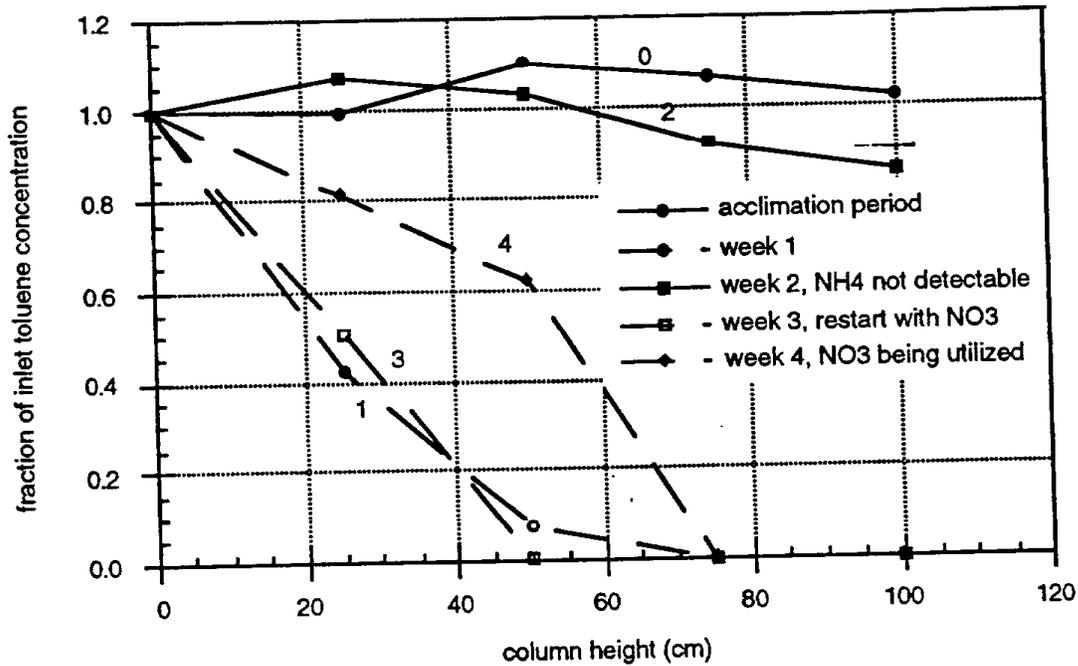


Figure 5.12. Toluene profiles for the first four weeks of COL2 operation showing acclimation period, and toluene utilization under nitrogen limited and nitrogen rich conditions.

The variable biomass density model, described in Chapter 3, was used to simulate TOL removal in COL2. Input model parameters, which reflected actual column operating conditions for 7/19 are shown in Table 5.3. The first order biodegradation rate,  $k$ , was determined at each node in the model by multiplying the microbial density ( $\rho_b$ , bacterial count/gram media) by the coefficient  $k'$  where:

$$k' = \frac{\mu_{max}}{K_s} = 3.1 \times 10^{-11} \text{ gram media/bacterial counts-min} \quad (5.4)$$

The biomass density at each node was determined by fitting a second order polynomial through the experimentally determined biomass density data of 7/19 (Figure 5.17). The coefficient,  $k'$ , was determined by a grid search technique. The best fit parameter was determined by minimizing the sum of absolute differences between the observed and predicted data of 7/19. The results, shown in Figure 5.18 indicate that the model over predicts the degradation rate near the inlet to the column and under predicts it near the outlet. The lack of fit indicates that, although biomass densities were low near the outlet, activity of the biomass near the outlet was disproportionate to their numbers. Similarly, a portion of the biomass near the inlet of the column was probably inactive. The results show that simple assumptions of biodegradation rates cannot be used to predict compound removal in a non-homogeneous biofiltration system.

5. RESULTS OF PHASE II: LABORATORY SCALE BIOFILTER EXPERIMENTS

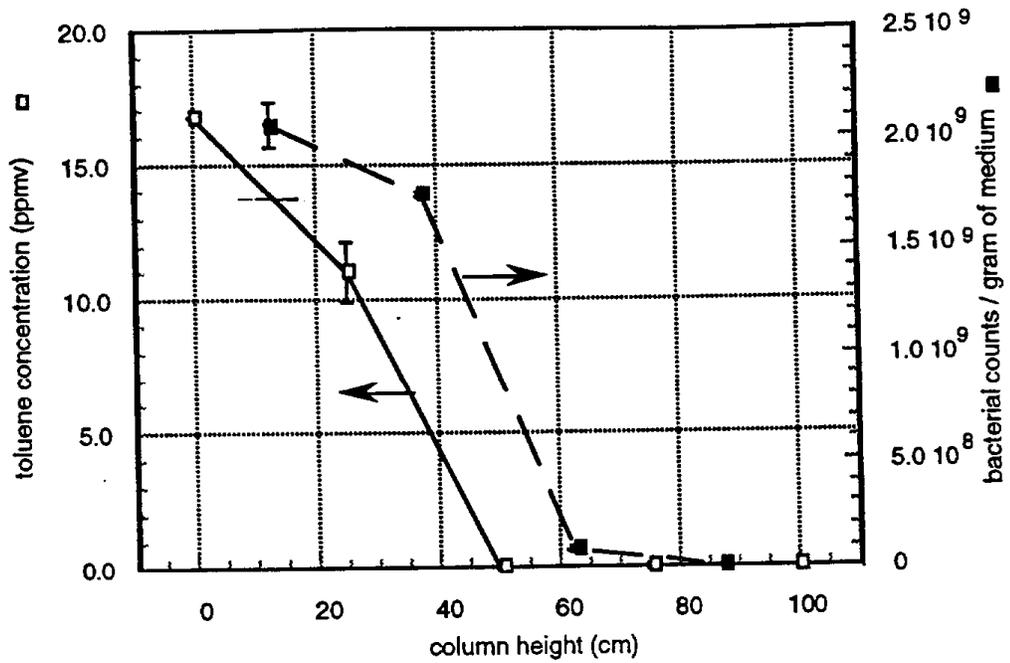


Figure 5.13. Bacterial counts and concentration profiles for toluene on 6/28.  $C_0 = 17 \text{ ppm}_V$ ,  $v = 1.5 \text{ m/min}$ .

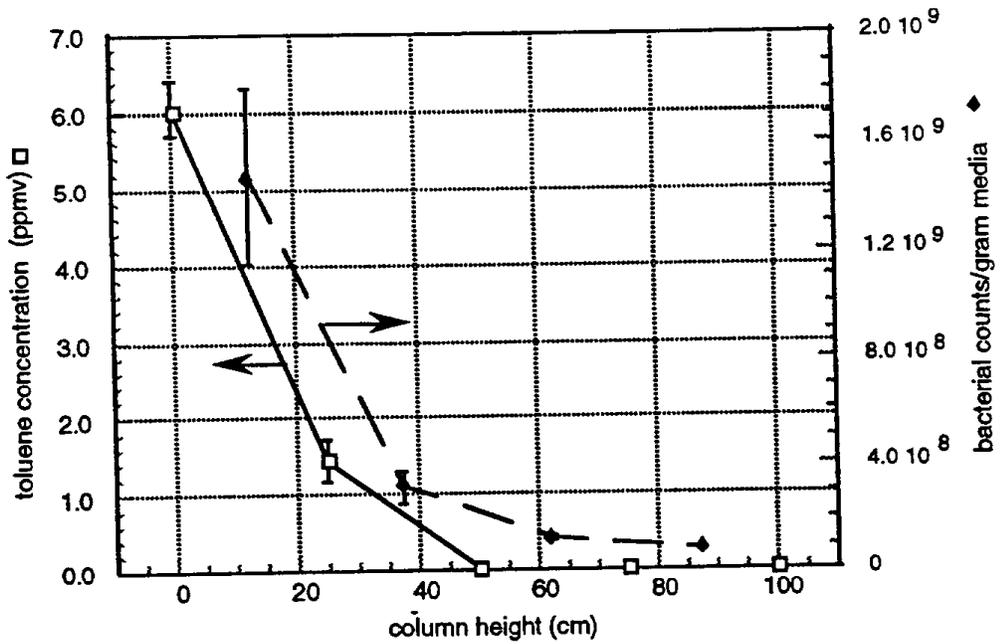


Figure 5.14. Bacterial counts and concentration profiles for toluene on 7/6.  $C_0 = 5 \text{ ppm}_V$ ,  $v = 1.5 \text{ m/min}$ .

Fig

5. RESULTS OF PHASE II: LABORATORY SCALE BIOFILTER EXPERIMENTS

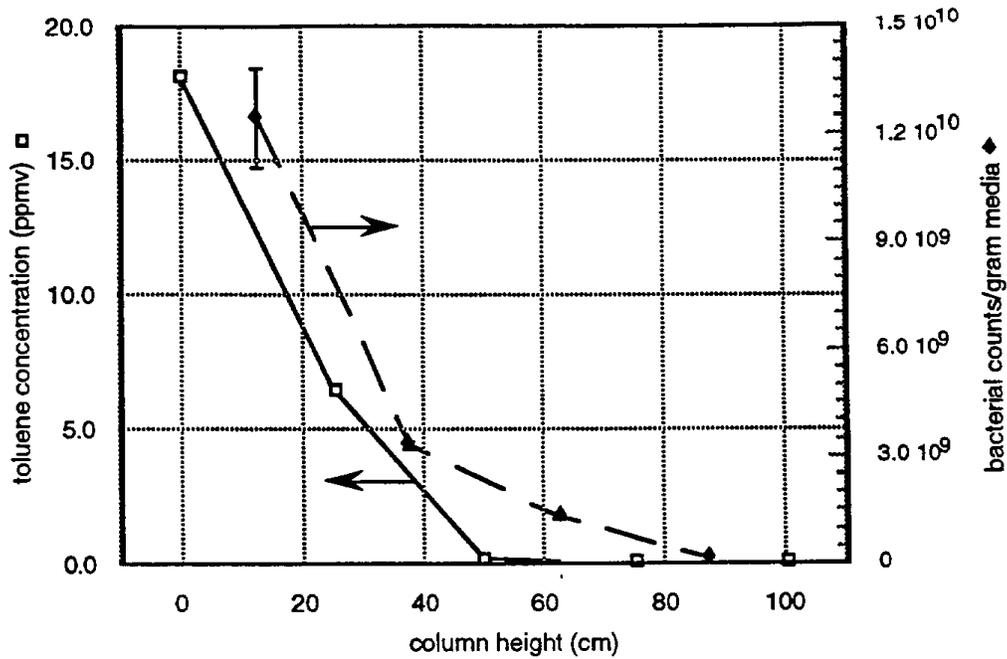


Figure 5.15. Bacterial counts and concentration profiles for toluene on 7/14.  $C_o = 18 \text{ ppm}_v$ ,  $v = 1.5 \text{ m/min}$ .

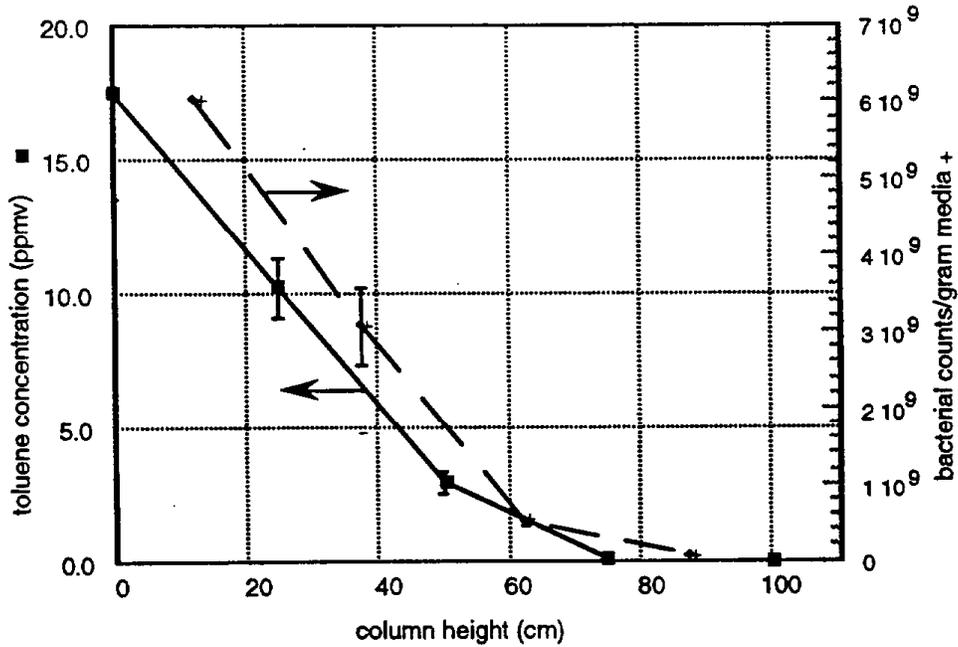


Figure 5.16. Bacterial counts and concentration profiles for toluene on 7/19.  $C_o = 17 \text{ ppm}_v$ ,  $v = 1.5 \text{ m/min}$ .

Model parameters used in variable biomass density model.

parameter	value	method of determination
$A_s$	$7.3 \times 10^5 \text{ m}^2/\text{m}^3$	B.E.T. analysis
$v$	3 m/min	gas flux/void ratio
$H$	0.27	reference a
$D$	$0.85 \times 10^{-9} \text{ m}^2/\text{s}$	Wilke-Chang method <sup>b</sup>
$L$	0.5 $\mu\text{m}$	water content/surface area
$k'$	$3.1 \times 10^{-11} \cdot \rho_b \text{ min}^{-1}$	grid search best fit

a - Certified Rubber Company, 1978; b - Reid and Prausnitz, 1977

## HEXANE DEGRADATION EXPERIMENTS

Acclimation of the biofilter to hexane required nearly three weeks of operation. After 33 days of operation removal efficiencies were approximately 85 percent but efficiencies then decreased with increasing operation time. Addition of the high concentrated nutrient solution SOL #2 (Table 4.10) resulted in increasing removal efficiencies above 99.9 percent. Removal efficiencies and other performance parameters are given in Figure 5.19 and Table 5.4. A detailed summary of operational changes is given in Appendix D. The pH remained constant at 7.4 throughout operation on hexane. Results of the biofilter performance are discussed in detail below.

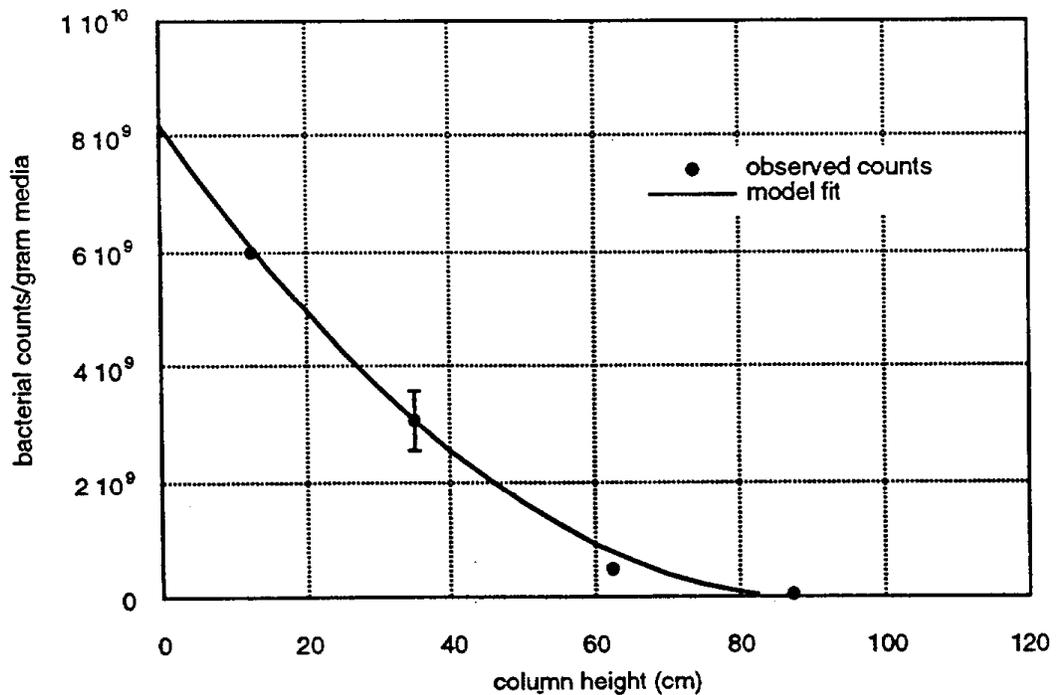


Figure 5.17. Biomass densities used in variable density biofilter model. Second order polynomial fit and observed bacterial counts for 7/19/93 (Figure 5.16 above).

## 5. RESULTS OF PHASE II: LABORATORY SCALE BIOFILTER EXPERIMENTS

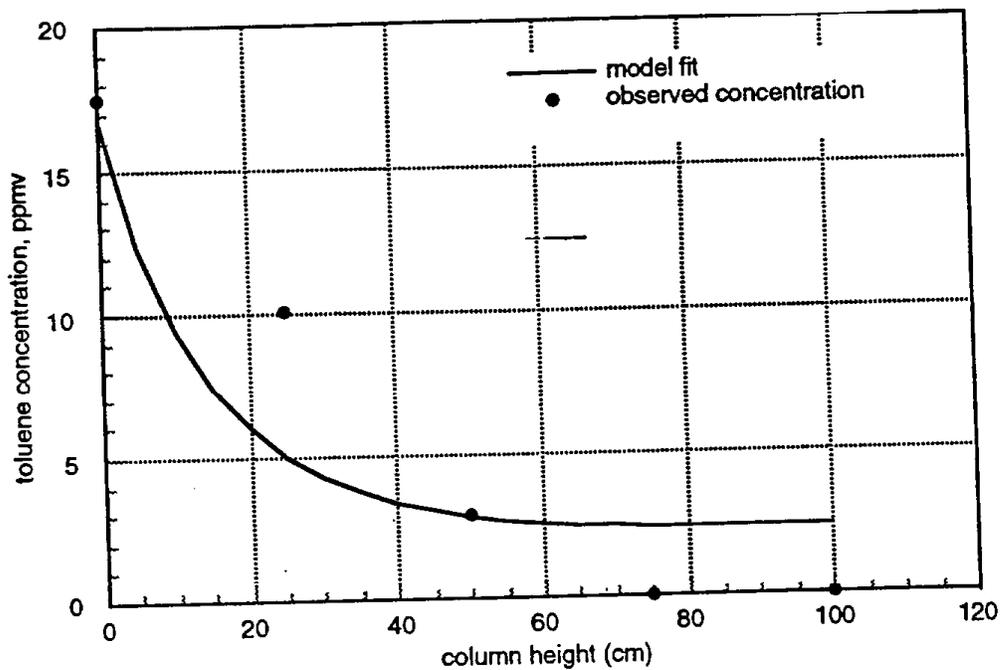


Figure 5.18. Variable density biofilter model. Model fit and observed concentrations for 7/19/93 (Figure 5.16 above).

Table 5.4  
Results of biofilter performance

	days of operation	Gas Flux ft <sup>3</sup> /ft <sup>2</sup> ·hr	Elimination			
			Efficiency, %	Capacity, g/m <sup>3</sup> h	$\alpha_1$ , m <sup>-1</sup>	$\alpha_1 \times v$ , hr <sup>-1</sup>
high flow	1 - 29	2.6	0 - 40	0 - 7	0.3	14.3
low flow	30 - 55	1.3	80 - 90	16 - 20	2.2	52.4
medium flow	56 - 68	2.0	55 - 70	9 - 14	1.4	50.1
low flow	69 - 103	1.3	40 - 70	7 - 14	1.0	23.8
low flow	104 - 118	1.3	> 99.9	17 - 26 <sup>1)</sup>	6-9	150 - 220
high flow	119 - 128	2.6	> 99.9	17 <sup>1)</sup>	7	300 - 320

<sup>1)</sup> Note that the elimination capacity was limited by the loading rate and measured loading rate ranged from 14 to 26 g/m<sup>3</sup>h (Figure 11). Higher elimination capacities can be expected for higher loading rates.

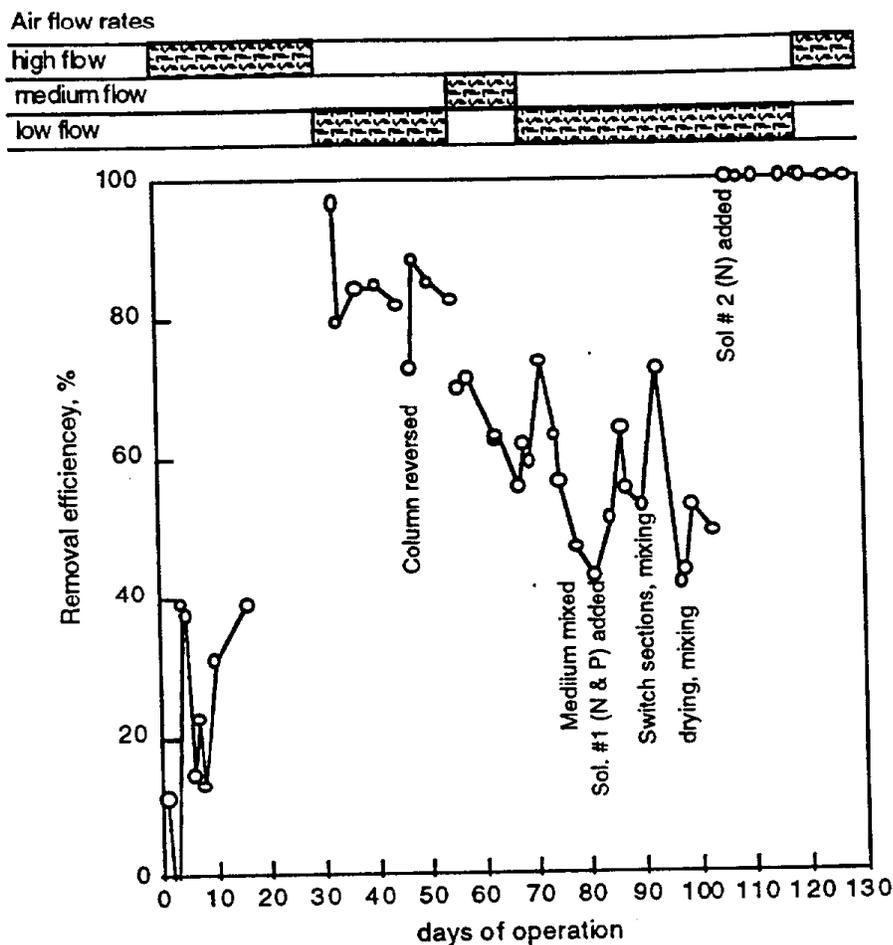


Figure 5.19  
Efficiency of the biofilter. Air flowrate was changed over the course of the experiments as shown above the graph. For detailed descriptions of the biofilter operation see Table D17 (Appendix D).

### Acclimation

Rapid acclimation of the biofilter was expected, because hexane is an easily biodegradable substrate for a large number of organisms [Gibson, 1984; Atlas, 1981]. In a batch test using unacclimated activated sludge from the UC Davis wastewater treatment plant, hexane was injected into the headspace of a sealed flask. Within a week, headspace hexane was decreased by 99 percent. Based on the results of the batch experiment, activated sludge that was used to inoculate the experimental compost biofilter. However in the first 16 days of operation, removal efficiencies in the biofilter were low and fluctuated between 0 and 40 percent, which was not considered significant (Figure 5.19). For a similar system Ergas [1993] reported acclimation periods of 1 and 4 weeks for toluene and dichloromethane, respectively. No measurements were made between the 16th and the 33rd day of operation. Removal efficiencies after the 33rd day of operation showed significant removal of 80 - 90 percent. Thus the biofilter required between 16 and 33 days to acclimate. Comparable results for butane removal were obtained by Kardono and Allen [1994], who reported a long acclimation period for the compost biofilter.

The long acclimation period was not expected for the removal of hexane. A reason for the long acclimation period may have been a low microbial population in the compost. Slow acclimation may have resulted from the low available nitrogen in medium, also.

### Effect of Gas Flux

Total air flux was varied in the hexane hexane, but the hexane loading rate was maintained constant at 21 g/m<sup>3</sup>h (see operating conditions in Table 4.8). Between day 30 and day 55 of operation the gas flux was low (23.8 m/h), while between day 56 and day 68 of operation the gas flux adjusted to medium flow (35.8 m/h). As can be seen in Figure 5.19 removal efficiencies were dependent on gas flux and efficiencies decreased when the total gas flux was increased. To verify dependents of the removal efficiency on gas flux, the gas flux was decreased again after day 69 of operation and it was expected that the removal efficiency would increase again to about 85 percent. The removal efficiency increased at first, but at day 71 of operation removal efficiency started to decrease again. Possible channeling was eliminated by drying and thoroughly mixing the media. A low concentration nutrient solution was added (SOL #1, Table 4.10) but removal efficiencies remained between 40 and 70 percent until a highly concentration nitrate solution (SOL #2, Table 4.10) was added on the 104th day of operation. After adding the highly concentrated nitrated solution the removal efficiencies were greater 99.9 percent for the next weeks. After 119 days of operation the gas flux was adjusted to high flow. Because removal efficiencies were extremely high, little effect was expected, and measured removal efficiencies did remain above 99.9 percent even after the increase in gas flux. Thus decrease of removal efficiency with increasing gas flux could be shown with the decrease after 56 days of operation. However this observation could not be verified, because nitrogen limitation dominated biofilter performance after 71 days of operation.

The influence of the gas flux at a constant loading rate can be evaluated from the analytical solution of the steady state model and is discussed in the following. Hexane concentrations in the biofilm were on the order of 0.01 mg/L and for the following discussion a first order removal rate equation is assumed. The result for the gas concentration as a function of the height,  $h$ , in the reactor was given by Morgenroth (1994) as:

$$C_g(h) = C_{g,0} e^{-\alpha_1 h} \quad (5.5)$$

where  $\alpha_1$  was the overall first order reaction rate:

$$\alpha_1 = \frac{A_s n \sqrt{kD}}{\sqrt{H}} \tanh \left( d \sqrt{\frac{k}{D}} \right) \quad (5.6)$$

The reaction rate  $\alpha_1$  is a function of the gas flux  $v$ , the first order reaction rate  $k$ , the thickness of the biofilm  $d$ , and properties of substrate or media  $A_s$ ,  $n$ ,  $D$ , and  $H$ . Greater removal efficiency are obtained for larger  $\alpha_1$ . The values of  $k$  and  $d$  are influenced by organism growth. The first order reaction rate,  $k$ , is proportional to the organism density and the biofilm thickness,  $d$ , will be increased by growing organisms. However if organism growth is not significant and kinetic parameters are constant during the time of the experiment, then the overall first order reaction rate  $\alpha_1$  is proportional to the inverse of  $v$  and thus the value of  $\alpha_1 v$  is a constant:

$$\alpha_1 v = \frac{A_s n \sqrt{kD}}{\sqrt{H}} = \text{constant} \quad (5.7)$$

From the experimental data the value of  $\alpha_1$  was determined from a regression of  $\ln(C/C_{g,0})$  versus column height,  $h$ . Results of  $\alpha_1$  and  $\alpha_1 \times v$  for different gas fluxes are given in Table 5.4 above. The value of  $\alpha_1$  increased significantly after the addition of nitrate at the 104th day of operation. The values of  $\alpha_1 \times v$  should be constant if the preceding assumptions of constant population density and constant kinetic parameters applies. After 55 days of operation the air flux was increased and as a result the value of  $\alpha_1$  decreased, however the value of  $\alpha_1 \times v$  remained approximately constant. After 71 days of operation nutrient limitation dominated biofilter performance. After a concentrated nitrate solution was added on the 104th day of operation the values of  $\alpha_1$  and  $\alpha_1 \times v$  increased approximately an order of magnitude.

### Elimination Capacity

The elimination capacity (EC) is an important parameter for the design of a biofilter because it determines the size and thus the price of the unit. Elimination capacity is a measure of the extent to which the biofilm is utilized and is a measure of the extent to which the system is reaction limited versus diffusion limited. A maximum value of elimination capacity is reached when the entire biofilm is consuming the VOCs at the maximum rate. Elimination capacity is shown as a function of inlet concentration in Figure 5.20. As expected, higher inlet concentrations resulted in higher elimination capacities up to the 71st day of operation, where nutrient limited performance of the biofilter. After adding the concentrated nitrate solution on the 104th day of operation, hexane removal in the biofilter was almost complete regardless of inlet concentration and thus the elimination capacity was equal to the loading rate. However inlet concentrations varied and thus calculated loading rates and elimination capacities ranged from 15 to 26 g/m<sup>3</sup> h. If the hexane loading rate is increased, the elimination capacity is also expected to increase and greater elimination capacities are expected for higher inlet concentrations.

For a first order reaction rate the elimination capacity is given by the following equation:

$$EC = \frac{C_{g,0} v}{H} (1 - e^{-\alpha_1 H}) \quad (5.8)$$

In this study a constant substrate flux ( $= C_{g,0} v$ ) was maintained and the elimination capacity increased with an increasing inlet concentration because  $\alpha_1$  is proportional to the inlet concentration.

### Nitrogen Limitation

After 71 days of operation, performance of the biofilter decreased rapidly. After 82 days of operation 1 L of a nutrient solution (Table 4.10) was added to the column which was equivalent to 5.1 g of nitrogen. Improvement could be observed immediately as an increase in removal efficiency (see Figure 5.19). Assuming a removal efficiency of 50 percent, the amount of hexane degraded per day was 3.2 g as organic carbon. Assuming no recycle of nitrogen and a substrate C:N ratio of 10 [Paul and Clark, 1989 page 138] the supplied nitrogen should have been sufficient for 16 days. However, if compost was being degraded also, the nitrogen added may have been insufficient for that period of operation. The removal efficiency did not increase to the expected 85 percent but started to drop down 5 days after nitrogen addition. When adding the nutrient solution, the moisture content was increased to a level where the media compacted and short circuiting was quite possible. Lowering the moisture content was difficult as described in the following section. On the 91st and the 98th day of operation the column was taken apart and media was mixed and large aggregates were broken down. The mixing always resulted in an

increase of removal efficiency. However after each increase, performance of the column dropped down again (Figure 5.19). Mixing of the media without addition of nutrients did not increase the removal. To evaluate whether compaction of the bed was the reason for the decrease in performance (after the 71st day of operation) the column was taken apart and the media was mixed thoroughly on the 76th day of operation. But the removal efficiency still decreased until nutrients were added on the 82nd day of operation (Figure 5.10). On the 104th day of operation a nitrate solution, having a ten times higher concentration (equivalent to 51 g of nitrogen), was mixed into the media. As a result removal efficiencies immediately increased to values greater than 99.9 percent. Removal efficiencies greater than 99.9 percent were achieved during the 24 days of operation.

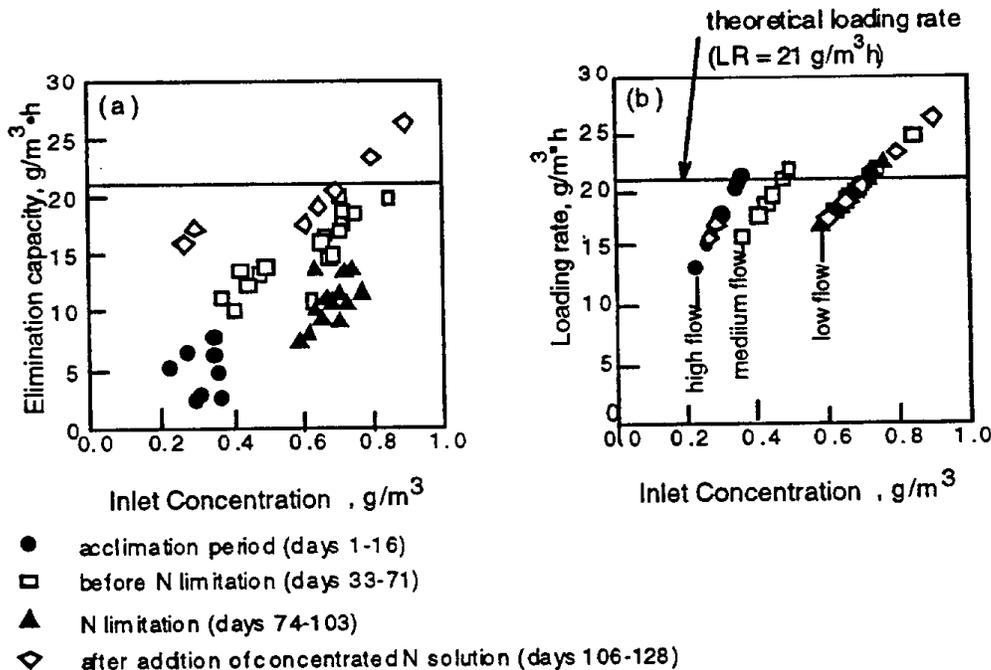


Figure 5.20  
 (a): Elimination capacity is given as a function of inlet concentration. (b): Fluctuations of the measured inlet concentration resulted in loading rates ranging from 14 to 26  $\text{g/m}^3 \cdot \text{h}$  while theoretical the loading rate was constant at 21  $\text{g/m}^3 \cdot \text{h}$ . The biofilter was operated at three different air flowrates.

Addition of a nutrient solution to the biofilter media can result in an adequate supply of nutrients. However, the added liquid will increase the moisture content of the media and repeated addition of nutrients to a full size plant is not practical. Ergas [1993] added a nutrient solution to a biofilter containing an artificial media on a weekly basis. No problems were encountered from an increased moisture content, because excess water was easily drained from the artificial media. For the compost media used in this study, the water holding capacity was about 70 percent moisture content and the optimal moisture content range was 45 to 60 percent. Thus draining is not sufficient to reduce the moisture content to the optimal range and drying with the main air stream resulted in problems due to uneven drying as discussed in the section.

A comparable decrease of removal efficiency, which may have been the result of nutrient limitation, has been reported in the literature. Operating a biofilter using peat moss as a media

for the removal of isopentane, Togna and Singh [1994] observed a decrease in performance after long operation. After 200 days of operation of their biofilter, removal efficiencies decreased from about 70 to 10 percent. Togna and Singh suggest nutrient limitation as one of the reasons for a decrease in performance of their biofilter. However Togna and Singh did not investigate nutrient limitation any further.

One reason for using compost as a filter medium is that nutrients from the compost would presumably be formed by mineralization and diffuse into the biofilm to replace what is consumed by microorganisms. In other studies [Ottengraf, 1983; Ergas, 1993] biofilters were operated for up to a year without observable nutrient limitation. However, compost is a very undefined material and the nutrient characteristics would be expected to vary between suppliers and between batches, and over time. Composts have a significant variation in the C:N ratio. Nutrient release may occur within a few weeks in some cases. Slower release rates occur also and can provide nutrients for years [Klaussen, 1994; Vogtmann et al., 1993]. When nutrient limitation was suspected in the hexane experiments an analysis of the compost in the experimental biofilter was performed. After 80 days of operation the total amounts of nitrogen, phosphorous, and carbon in the compost media were 1.222 percent, 11,294 ppm, and 15.2 percent respectively.

A simple method to evaluate the nitrogen available to microorganisms is the potentially mineralizable nitrogen (PMN), which is the net ammonia-nitrogen production under waterlogged conditions [Soil Science Society of America, 1982]. The measurement is representative of the labile pool of organic forms of nitrogen. The  $\text{NH}_4$  concentration measured before incubation is a measure of the inorganic nitrogen.

Measurements were conducted on fresh media and media that had been used for 100 days. Also, compost from two batches of Nitrohumus™ compost, which was used in this biofilter study, were analyzed for PMN with results given in Table 5.5. The PMN of the compost media was very low, measurements for fresh and used media were below 10 mg  $\text{NH}_4\text{-N}$ . The extractable inorganic nitrogen was considerably lower in the used than in the fresh compost media. Thus, as expected from biofilter performance, the total nitrogen of 1.222 percent measured after 80 days of operation was not readily available for the microorganisms and may have been bound in complex humic molecules. Available nitrogen two batches of Nitrohumus™ compost were considerably different. Compost #1 had a higher PMN than compost #2, whereas the inorganic nitrogen in compost #2 was an order of magnitude larger than in compost #1. Compost #2 was probably old compost and a large fraction of the organic nitrogen had already been released over time. For a compost biofilter a younger compost with a high PMN should be used as a media, because organic nitrogen is released slowly and over a long period of time.

### Moisture Content

During operation of the reactor, moisture content ranged from 43 to 67 percent and moisture content was not always uniform throughout the column. At startup, the media had a spatially constant moisture content of 50 percent. During the first 7 weeks of operation the average moisture content in section 1 was higher, at 55 percent, than in section 4, at 45 percent. After the first 7 weeks of operation, however the moisture content in section 4 was higher, with average moisture contents in section 1 and 4 at 60 and 65 percent, respectively. A higher temperature in the humidifier allows the air to hold more water than cold air. At startup the water in the humidifier was heated to 3 to 5°C above room temperature. The average moisture content in the column increased after startup and thus the humidifier was not heated any more after the 68th day of operation. Even after switching the heater off, the moisture content of the media still increased, however no explanation for the increase was evident. After 119 days of operation the heater for the humidifier was switched on again.

## 5. RESULTS OF PHASE II: LABORATORY SCALE BIOFILTER EXPERIMENTS

Table 5.5  
Potentially mineralizable nitrogen (PMN) for biofilter media and composts

	NH <sub>4</sub> -N, mg/L (± SD)		
	before incubation	after incubation	difference = potentially mineralizable nitrogen (PMN)
Biofilter media <sup>1</sup> before startup	21.9 (±0.9)	28.3 (±2.0)	6.4
Biofilter media after 100 days of operation <sup>2</sup>	1.0 (±0.2)	9.3 (±1.9)	8.3
Compost #1	21.9	58.7 (±5.0)	36.8 (±16.5)
Compost #2	513	511 (±20.9)	- 0 (±40.0)

<sup>1</sup> Media samples are with perlite

<sup>2</sup> Note that nitrogen had been added after 82 days of operation  
b.d. = below detection limit, which was 5 mg-N/L

Measurement of moisture content in the biofilter posed two difficulties: (1) measurement required taking a 2 - 5 g sample from the middle of a section and (2) samples were limited to locations in the center of each section. Medium samples were discarded after moisture measurement, thus for every measurement, active media was lost from the column. As discussed below, drying of the media did not occur homogeneously within a section and thus the sample was not representative for the whole section.

One liter of nutrient solution was added to the medium on the 82nd day of operation to test the nutrients limitation hypothesis. Before the nutrient addition the moisture content of the media was 62 percent. To reduce the moisture content, the inlet air bypassed the humidifier for approx. 2 hours per day. Assuming that air with no humidity is fed into the reactor and leaves the reactor at 100 percent moisture content, then the water removed at an air flow rate of 7.5 L/min from the column would be 0.194 L / day [Viessman et al., 1977]. Increasing the temperature of the dry air would allow removal of more water from the column (e.g. 0.281 L / day at 30°C).

The moisture content of the media did not decrease. Therefore the column was taken apart on the 91st day of operation. It was observed that the first 3 cm of section 1 were already extremely dry even though the sample taken from the middle of the section had a moisture content of 62 percent. The remaining sections 2, 3, and 4 looked very wet. Because of the presence of a very dry zone at the beginning of the 1st section with a distinct border between the dry and wet portions it was concluded that the column could not be dried out homogeneously. On the 91st day of operation, sections 1 and 2 and sections 3 and 4 were exchanged with respect to relative position in the column (See Table 4.9) to allow drying of the wet media in section 2 and to prevent section 1 from further drying out. On the 98th day of operation the column was taken apart and the media still looked very wet. Because drying with the air blown through the reactor was not successful the media was removed from the column, spread out to a depth of 2 cm, and was turned frequently. The larger mass of moving ambient air allowed a faster and more homogenous drying than in the column. The media was allowed to dry for 2 1/2 hours and after

## 5. RESULTS OF PHASE II: LABORATORY SCALE BIOFILTER EXPERIMENTS

that it was well mixed. The moisture content after this drying procedure was 60 percent throughout the entire column.

# 6. CONCLUSIONS

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The objective of this study was to assess applicability of biofilters for treatment of low concentration volatile organic compound (VOC) emissions. Specific objectives included:

- Determination of compound removal for a selected group of compounds including aromatic hydrocarbons, aliphatics, and chlorinated aliphatic compounds;
- Determination of the factors that affect biofilter performance, including compound characteristics, microbiological factors, and operating parameters; and
- Development and verification of theoretical models which describe transport and transformation of VOCs in biofilters.

Biofilters were found to be effective in degrading low concentration emissions of aromatic hydrocarbons. Greater than 99 percent removal efficiency was obtained for toluene (TOL) at superficial velocities from 1 to 3 m<sup>3</sup>/m<sup>2</sup>·min. Acclimation of microbial populations to aromatic compounds occurred within a short time of operation start-up. Steady state conditions were observed within two weeks of start-up of operations and systems were able to recover after shut-downs of over one week. Toluene removal was high, both in compost media amended with activated sludge and media inoculated with a specialized microbial culture. Biodegradation rates were higher after bioaugmentation.

The response of the experimental biofilter system to rapid changes in inlet concentrations was excellent. During periods of extreme loading high mass removals were observed even when breakthrough of target compounds occurred. Increased removal efficiencies during peak loadings might be obtained by increasing the adsorption capacity of the filter media or by increasing the population density of VOC degraders near the outlet. Further research is needed to determine whether these strategies would be successful.

Dichloromethane degradation was found to be dependent on the presence of particular organisms capable of degrading DCM. Once populations of DCM degraders were established in the reactor, DCM removal efficiencies of greater than 98 percent were achieved. Furthermore, DCM degrading organisms were capable of withstanding shock loads and interruptions in operations. Further research is needed to determine whether inoculation of biofilters with specific strains of bacteria capable of degrading DCM results in consistent DCM removal in field situations.

Removal of TCE in laboratory column experiments was not observed, even after conditions favorable to TCE cometabolism were established in the biofilter. Specifically, bioaugmentation with bacteria capable of cometabolizing TCE in the presence of TOL and establishing an inlet TOL/TCE ratio favorable to cometabolism did not result in measurable TCE removals. Removal of TCE, observed in the pilot system [Ergas et al., 1992b] as well as in liquid culture, suggests the TOL/TCE ratio required for TCE cometabolism could not be maintained throughout the column length.

Further research is required to refine and improve the process for TCE removal. One strategy that may be applied is to add TOL at several points over the length of the column to keep the TOL/TCE ratio at optimum for TCE degradation. Another strategy would be to

continuously reinoculate the column with organisms which have been induced with TOL or another co-substrate such as phenol or methane. Within the context of POTW emission control, however, it is unlikely that a full scale system designed to optimize TCE removal would be practical given that TCE represents a small fraction of the VOCs of concern. An alternative approach is to investigate solution phase removal of TCE and utilization of a biofilter to remove excess co-metabolite.

Hexane was used as a model aliphatic compound and one that is particularly representative of aliphatic compounds in gasoline. Mass transfer limitations were expected to control biodegradation of hexane in the biofilter because of the compounds relatively low solubility in water (13 mg/L). However, removals of greater than 99 percent were achieved using inlet concentrations up to 200 ppm<sub>v</sub> and contact times of less than one minute. Hexane removal rates were greater than those observed for toluene, although the maximum toluene degradation rate was not determined.

A biofilm model incorporating first order biodegradation kinetics and homogeneous biomass population density accurately predicted DCM concentration profiles in the compost column system. Calibration and verification of the model was not possible using TOL profiles due to the high degradation rate for this compound. Nearly all TOL was degraded between the inlet and first sample port. The model did accurately predict that column removal efficiency for TOL was independent of inlet concentrations. The results suggest, that for compounds which support growth at concentrations in the range of 50 ppm<sub>v</sub> and below, an increase in bed depth is not required to obtain the same removal efficiency at higher concentrations.

The model indicated that bed depth, media specific surface area, biofilm thickness, biodegradation rate, and gas velocity are the important operational parameters for determining compound removal in biofilters. For a constant residence time, increased removal efficiency could be obtained either by increasing the specific surface area of the media or by increasing the biodegradation rate. Decreasing biofilm film thickness is not recommended given that the systems are prone to drying resulting in decreased removal efficiency. There is, however, a potential to increase mass transfer efficiency by increasing the specific surface of biofilter media. High surface area materials include activated carbon adsorbents and hydrophobic polymers. The pore diameters of activated carbon, however, are generally less than 1.0 μm and may be unavailable for colonization by bacteria. However, benefits from increased mass transfer efficiency must be weighed against potential higher energy costs for overcoming pressure drops or costs of providing nutrients to populations growing on inert media. Higher biodegradation rates may be possible with specialized strains of organisms or higher biomass densities.

In biofilters utilizing inert filter media, biomass densities were shown to vary with column height. The greatest biomass concentrations existed near the biofilter inlet where substrate concentrations were highest. This indicates that much of the column was underutilized due to low population densities near the outlet. During peak loadings, when inlet concentrations exceed the degradation capacity of populations near the inlet, percent removals decrease. A potential solution to this problem is to increase the biomass density near the outlet by periodically switching from up-flow to down-flow operation or to supplement the upper parts of the column with appropriate substrates. A variable biomass density model failed to predict TOL removal in the inert media system.

An important conclusion of this research is that commercial composts may be nitrogen limited media. The development of a method of adding nitrogen to biofiltration systems using either compost or porous ceramic media will be useful in the management of full scale operations. More important is the information that nitrogen analysis is an important feature of design and operation of compost biofiltration systems. A simple method for determining

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potentially mineralizable nitrogen (PMN) can be applied to evaluate the amount of nitrogen available to microorganisms in the compost media.

Acclimation times for low solubility compounds, such as hexane, may be very long. Research on shortening acclimation time is needed. The most promising avenue of shortening acclimation time is the development of microbial populations in liquid culture and using those cultures to "seed" the compost medium at start-up.



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***APPENDIX:  
Toluene and DCM Data***



Compost Column Data								
height (cm)	TOL-1 (ppmv)	TOL-2 (ppmv)	TOL-C/Co	St Dev	DCM-1 (ppmv)	DCM-2 (ppmv)	DCM-C/Co	St Dev
	23-Nov	v=3 ft/min			biofilter start-up date			
0	2.67	2.40	1.00	0.07	2.39	2.40	1.00	0.00
100	3.17	2.99	1.22	0.05	2.67	2.79	1.14	0.03
	24-Nov	v=3 ft/min						
0	2.36	2.40	1.00	0.01	2.52	2.27	1.00	0.07
100	3.20	3.20	1.34	0.00	2.96	2.96	1.24	0.00
	25-Nov							
0	2.52	2.52	1.00	0.00	2.65	2.65	1.00	0.00
100	2.08	2.49	0.91	0.12	2.15	2.55	0.89	0.11
	30-Nov	v=3 ft/min						
0	1.88		1.00		2.35		1.00	
25	1.90		1.01		2.38		1.01	
50	1.04		0.55		2.32		0.99	
75	0.72		0.38		2.03		0.86	
100	0.28		0.15		1.74		0.74	
	2-Dec	v=3 ft/min						
0	3.05		1.00		2.86		1.00	
25	1.75		0.57		3.37		1.18	
50	1.02		0.33		2.21		0.77	
75	0.42		0.14		2.54		0.89	
100	0.10		0.03		2.23		0.78	
	7-Dec	v=3 ft/min						
0	3.45	2.16	1.00	0.32	2.64	2.22	1.00	0.12
25	1.27	1.35	0.47	0.02	2.26	2.48	0.98	0.06
50	0.32	0.19	0.09	0.03	2.35	2.30	0.96	0.01
75	0.01	0.01	0.00	0.00	2.33	2.02	0.89	0.09
100	0.01	0.00	0.00	0.00	2.49	2.38	1.00	0.03
	10-Dec	v=3 ft/min						
0	1.61	2.27	1.00	0.24	1.80	2.25	1.00	0.16
25	1.23	0.99	0.57	0.09	1.92	2.08	0.99	0.06
50	0.11	0.10	0.06	0.00	2.17	2.28	1.10	0.04
75	0.00	0.00	0.00	0.00	2.09	2.07	1.03	0.01
100	0.02	0.04	0.02	0.01	2.11	2.34	1.10	0.08
	14-Dec	v=3 ft/min			innoculation with TOL1A culture			
0	1.85	2.09	1.00	0.09	1.88	2.22	1.00	0.12
25	1.04	0.93	0.50	0.04	2.50	2.39	1.19	0.04
50	0.04	0.07	0.03	0.01	2.17	2.39	1.11	0.08
75	0.01	0.00	0.00	0.00	2.29	2.02	1.05	0.09
100	0.00	0.02	0.01	0.01	2.05	2.21	1.04	0.05
	17-Dec	v=3 ft/min						
0	2.32	1.61	1.00	0.25	2.27	2.28	1.00	0.01
25	0.80	0.98	0.45	0.07	2.28	2.54	1.06	0.08
50	0.07	0.09	0.04	0.01	2.15	2.31	0.98	0.05
75	0.02	0.03	0.01	0.00	2.15	2.14	0.94	0.00
100	0.01	0.00	0.00	0.00	1.87	1.79	0.80	0.03

col height (cm)	TOL-1 (ppmv)	TOL-2 (ppmv)	TOL-C/Co	St Dev	DCM-1 (ppmv)	DCM-2 (ppmv)	DCM-C/Co	St Dev
	28-Dec v = 3 ft/min							
0	2.05	2.35	1.00	0.10	1.96	1.93	1.00	0.01
25	0.34	0.16	0.11	0.06	2.04	1.90	1.01	0.05
50	0.07	0.09	0.04	0.01	1.90	1.72	0.93	0.07
75	0.03	0.03	0.01	0.00	1.74	1.71	0.88	0.01
100	0.01	0.02	0.01	0.00	0.22	0.17	0.10	0.02
	31-Dec v = 3 ft/min							
0	1.39	1.43	1.00	0.02	1.88	1.85	1.00	0.01
25	0.06	0.06	0.04	0.00	1.63	1.82	0.92	0.07
50	0.01	0.00	0.00	0.00	1.65	1.65	0.89	0.00
75	0.00	0.00	0.00	0.00	1.41	1.41	0.76	0.00
100	0.00	0.03	0.01	0.01	0.08	0.11	0.05	0.01
	4-Jan v = 3 ft/min							
0	1.04	1.46	1.00	0.23	1.77	1.43	1.00	0.15
25	0.17	0.12	0.12	0.03	1.31	1.34	0.83	0.02
50	0.02	0.02	0.02	0.00	1.17	1.43	0.81	0.11
75	0.00	0.00	0.00	0.00	0.94	0.88	0.57	0.03
100	0.01	0.01	0.01	0.00	0.34	0.34	0.21	0.00
	7-Jan v=3 ft/min				increased TOL to 50 ppmv			
reservoir	45.69	54.57			3.54	1.20		0.70
0	38.64	35.45	1.00	0.06	1.93	2.30	0.26	0.11
25	2.77	1.82	0.74	0.02	1.94	1.59	0.25	0.10
50	0.05	0.05	0.05	0.00	1.29	1.60	0.22	0.09
75	0.04	0.04	0.00	0.00	0.79	0.88	0.06	0.03
100	0.04	0.05	0.00	0.00	0.00	0.00	0.00	
	11-Jan v=3 ft/min							
reservoir	42.69				2.14			
0	27.89	27.89	1.00	0.00	1.47	1.47	1.00	0.00
25	0.95	0.79	0.03	0.00	1.50	1.52	1.03	0.01
50	0.02	0.00	0.00	0.00	0.74	0.84	0.54	0.05
75	0.00	0.00	0.00	0.00	0.36	0.33	0.23	0.01
100	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00
	14-Jan v=3 ft/min							
reservoir	43.68				3.29			
0	39.43	35.01	1.00	0.08	2.00	1.97	1.00	0.01
25	1.95	2.22	0.06	0.01	1.78	2.01	0.95	0.08
50	0.02	0.00	0.00	0.00	0.59	0.67	0.31	0.03
75	0.00	0.00	0.00	0.00	0.25	0.27	0.13	0.01
100	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	18-Jan v=3 ft/min							
0	35.46	36.71	1.00	0.02	2.48	2.27	1.00	0.06
25	0.14	0.22	0.00	0.00	2.15	1.86	0.84	0.09
50	0.02	0.00	0.00	0.00	0.34	0.35	0.14	0.00
75	0.00	0.04	0.00	0.00	0.19	0.20	0.08	0.00
100	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00

col height (cm)	TOL-1 (ppmv)	TOL-2 (ppmv)	TOL-C/Co	St Dev	DCM-1 (ppmv)	DCM-2 (ppmv)	DCM-C/Co	St Dev
	21-Jan	v=3 ft/min						
reservoir	57.98	61.85			3.71	4.30		
0	49.50	50.40	1.00	0.01	2.27	2.77	1.00	0.14
12.5	18.73	19.66	0.83	0.01	2.54	2.57	0.63	0.01
25	1.42	1.13	0.32	0.00	2.44	1.80	0.64	0.18
37.5	0.57	0.74	0.02	0.00	0.61	0.63	0.53	0.01
	26-Jan	v=3 ft/min						
0	27.41	24.32	1.00	0.08	1.38	1.36	1.00	0.01
25	1.02	1.84	0.06	0.02	1.18	1.34	0.92	0.08
50	0.04	0.00	0.00	0.00	0.13	0.15	0.10	0.01
75	0.00	0.00	0.00	0.00	0.09	0.09	0.07	0.00
100	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	2-Feb	v=3 ft/min						
0	31.51	24.27	1.00	0.18	1.81	1.30	1.00	0.23
12.5	10.52	10.62	0.38	0.00	1.89	1.77	1.17	0.06
25	6.59	5.44	0.22	0.03	1.12	1.12	0.72	0.00
50	0.02	0.16	0.00	0.00	0.17	0.11	0.09	0.03
75	0.00		0.00		0.00		0.00	
100	0.01		0.00		0.00		0.00	
	9-Mar	v=4.5ft/min			shut down 2/25-3/8			
0	53.00	58.17	1.00	0.07	2.30	2.63	1.00	0.09
25	15.30	14.35	0.27	0.01	1.31	1.31	0.53	0.00
50	1.84	2.12	0.04	0.00	0.51	0.70	0.25	0.05
75	1.70	1.05	0.02	0.01	0.52	0.45	0.20	0.02
100	0.05	0.06	0.00	0.00	0.27	0.31	0.12	0.01
	11-Mar	v=4.5ft/min			shock load on 3/10			
0	49.85	50.97	1.00	0.02	2.45	2.72	1.00	0.07
25	27.74	27.34	0.55	0.01	1.36	1.29	0.51	0.02
50	14.46	16.40	0.31	0.03	0.49	0.57	0.20	0.02
75	2.31	1.59	0.04	0.01	0.39	0.39	0.15	0.00
100	0.39	0.10	0.00	0.00	0.20	0.20	0.08	0.00
	15-Mar	v=4.5ft/min						
0	75.16	57.64	1.00	0.19	3.22	3.30	1.00	0.02
25	37.63	37.87	0.57	0.00	1.65	1.61	0.50	0.01
50	20.31	31.38	0.39	0.12	0.50	0.67	0.18	0.04
75	18.65	17.32	0.27	0.01	0.39	0.45	0.13	0.01
100	19.32	22.30	0.31	0.03	0.21	0.23	0.07	0.01
	19-Mar	v=4.5ft/min						
0	58.40		1.00		2.87	1.00		
25	29.33		0.50		1.35	0.47		
50	24.95		0.43		0.51	0.18		
75	22.20		0.38		0.32	0.11		
100	26.71		0.46		0.16	0.06		

height (cm)	TOL-1 (ppmv)	TOL-2 (ppmv)	TOL-C/Co	St Dev	DCM-1 (ppmv)	DCM-2 (ppmv)	DCM-C/Co	St Dev
23-Mar v=4.5ft/min took TCE out of mix 3/19								
0	68.44	68.44	1.00	0.00	4.19	4.19	1.00	0.00
25	39.67	34.56	0.54	0.05	2.38	1.87	0.51	0.09
50	27.58	31.47	0.43	0.04	0.89	1.00	0.23	0.02
75	20.74	20.06	0.30	0.01	0.56	0.52	0.13	0.01
100	21.77	23.53	0.33	0.02	0.23	0.24	0.06	0.00
30-Mar v=4.5ft/min								
0	70.78	69.75	1.00	0.01	3.96	3.85	1.00	0.02
25	38.86	33.28	0.51	0.06	2.26	1.93	0.54	0.06
50	30.55	30.33	0.43	0.00	0.77	0.91	0.22	0.03
75	11.88	7.95	0.14	0.04	0.39	0.30	0.09	0.02
100	4.29	9.11	0.10	0.05	0.11	0.13	0.03	0.00
19-Apr v=4.5ft/min moisture content in lower section 43%								
0	73.49		1.00		4.08		1.00	
25	40.36		0.55		1.91		0.47	
50	29.32		0.40		0.82		0.20	
75	32.87	30.12	0.43		0.77	0.79	0.19	
100	26.25		0.36		0.28		0.07	
29-Apr v=3 ft/min re-innoculated column 4/26								
0	65.03		1.00		3.95		1.00	
25	56.42		0.87		3.04		0.77	
50	28.82		0.44		1.30		0.33	
75	30.41		0.47		1.03		0.26	
100	27.44		0.42		0.46		0.12	
4-May								
0	17.97	19.21	1.00	0.05	2.96	2.64	1.00	0.08
25	3.37	6.88	0.28	0.13	0.62	2.09	0.48	0.37
50	2.91	2.91	0.16	0.00	0.54	0.61	0.21	0.02
75	0.21	0.09	0.01	0.00	0.25	0.17	0.07	0.02
100	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00
11-May								
0	19.93	24.25	1.00	0.14	3.26	3.46	1.00	0.04
25	3.06	3.06	0.14	0.00	1.23	1.23	0.37	0.00
50	1.07	2.84	0.09	0.06	0.59	0.76	0.20	0.04
75	0.10	0.11	0.00	0.00	0.19	0.20	0.06	0.00
100	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
18-May								
0	24.27	33.44	1.00	0.22	2.80	4.25	1.00	0.29
25	8.68	7.51	0.28	0.03	1.94	1.67	0.51	0.06
50	3.54	4.51	0.14	0.02	0.66	0.86	0.22	0.04
75	0.10	0.06	0.00	0.00	0.23	0.17	0.06	0.01
100	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
20-May 4.5 ft/min								
0	40.68	35.92	1.00	0.09	3.57	3.39	1.00	0.04
25	23.86	19.35	0.56	0.08	2.47	2.11	0.66	0.07
50	6.04	6.04	0.16	0.00	0.47	0.71	0.17	0.05
75	2.29	2.29	0.06	0.00	0.49	0.49	0.14	0.00

height (cm)	TOL-1 (ppmv)	TOL-2 (ppmv)	TOL-C/Co	St Dev	DCM-1 (ppmv)	DCM-2 (ppmv)	DCM-C/Co	St Dev
	21-May	v=4.5						
0	40.68	35.92	1.00	0.09	3.57	3.39	1.00	0.04
25	13.54	15.15	0.37	0.03	0.86	0.99	0.27	0.02
50	1.05	1.21	0.03	0.00	0.34	0.32	0.09	0.00
75	0.73	0.42	0.02	0.01	0.08	0.00	0.01	0.02
	25-May	v=4.5						
0	41.20	34.85	1.00	0.12	2.58	2.19	1.00	0.12
25	12.19	22.83	0.46	0.20	0.89	1.45	0.49	0.17
50	4.89	8.10	0.17	0.06	0.39	0.41	0.17	0.01
75	5.28	4.28	429.41	0.02	0.10	0.15	0.05	0.01
	27-May	v=4.5			took column apart and repacked it 5/25			
0	30.03	31.66	1.00	0.04	2.46	2.52	1.00	0.02
25	0.06	0.08	0.00	0.00	1.78	1.89	0.74	0.03
50	0.03	0.04	0.00	0.00	0.67	0.60	0.26	0.02
75	0.00	0.00	0.00	0.00	0.31	0.34	0.13	0.01
100	0.00	0.02	0.00	0.00	0.16	0.16	0.06	0.00
	1-Jun	v=4.5						
0	29.60	29.22	1.00	0.01	2.66	2.49	1.00	0.05
25	3.42	3.24	0.11	0.00	1.01	0.87	0.37	0.04
50	0.00	0.00	0.00	0.00	0.11	0.14	0.05	0.01
75	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
100	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	3-Jun	v=4.5						
0	20.40		1.00		1.21		1.00	
25	2.80		0.14		0.56		0.46	
50	0.00		0.00		0.10		0.09	
75	0.00		0.00		0.08		0.07	
100	0.10		0.00		0.00		0.00	
	8-Jun	6 ft/min						
0	26.58	24.79	1.00	0.05	2.07	1.65	1.00	0.16
25	11.73	10.84	0.44	0.02	0.91	0.74	0.44	0.06
50	0.03	0.03	0.00	0.00	0.18	0.18	0.10	0.00
75	0.00	0.00	0.00	0.00	0.09	0.09	0.05	0.00
100	0.00	0.00	0.00	0.00	0.06	0.06	0.03	0.00
	8-Jun	6 ft/min			stepped up inlet concentration			
0	57.16	51.95	1.00	0.07	4.82	3.33	1.00	0.26
25	37.81	36.00	0.68	0.02	2.00	2.39	0.54	0.07
50	10.75	11.40	0.20	0.01	0.42	0.43	0.11	0.00
75	10.51	8.00	0.17	0.03	0.27	0.23	0.06	0.01
100	7.15	6.93	0.13	0.00	0.16	0.13	0.04	0.00
	10-Jun				column drying			
0	43.85	50.00	1.00	0.09	2.57	3.76	1.00	0.27
25	37.11	39.01	0.81	0.03	2.45	2.49	0.78	0.01
50	4.98	4.92	0.11	0.00	0.52	0.50	0.16	0.00
75	0.01	0.00	0.00	0.00	0.24	0.29	0.08	0.01
100	0.00	0.00	0.00	0.00	0.18	0.18	0.06	0.00

height (cm)	TOL-1 (ppmv)	TOL-2 (ppmv)	TOL-C/Co	St Dev	DCM-1 (ppmv)	DCM-2 (ppmv)	DCM-C/Co	St Dev
	18-Jun							
0	50.20	45.89	1.00	0.06	4.19	2.70	1.00	0.31
25	49.50	48.93	1.02	0.01	3.96	3.51	1.08	0.09
50	44.10	39.00	0.86	0.08	3.21	2.71	0.86	0.10
75	16.43	18.97	0.37	0.04	1.10	1.28	0.35	0.04
100	0.26	0.23	0.01	0.00	0.44	0.40	0.12	0.01
	24-Jun 6 ft/min wet down column							
0	29.27		1.00		2.55		1.00	
25	2.19		0.07		0.99		0.39	
50	1.22		0.04		1.03		0.40	
75	0.04		0.00		0.57		0.22	
100	0.04		0.00		0.19		0.07	
	29-Jun 6 ft/min							
0	20.50	24.00	1.00	0.11	2.09	3.75	1.00	0.40
25	1.87	2.09	0.09	0.01	0.82	0.82	0.28	0.00
50	1.00	0.95	0.04	0.00	0.70	0.75	0.25	0.01
75	0.03	0.02	0.00	0.00	0.31	0.29	0.10	0.01
100	0.01	0.01	0.00	0.00	0.14	0.12	0.04	0.01
	8-Jul 6 ft/min col dry							
0	29.10	29.98	1.00	0.02	2.40	2.44	1.00	0.01
25	26.28	26.24	0.89	0.00	2.08	2.04	0.85	0.01
50	10.82	11.24	0.37	0.01	1.20	1.32	0.52	0.03
75	0.38	0.09	0.01	0.01	0.45	0.39	0.17	0.02
100	0.00	0.00	0.00	0.00	0.09	0.08	0.03	0.00

col height (cm)	TCE-1 (ppmv)	TCE-2 (ppmv)	TCE-C/Co	St Dev
	23-Nov	v =3 ft/min	biofilter start-up date	
0	2.49	2.40	1.00	0.03
100	2.89	3.30	1.27	0.12
0	2.41	2.60	1.00	0.05
100	3.17	3.17	1.27	0.00
0	2.80	2.80	1.00	0.00
100	2.37	2.68	0.90	0.08
	30-Nov	v=3 ft/min		
0	2.44			
25	2.55			
50	2.60			
75	2.46			
100	1.94			
	2-Dec	v = 3 ft/min		
0	3.06			
25	3.43			
50	2.86			
75	2.69			
100	2.32			
	7-Dec	v = 3 ft/min		
0	2.84	2.50	1.00	0.09
25	2.46	2.55	0.94	0.02
50	2.58	2.61	0.97	0.01
75	2.49	2.22	0.88	0.07
100	2.83	2.60	1.02	0.06
	10-Dec	v = 3 ft/min		
0	1.93	2.57	1.00	0.20
25	2.28	2.21	1.00	0.02
50	2.39	2.41	1.07	0.01
75	2.18	2.13	0.96	0.02
100	2.46	2.34	1.06	0.04
	14-Dec	v=3 ft/min	innoculation with TOL1A culture	
0	2.45	2.65	1.00	0.05
25	2.78	2.64	1.06	0.04
50	2.32	2.83	1.01	0.14
75	2.46	2.23	0.92	0.07
100	2.30	2.72	0.98	0.12
	17-Dec	v = 3 ft/min		
0	2.54	2.49	1.00	0.01
25	2.47	3.26	1.14	0.22
50	2.50	2.66	1.03	0.04
75	2.48	2.66	1.02	0.05
100	2.47	2.37	0.96	0.03

col height (cm)	TCE-1 (ppmv)	TCE-2 (ppmv)	TCE-C/Co	St Dev
	28-Dec	v = 3 ft/min		
0	2.17	2.36	1.00	0.06
25	2.56	1.95	0.99	0.19
50	2.19	2.15	0.96	0.01
75	2.21	2.29	0.99	0.02
100	2.37	2.43	1.06	0.02
	31-Dec	v = 3 ft/min		
0	2.09	2.14	1.00	0.01
25	2.00	2.19	0.99	0.06
50	2.21	2.21	1.04	0.00
75	2.11	2.11	1.00	0.00
100	2.00	2.14	0.98	0.05
	4-Jan	v = 3 ft/min		
0	2.20	2.24	1.00	0.01
25	2.00	1.86	0.87	0.04
50	1.76	2.08	0.87	0.10
75	1.90	1.90	0.86	0.00
100	2.23	2.23	1.01	0.00
	7-Jan	v=3 ft/min	increased TOL to 50 ppmv	
reservoir	3.48	2.71		
0	2.50	2.71	1.00	0.06
25	2.46	2.51	0.84	0.01
50	2.42	2.67	0.80	0.07
75	2.75	2.74	0.82	0.00
100	2.72	2.94	0.89	0.06
	11-Jan	v=3 ft/min		
reservoir	2.89			
0	1.86	1.86	1.00	0.00
25	1.73	1.75	0.94	0.00
50	1.74	2.11	1.04	0.14
75	2.06	1.94	1.08	0.05
100	2.09	2.16	1.14	0.03
	14-Jan	v=3 ft/min		
reservoir	2.27			
0	2.56	2.58	1.00	0.00
25	2.17	2.57	0.92	0.11
50	2.31	2.72	0.98	0.11
75	2.82	2.79	1.09	0.01
100	2.86	2.94	1.13	0.02
	18-Jan	v=3 ft/min		
0	2.91	2.76	1.00	0.04
25	2.73	2.47	0.92	0.06
50	2.25	2.48	0.83	0.06
75	2.76	2.45	0.92	0.08
100	2.77	2.77	0.98	0.00

col height (cm)	TCE-1 (ppmv)	TCE-2 (ppmv)	TCE-C/Co	St Dev
	21-Jan	v=3 ft/min		
reservoir	4.28	4.38		
0	3.19	3.45	1.00	0.06
12.5	2.99	3.21	0.77	0.05
25	3.42	2.58	0.72	0.18
37.5	2.13	2.41	0.69	0.06
	26-Jan	v=3 ft/min		
0	1.65	1.62	1.00	0.02
25	1.59	1.83	1.04	0.10
50	1.62	1.83	1.05	0.09
75	1.72	1.92	1.11	0.09
100	1.88	1.92	1.16	0.02
	2-Feb	v=3 ft/min		
0	2.14	1.60	1.00	0.20
12.5	2.19	2.09	1.14	0.04
25	1.58	1.70	0.87	0.05
50	1.44	1.36	0.75	0.03
75	1.43		0.76	0.54
100	1.13		0.60	
	9-Mar	v=4.5ft/min	shut down 2/25-3/8	
0	3.17	3.59	1.00	0.09
25	3.39	3.29	0.99	0.02
50	2.52	3.53	0.89	0.21
75	3.62	3.27	1.02	0.07
100	3.26	3.55	1.01	0.06
	11-Mar	v=4.5 ft/min	shock load on 3/10	
0	2.92	3.39	1.00	0.11
25	3.67	3.35	1.11	0.07
50	2.91	3.38	1.00	0.11
75	3.40	3.58	1.10	0.04
100	3.59	3.41	1.11	0.04
	15-Mar	v=4.5 ft/min		
0	4.44	4.41	1.00	0.01
25	4.33	4.67	1.02	0.05
50	3.02	4.46	0.85	0.23
75	4.29	4.35	0.98	0.01
100	4.56	4.96	1.08	0.06

Porous Ceramic Column Data				
column height (cm)	TOL-1 (ppmv)	TOL-2 (ppmv)	C/Co	St Dev
29-Apr		started system 4/28		
0	53.73		1.00	
25	53.42		0.99	
50	59.16		1.10	
75	57.35		1.07	
100	55.01		1.02	
4-May				
0	15.30	25.64	1.00	0.36
25	8.80	8.60	0.43	0.01
50	1.56	1.70	0.08	0.00
75	0.05	0.05	0.00	0.00
100	0.03	0.03	0.00	0.00
11-May		NH3 analysis showed no N in media		
0	54.85	62.51	1.00	0.09
25	66.35	59.25	1.07	0.09
50	57.19	64.33	1.04	0.09
75	55.50	52.86	0.92	0.03
100	51.51	49.36	0.86	0.03
25-May		added nutrients 5/18		
0	57.53	60.74	1.00	0.04
25	29.31	29.86	0.50	0.01
50	0.37	0.40	0.01	0.00
75	0.09	0.09	0.00	0.00
100	0.04	0.04	0.00	0.00
1-Jun				
0	49.91	48.13	1.00	0.03
25	40.32	39.44	0.81	0.01
50	37.53	23.23	0.62	0.21
75	0.06	0.11	0.00	0.00
100	0.00	0.00	0.00	0.00
3-Jun		added nutrients 6/3		
0	60.58		1.00	
25	48.24		0.80	
50	1.44		0.02	
75	0.15		0.00	
100	0.08		0.00	
8-Jun		started weekly nutrient addition		
0	56.18	61.74	1.00	0.07
25	28.62	28.37	0.48	0.00
50	0.54	0.47	0.01	0.00
75	0.19	0.11	0.00	0.00
100	0.05	0.07	0.00	0.00

column height (cm)	TOL-1 (ppmv)	TOL-2 (ppmv)	C/Co	St Dev
18-Jun				
0	72.60	69.40	1.00	0.03
25	45.97	40.15	0.61	0.06
50	12.43	14.09	0.19	0.02
75	4.18	4.30	0.06	0.00
100	2.24	2.38	0.03	0.00
22-Jun				
0	64.89	65.79	1.00	0.01
25	43.89	43.34	0.67	0.01
50	2.88	3.17	0.05	0.00
75	0.03	0.02	0.00	0.00
100	0.00	0.01	0.00	0.00
24-Jun				
0	35.80			
25	25.52			
50	6.65			
75	0.25			
100	0.14			
28-Jun				
0	16.72	16.72	1.00	0.00
25	10.22	11.79	0.66	0.07
50	0.06	0.05	0.00	0.00
75	0.03	0.02	0.00	0.00
100	0.01	0.01	0.00	0.00
6-Jul				
0	5.81	6.32	1.00	0.06
25	1.64	1.24	0.24	0.05
50	0.04	0.04	0.01	0.00
75	0.02	0.01	0.00	0.00
100	0.02	0.02	0.00	0.00
13-Jul				
0	14.23	21.82	1.00	0.30
25	7.65	5.37	0.36	0.09
50	0.19	0.19	0.01	0.00
75	0.01	0.01	0.00	0.00
100	0.00	0.00	0.00	0.00
19-Jul				
0	14.62	20.31	1.00	0.23
25	10.90	9.37	0.58	0.06
50	2.61	3.19	0.17	0.02
75	0.01	0.02	0.00	0.00
100	0.00	0.00	0.00	0.00

## Bacterial Counts Data

column height (cm)	counts/gram media 1	counts/gram media 2	mean	St Dev
28-Jun				
12.5	2.13E+09	1.98E+09	2.06E+09	1.02E+08
37.5	1.73E+09	1.74E+09	1.74E+09	9.49E+06
62.5	9.26E+07	7.22E+07	8.24E+07	1.45E+07
87.5	8.49E+06	8.04E+06	8.26E+06	3.16E+05
6-Jul				
12.5	1.25E+09	1.71E+09	1.48E+09	3.29E+08
37.5	2.72E+08	3.58E+08	3.15E+08	6.07E+07
62.5	1.20E+08	1.35E+08	1.27E+08	1.03E+07
87.5	8.48E+07	7.96E+07	8.22E+07	3.63E+06
13-Jul				
12.5	1.14E+10	1.34E+10	1.24E+10	1.39E+09
37.5	3.40E+09	3.24E+09	3.32E+09	1.09E+08
62.5	1.35E+09	1.28E+09	1.31E+09	5.02E+07
87.5	1.21E+08	1.26E+08	1.24E+08	3.72E+06
19-Jul				
12.5	6.00E+09	6.00E+09	6.00E+09	0.00E+00
37.5	2.70E+09	3.41E+09	3.06E+09	5.03E+08
62.5	4.68E+08	5.26E+08	4.97E+08	4.13E+07
87.5	6.27E+07	6.27E+07	6.27E+07	0.00E+00