BIOFILTRATION OF VOCs:

LABORATORY STUDIES

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April, 1995

Citation for this report should read as:

GASReP - Groundwater and Soil Remediation Program. Unpublished Report, No. 9284. (1995). "Biofiltration of VOCs: Laboratory Studies", 167p.

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ACKNOWLEDGEMENTS

GASReP sponsored the work resulting in this report entitled "Biofiltration of VOCs: Laboratory Studies".

Agencies that participate in GASReP are listed below alphabetically.

Alberta Environmental Protection
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Environment Canada, Environmental Technology Centre (ETC)
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Prince Edward Island Ministry of the Environment
United States Environmental Protection Agency (USEPA)
Wastewater Technology Centre (WTC)

Environment Canada's Burlington Environmental Technology Office manages GASReP on behalf of the participants.

GASReP co-funded this project with financial support from the Canadian federal government's interdepartmental Program on Energy Research and Development (PERD). Other co-funders were:

Canadian Petroleum Products Institute
Ontario Ministry of Environment and Training

April 1995

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Introduction

La biofiltration est une technique de réduction de la pollution atmosphérique qui utilise des microorganismes immobilisés sur un milieu filtrant comme la sphaigne ou le compost. Il a été démontré que l'utilisation des biofiltres était une méthode efficace et bon marché pour l'élimination des odeurs de nombreuses émanations gazeuses résiduaires. Depuis peu, on s'intéresse davantage à l'utilisation de biofiltres pour le traitement d'émanations gazeuses contaminées par des composés organiques volatils (COV) provenant de diverses activités industrielles. En effet, l'utilisation de l'extraction à la vapeur pour l'assainissement de sols contaminés par les hydrocarbures produit de grandes quantités d'émanations gazeuses contaminées par le benzène, le toluène, l'éthylbenzène et les xylènes (BTEX). Les méthodes traditionnelles de traitement des émanations gazeuses issues de l'extraction des sols par la vapeur (ESV) sont caractérisées par des coûts d'exploitation élevés et dans certains cas, il a production de sous-produits résiduaires dangereux (p. ex. adsorbés sur du charbon activé). La biofiltration peut devenir une méthode peu coûteuse de traitement des émanations gazeuses de l'ESV. Cependant, des études supplémentaires sont nécessaires afin de déterminer son utilité et d'optimiser les paramètres de conception.

Objectifs de recherche

Les objectifs du programme de recherche étaient de mieux comprendre la réponse du système du biofiltre et de déterminer les caractéristiques de conception et d'utilisation requises pour obtenir un rendement efficace du filtre.

Dans cette étude, on s'est penché sur la capture du toluène, du benzène et du xylène à l'aide d'un biofiltre expérimental de laboratoire. Le programme de recherche était divisé en quatre phases principales: i) conception et construction d'un système de biofiltration à l'échelle expérimentale, ii) comparaison et évaluation de milieux filtrants organiques, iii) effet de la vitesse d'écoulement de l'air sur l'efficacité de la capture du toluène et iv) biofiltration de mélanges de BTX.

Système de biofiltration

Le système expérimental est illustré à la figure 3.1 et décrit en détail dans la partie principale du chapitre 3.1 de la thèse. Le système de biofiltration comportait les éléments suivants : 1) système de préhumidification, 2) système d'injection des échantillons et 3) colonnes de biofiltration.

Chaque colonne de biofiltration était constituée d'un biofiltre à trois paliers et d'une section de distribution d'air. Chaque palier du biofiltre était fait de sections de tuyaux de 6 po (diamètre interne, 15,4 cm) en acier inoxydable de la nomenclature 40, d'une longueur de 34 cm, et ce dernier était garni de milieu

filtrant sur une profondeur de 30 cm, ce qui donnait, pour l'ensemble du biofiltre, une hauteur de lit de 90 cm et un volume de 16,3 L.

On humidifiait de l'air de laboratoire filtré à l'aide d'une tour chargée à contre-courant avant l'injection des agents chimiques. Pour l'introduction de contaminants dans le courant d'air, on utilisait un pousse-seringue programmable Harvard modèle 22, équipé de seringues étanches de 50 mL.

On surveillait les températures d'entrée du courant d'air et du lit bactérien à l'aide de thermocouples, et la perte de charge entre les lits du filtre à l'aide d'un manomètre. On a prélevé des échantillons de la partie centrale du lit pour déterminer le taux d'humidité et les teneurs en substances nutritives dans le lit bactérien.

On a utilisé un détecteur portatif à photoionisation (DPI) pour mesurer la concentration totale d'hydrocarbures dans le courant gazeux, ainsi qu'un système CG-DPI en ligne pour doser les divers BTX. On a dosé le dioxyde de carbone dans le courant gazeux du filtre à l'aide d'un système CG-DCT (détecteur à conductivité thermique). On a évalué la contamination par les hydrocarbures du milieu filtrant usagé du biofiltre en effectuant une extraction au chlorure de méthylène suivie d'un dosage à l'aide d'un système CG-DIF (détecteur à ionisation de flamme).

Résultats

À ce jour, ces recherches ont donné plusieurs résultats importants; on trouvera ci-dessous de brèves descriptions des résultats obtenus.

1. On a évalué le rendement du biofiltre obtenu avec cinq lits bactériens filtrants différents. Les milieux utilisés au cours de l'étude étaient notamment des ordures ménagères compostées, des boues d'égout compostées, des déchets de jardin et des feuilles compostés, des déchets de jardin et des déchets alimentaires compostés, ainsi que de l'écorce compostée. On a ajouté de la perlite, une cendre volcanique inerte, afin d'accroître la porosité et de réduire la perte de charge à travers le lit bactérien (mélange milieu/perlite de 60:40, en volume). On a choisi la perlite parce qu'il s'agit d'un amendement facilement disponible et peu coûteux qui devrait réduire les coûts d'exploitation du biofiltre. On a fait un essai initial de chaque milieu de lit bactérien sans ensemencement microbien ou addition d'éléments nutritifs. Les ordures ménagères et les boues d'égout compostées donnaient incontestablement les meilleurs taux de capture pour le toluène et, pour ces deux milieux de lit bactérien, le temps d'acclimatation était inférieur à quatre jours.

2. On a ensemencé les feuilles et les déchets de jardin compostés, ainsi que les particules fines d'écorce compostée, avec de la liqueur mixte de la station d'épuration des eaux usées de la ville de Guelph. L'ensemencement microbien du milieu filtrant n'avait pas d'effet sur la capture du toluène.

3. On a modifié davantage le mélange de feuilles et de déchets de jardin compostés par l'addition de substances nutritives, en l'occurrence des fertilisants commerciaux. On a constaté que le rendement du biofiltre mesuré ensuite s'était amélioré et qu'il atteignait des valeurs correspondant à celles obtenues avec des ordures ménagères et des boues d'égout compostées. Cette constatation, couplée avec les résultats de l'analyse des milieux, indiquait que la disponibilité des substances nutritives pourrait bien être le facteur limitant pour une dégradation efficace des BTEX sur le biofiltre. On a constaté que les teneurs en azote disponible (azote à l'état d'ammonium et à l'état de nitrate) étaient notablement supérieures dans les milieux de biofiltration efficaces.

4. On a évalué la capture du toluène sur une plage de concentrations comprise entre 50 et 600 ppm, avec une vitesse superficielle dans le lit bactérien comprise entre 30 et 90 m/h. Les vitesses superficielles donnaient des temps de rétention, dans le lit vide du biofiltre, compris entre 0,6 et 1,8 min. On a calculé des capacités de capture du toluène de 59, 47, et 37 g/m^3 pour des vitesses superficielles de 30, 60 et 90 m/h, respectivement. On a observé des valeurs d'efficacité de capture de 97 % ou plus pour des taux de charge massiques de toluène de 40 $g/m^3/h$ ou moins.

5. On a effectué des expériences qui portaient sur la capture de mélanges de benzène (B), de toluène (T) et d'*o*-xylène (X). On a utilisé les combinaisons suivantes des contaminants dans cette portion de l'étude : B, T, X, BT, BTX et TX. On a noté les quatre observations principales suivantes : i) accroissement de la période d'acclimatation d'un jour, pour le toluène utilisé comme seul contaminant du courant gazeux, à neuf jours pour le mélange de BTX; ii) l'accroissement de la période d'acclimatation était dû à la présence d'*o*-xylène dans le courant gazeux; iii) on a constaté que, après acclimatation, les valeurs d'efficacité de capture du carbone pour le mélange de BTX étaient semblables à celles obtenues avec des émanations gazeuses contaminées par du toluène; et iv) le profil de dégradation correspondant à la capture des contaminants était cohérent et présentait une capture préférentielle du toluène, du benzène et de l'*o*-xylène, dans cet ordre.

6. On a constaté qu'il y avait dégradation du rendement du filtre avec le temps dans le cas des filtres utilisés pour traiter les émanations gazeuses contaminées par les BTX et le toluène lorsque les taux de charge du filtre étaient supérieurs à 30 g de carbone/m^3/h. On a attribué les taux réduits de capture à la formation de canaux dans le milieu filtrant ou au séchage du milieu.

7. On a évalué la production de dioxyde de carbone dans les lits des biofiltres avant l'introduction des contaminants et pendant leur capture. L'écart entre les concentrations prévues de CO_2 (évaluées d'après la dégradation des contaminants) et les valeurs mesurées atteignait 15 %. Ces bilans massiques, ainsi que les données de température du lit bactérien, ont confirmé que la biodégradation était responsable de la capture des contaminants.

8. Après la fin des essais, on a recherché la présence de COV dans le milieu du biofiltre. On n'a pas détecté de contamination résiduelle dans des extraits d'échantillons provenant de milieux de biofiltres usagés.

Conclusions et recommandations

Les résultats expérimentaux indiquaient que la biofiltration pourrait peut-être servir au traitement des émanations gazeuses issues de l'ESV, mais que son utilisation serait limitée aux faibles concentrations de BTX (moins de 600 ppm).

On a constaté que la disponibilité de l'azote était un facteur limitant pour une biofiltration efficace dans certains milieux à base de compost. De plus, on n'a pas suffisamment étudié la question de la disponibilité des substances nutritives au cours des recherches portant sur les biofiltres; des travaux supplémentaires sont nécessaires pour déterminer le type, la quantité et la fréquence des apports de substances nutritives à fournir.

Bien que l'on ait mesuré des taux de capture massiques (en carbone) de BTX et de toluène de 60 $g/m^3/h$ ou plus, on a constaté qu'il était difficile de maintenir des taux de capture élevés. Les taux de capture réduits étaient attribuées à la formation de canaux dans les milieux filtrants ou au séchage des milieux. La mise au point de biofiltres à taux de capture élevés pour les COV nécessite des stratégies améliorées de régulation de l'humidité. Le développement de capteurs et de systèmes de régulation en ligne efficaces faciliterait la tenue d'essais futurs sur les biofiltres. En outre, il faudrait effectuer des études portant sur les changements hydrodynamiques pendant l'utilisation des filtres afin d'évaluer pleinement le rendement à long terme.

Au cours de la présente étude, des périodes d'acclimatation plus longues étaient requises pour la capture de mélanges de BTX par rapport à celle du toluène (études avec un seul contaminant). L'effet des mélanges de COV sur le rendement du biofiltre requiert des études supplémentaires. Dans le cas du traitement des émanations gazeuses issues de l'ESV, il pourrait y avoir une vaste gamme de contaminants ayant des effets sur la capture des BTEX.

EXECUTIVE SUMMARY

Introduction

Biofiltration is an air pollution control technology that utilizes microorganisms immobilized on a filter medium, such as peat or compost. The use of biofilters has proven to be an effective and inexpensive method for removing odorous compounds from many waste gas streams. Recently there has been increased interest in the use of biofilters for the treatment of off-gas contaminated with volatile organic compounds (VOCs) arising from various industrial activities. The remediation of petroleum-contaminated soil by vapour extraction produces large quantities of off-gas contaminated with benzene, toluene, ethylbenzene and xylenes (BTEX). Traditional methods of SVE off-gas treatment are characterised by high operating costs and in some cases a hazardous waste byproduct is generated (i.e. carbon adsorption). Biofiltration has the potential to be a low-cost treatment technology for SVE off-gas. However, additional research is needed to determine its utility and to optimize design parameters.

Research Objectives

The objectives of the research program were to develop a improved understanding of biofilter system response and to identify filter design and operating characteristics required for efficient filter performance.

In this study the removal of toluene, benzene and xylene was examined using an experimental laboratory-scale biofilter. The research program was divided into four main phases: i) design and construction of a lab-scale biofiltration system, ii) comparison and assessment of organic filter media, iii) effect of airflow rate on toluene removal efficiency, and iv) biofiltration of BTX mixtures.

Biofiltration System

The experimental system is illustrated in Figure 3.1 and described in detail in Chapter 3.1 in the thesis. The biofiltration system consisted of the following components: 1) pre-humidification system, 2) sample injection system and 3) biofilter columns.

Each biofilter column consisted of three biofilter stages and an air distribution section. Each stage was constructed from sections of 6" schedule 40 stainless steel pipe (inside diameter of 15.4 cm) with a length of 34 cm. Each biofilter stage was packed with filter material to a depth of 30 cm providing an overall bed depth for the biofilter of 90 cm, and an overall filter volume of 16.3 L.

Filtered laboratory air was humidified in a counter-current packed tower prior to chemical dosing. A Harvard model 22 programmable syringe pump, equipped with 50 mL gas-tight syringes, was used for contaminant introduction into the air stream.

Inlet air stream and bed temperatures were monitored using thermocouples. Headloss across the filter beds was monitored using a manometer. Core bed samples were used to determine moisture content and nutrient levels in the filter bed.

A portable photoionization detector (PID) was used to measure total hydrocarbon concentration in the gas stream. An on-line GC-PID was used to quantify levels of

individual BTX components. Carbon dioxide concentrations in the filter gas stream were determined using a GC-TCD (Thermal Conductivity Detector). Hydrocarbon contamination of used biofilter material was evaluated using methylene chloride extraction followed by GC-FID (Flame Ionization Detector) analysis.

Results

To date, research has lead to several significant findings. Brief descriptions of research results are provided below.

1. Biofilter performance was evaluated using five separate bed materials. The media used in the study included composted municipal solid waste (MSW), composted sewage sludge, composted leaf and yard waste, composted food and yard waste, and composted bark. Perlite, an inert volcanic ash, was added to increase porosity and reduce headloss across the filter bed (60:40 media:perlite mixture by volume). Perlite was selected as a readily available, low-cost amendment that should reduce biofilter operating costs. Each bed packing was initially tested without microbial seeding or nutrient addition. Composted MSW and sewage sludge clearly exhibited the highest removal rates for toluene; acclimation time for each of these two bed materials was less than four days.

2. Composted leaf and yard wastes, as well as composted bark fines were seeded with mixed-liquor from the City of Guelph wastewater treatment plant. Microbial seeding of the filter material had no effect on toluene removal.

3. Composted leaf and yard waste was further amended with the addition of nutrients in the form of commercial fertilizer. Subsequent biofilter performance was found to improve to a level consistent with composted MSW and sewage sludge. This finding, coupled with the results of media analysis indicated that nutrient availability may be the limiting factor for effective biofilter degradation of BTEX. Available nitrogen levels (ammonium-nitrogen and nitrate-nitrogen) were found to be significantly higher in effective biofilter media.

4. Toluene removal was evaluated over a concentration range of 50 to 600 ppm and a filter bed superficial velocity range of 30 to 90 m/h. The superficial velocities resulted in biofilter empty bed retention times of 0.6 to 1.8 min. Toluene elimination capacities of 59, 47 and 37 $g/m^3/h$ were calculated for superficial velocities of 30, 60, and 90 m/h respectively. Removal efficiencies of 97% or greater were observed for toluene mass loading rates of 40 $g/m^3/h$ or less.

5. Experiments which examined the removal of mixtures of benzene (B), toluene (T) and *o*-xylene (X) were conducted. The following contaminant combinations were utilized in this portion of the study: B, T, X, BT, BTX, and TX. Four main observations were noted: i) acclimation period increased from 1 day, for toluene as a single gas stream contaminant, to 9 days for the BTX mixture; ii) the increased acclimation period was due to the presence of *o*-xylene in the gas stream; iii) once acclimated, carbon removal efficiencies for the BTX mixture were found to be similar to toluene-contaminated gas streams; and (iv) contaminant removal followed a consistent degradation pattern with preferential

removal in the order of toluene, benzene and *o*-xylene.

6. Filter performance was found to degrade over time in filters treating BTX and toluene-contaminated gas streams when filter loading rates were greater than 30 g-carbon/m^3/h. Reduced removal rates were attributed to filter channelling or media drying.

7. Carbon dioxide production in the biofilter beds was evaluated before contaminant introduction and during contaminant removal. Predicted CO_2 concentrations, based on contaminant degradation were within 15% of the measured values. These mass balances, coupled with filter bed temperature data confirmed biodegradation was responsible for contaminant removal.

8. Biofilter media were tested for the presence of VOCs following the termination of experiments. No residual contamination was detected in sample extracts obtained from used biofilter media.

Conclusions and Recommendations

Experimental results indicated that biofiltration may be feasible for the treatment of SVE off-gas, but would be restricted for use with low BTX concentrations (less than 600 ppm).

Nitrogen availability was found to be a limiting factor for effective biofiltration in some compost-based media. The issue of nutrient availability has not been sufficiently addressed in biofilter research. Further research is required to identify the appropriate type, amount and frequency of nutrient supplementation.

Although toluene and BTX carbon mass removal rates of 60 g/m^3/h or greater were observed, maintaining high removal rates was found to be difficult. Reduced removal rates were attributed to filter channelling or media drying. The development of efficient high-rate biofilters for VOC removal requires improvements in moisture control strategies. The development of effective on-line sensors and control systems would be beneficial to future biofilter testing. Furthermore, studies examining hydrodynamic changes during filter operation are required to fully evaluate long-term filter performance.

In this study longer acclimation periods were required for the removal of BTX mixtures compared with toluene as a single contaminant. The effect of VOC mixtures on biofilter performance requires further study. In the case of SVE off-gas treatment, a wide range of contaminants may be present which could affect BTEX removal.

ABSTRACT

BIOFILTRATION OF VOCs: LABORATORY STUDIES

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The purpose of this research was to investigate the removal of toluene, benzene and *o*-xylene using an experimental lab-scale biofiltration system. The biofiltration system consisted of three parallel multi-stage biofilters. The research program was divided into 3 main sections: i) media effects, ii) effects of flow rates, and iii) biofiltration of BTX mixtures. Nutrient limitation was found to be the main factor responsible for poor filter performance of some compost-based media. Toluene removal was investigated at three superficial velocities: 28, 58, and 87 m/h. All filters demonstrated greater than 97% removal at mass loading rates up to 40 $g/m^3/h$. Filter drying and flow channelling created a reduction in filter removal efficiency with time. An acclimation period of 9 days was encountered during the biofiltration of mixtures of benzene, toluene and *o*-xylene compared with 1 day for toluene alone. Once acclimated, carbon mass removal efficiencies were found to be similar for BTX mixtures and single component gas streams.

BIOFILTRATION OF VOCs: LABORATORY STUDIES

A Thesis

Presented to

The Faculty of Graduate Studies

of

The University of Guelph

by

LEONARD PAUL SEED

In partial fulfilment of requirements

for the degree of

Master of Science

April, 1995.

ACKNOWLEDGEMENTS

This research work was funded by the Canadian Petroleum Products Institute and the Ontario Ministry of Education and Training.

I wish to thank my supervisor, Dr. Richard Corsi for his support and encouragement, and the rest of my advisory committee, Dr. Gordon Hayward and Dr. Lambert Otten for their input. Dr. Wayne Parker (Carleton University) also provided helpful technical advice during this research effort.

The research work could not have been completed without the assistance of the School of Engineering technical staff, Paul Found, Bill Verspagen and Sandra Ausma. Jeff Kemp and Perry Martos provided valuable assistance in laboratory experiments.

Finally I would like to thank my wife, Lenore, for all of her help and understanding.

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NOMENCLATURE

Abbreviations

ANOVA	analysis of variance
BP	boiling point
BTEX	benzene, toluene, ethylbenzene and xylenes
BTX	benzene, toluene, and xylenes
CB	composted bark
cfm	cubic feet per minute
CF&Y	composted food and yard waste
CL&Y	composted leaf and yard waste
CMSW	composted municipal solid waste
CSS	composted sewage sludge
EBRT	empty bed retention time
GC	gas chromatograph
HC	hydrocarbons
HPLC	high performance liquid chromatography
MLVSS	mixed liquor volatile suspended solids
MW	molecular weight
NH_4-N	ammonium nitrogen
NO_3-N	nitrate nitrogen
PID	photoionization detector
sd	standard deviation
SS	stainless steel
SVE	soil vapour extraction
TCD	thermal conductivity detector
THC	total hydrocarbons
TOC	total organic carbon
TPH	total petroleum hydrocarbons
TX	toluene and xylene
UHP	ultra-high purity
VOC	volatile organic compound
VP	vapour pressure

Mathematical Nomenclature

A	area integrated from sorption curve (1/min)
a	specific area for packed bed particles (m^2/m^3)
C_{ge}	gas phase concentration at exit of biofilter bed (g/m^3)
C_{go}	gas phase concentration at inlet of biofilter bed (g/m^3)
C_g	gas phase concentration (g/m^3)
C_l	liquid phase concentration (g/m^3)
C	contaminant concentration (g/m^3)
D_e	effective diffusion coefficient (m^2/s)

h	height of biofilter bed (m)
H_c	Henry's law coefficient (m^3-liquid/m^3-gas)
k_0	zero-order biodegradation rate constant (g/m^3*s)
K_0	apparent zero-order reaction rate constant (g/m^3*s)
k_1	first-order biodegradation rate constant (1/s)
K_1	apparent first-order reaction rate constant (1/s)
k_d	endogenous decay coefficient (1/day)
K_{ow}	octanol-water partition coefficient (-)
M	biomass concentration (g/m^3)
Q	gas flow rate (L/min)
q_t	adsorption capacity (g-compound/g-bed material)
R	rate of contaminant biodegradation in the biofilm (g/m^3*s)
U_g	superficial velocity (m/h)
V_R	reactor volume (m^3)
W	mass of filter material (g)
Y	yield coefficient (g-biomass/g-substrate utilized)
z	vertical distance in the filter bed (m)
δ	biolayer thickness (m)
ϕ	Thiele number (-)
λ	contaminant penetration into the biofilm (m)

1.0 INTRODUCTION

Soil vapour extraction (SVE), when applied to petroleum-contaminated soil, produces off-gas contaminated with benzene, toluene, ethylbenzene and xylenes (BTEX) (USEPA 1992). This off-gas must often be treated in order to comply with emission permit requirements, which add to the overall cost of soil remediation. Current technologies for the treatment of SVE off-gas, such as carbon adsorption and thermal oxidation, are characterized by high capital and operating costs. In the case of carbon adsorption a secondary treatment or disposal problem exists.

Biofiltration, a process by which contaminants are aerobically degraded by microorganisms, has proven to be an effective and inexpensive method of removing odorous compounds from many waste gas streams (Allen and Yang, 1991; Frechen, 1993; Williams and Miller, 1992). Recent research has indicated that biofilters have the potential to remove volatile organic compounds (VOCs) from waste gas streams (Leson *et al.*, 1991; Yavorsky, 1993; Zurlinden *et al.*, 1993). However, research related to BTEX removal in biofilters is scarce.

1.1 Objectives

The purpose of this study was to enhance knowledge related to the biofiltration of VOCs, and to identify filter design and operating characteristics required for efficient filter performance. The specific research objectives were:

1) to compare and assess various organic media for use in biofilters,

2) to evaluate the effects of airflow rate on biofilter performance, and

3) to examine the biofiltration of mixtures of benzene, toluene and xylene (BTX).

1.2 Scope of Research

A bench-scale experimental biofiltration system, consisting of three parallel biofilters, was designed and constructed. Laboratory experiments, totalling ten in number, were conducted utilizing the experimental system.

Five different types of composted material amended with perlite were evaluated based on filter acclimation periods and toluene removal efficiencies. Long-term filter performance of the various media was not investigated. Experimental periods varied from 6 to 18 days of filter operation.

Toluene removal rates, for a single type of filter media, were calculated at three different airflow rates and two different toluene mass loadings. The airflow rates used in the study corresponded to filter empty-bed retention times of approximately 0.7, 1 and 2 minutes.

Investigations into the biofiltration of BTX mixtures were restricted to the following two combinations: benzene, toluene and *o*-xylene (1:1:1 by volume), and toluene and *o*-xylene (1:1 by volume). Carbon mass removal rates were calculated for the mixture of benzene, toluene and *o*-xylene and compared with the removal of toluene as a single gas stream contaminant.

1.3 Organization

Chapter 2 summarizes literature related to the biofiltration of VOCs, particulary BTEX compounds. Also, a brief summary of emissions from SVE activities is provided. Chapter 3 describes the experimental system and analytical methods used in the experiments, as well as providing an overview of experiments which were conducted. Experimental conditions, results and discussions are included in chapters 4 to 8. Chapters 9 and 10 summarize conclusions and present recommendations arising from the research program.

2.0 LITERATURE REVIEW

2.1 Introduction

The purpose of this review is to provide a summary of information related to the biofiltration of BTEX in soil vapour extraction (SVE) off-gas. Characteristics of SVE off-gas and a brief summary of current control technologies are presented in the first part of the chapter. The main focus of the chapter is on biofiltration as a method for treating BTEX. Also, some simple biofilter models will be briefly discussed.

2.2 Characteristics of SVE Off-Gas

Contaminant Emissions From SVE

The amount of VOCs emitted from SVE systems depends upon the size of the contaminated zone and the age of the spill. Initial off-gas concentrations of VOCs can vary from percent levels for a fresh spill to hundreds of parts per million by volume (ppm) of contaminant for a weathered site. Off-gas concentrations typically follow a first-order decay pattern over time; there is an initial rapid decrease in off-gas concentration followed by a prolonged tailing off (Buck and Seider, 1991).

Table 2.1 summarizes a range of typical operating conditions for SVE systems.

Table 2.1. Example Scenarios for SVE

Parameter	Units	Scenario[1]			
		Very Small	Small	Medium	Large
Exhaust Gas Flowrate	m^3/min	1.4	14	85	425
	cfm	50	500	3000	15000
Exhaust gas velocity	m/s	3.0	7.4	12.5	14.2
Exhaust gas Temp.	^{0}C	50	50	50	50

[1]Size of contaminated zone.
From USEPA 1992.

The BTEX group are the compounds of greatest concern when remediating petroleum contaminated soil. However, data describing BTEX concentrations in SVE off-gas are scarce. Table 2.2 summarizes total VOC levels from a variety of SVE systems as reported in a review by Eklund *et al.* (1992). Tables 2.3 and 2.4 present BTEX concentrations observed in field applications of SVE.

Table 2.2. VOC Concentrations in SVE Off-gas

Number of systems surveyed	Flowrate (cfm)		Total VOC Concentration (ppm)	
	Range	Average	Range	Average
13	5.3 - 300 per well	80 (2.2 m^3/min)	20 - 350	100
17	25 - 11300 total	2200 (62 m^3/min)	150 - 38000	4000

From Eklund *et al.*, (1992).

Table 2.3. BTX Concentrations in SVE Off-gas

Week	Flow Rate (m^3/h)	Air Concentration (mg/L)		
		Benzene	Toluene	Xylene
0	19.2	2.37	4.71	1.84
1	24.8	0.44	1.64	1.23
7	29.8	0.09	0.37	0.52
38	47.7	0.042	0.169	0.296
56	39.8	0.007	0.008	0.075

From van Eyk, 1992. Data from a contaminated retail gasoline station.

Table 2.4. Off-Gas BTEX Levels

Time (days)	Approximate Air Concentration (mg/L)			
	Benzene	Toluene	Ethylbenzene and m/p-xylene	*o*-Xylene
10	0.3	2	2	1
20	0.15	1.3	2.	.9
40	0.1	0.75	1.5	0.7
135	<0.05	0.3	0.5	0.5

From Parker 1993.

From Tables 2.3 and 2.4 it is apparent that of the BTEX compounds, toluene is often present at the highest concentration. The xylenes are initially present at the lowest levels, but their concentration does not decrease as rapidly as the other BTEX constituents. The implication of this shift in off-gas composition is that the biodegradability of the gas stream may change over time.

VOC Treatment Technologies

The choice of an appropriate BTEX control technology depends on the off-gas flow rate and VOC concentration. The most widely used control technologies for the treatment of VOCs in SVE off-gas include:

- activated carbon adsorption
- catalytic oxidation
- thermal incineration
- internal combustion engines (ICEs).

A detailed comparison of treatment technologies is beyond the scope of this review. Operational characteristics of current treatment technologies relevant to the treatment of SVE off-gas are summarized in Table 2.5. The main disadvantages of current treatment technologies are additional fuel requirements and the production of nitrogen oxides for incineration or combustion treatment methods, and the need for activated carbon disposal or regeneration.

While contaminants can be recovered as a liquid stream from the regeneration of carbon or from condensation technologies, VOCs from SVE off-gas are not of sufficient purity or value to warrant recycling (USEPA, 1992).

Table 2.5. Operational Characteristics of VOC Treatment Technologies

Treatment Technology	Process Characteristics
Activated Carbon Adsorption	• most common control technology • applicable VOC conc. < 1000 ppm • removal efficiency 70-90% • flowrates < 100,000 scfm (2800 m^3/min) • off-gas relative humidity < 50% • off-gas temp < 38 ^{0}C • contaminant MW 50-150 g/g-mol • secondary treatment or disposal
Thermal Incineration	• applicable high VOC conc. • >98% removal efficiency • auxiliary fuel required • requires a constant off-gas flow rate • NO_x production
Catalytic Oxidation	• 95-99% removal efficiency • requires VOC conc < 3000 ppm • catalyst can be damaged by trace contaminants
Internal Combustion Engines	• >99% removal efficiency • off-gas flowrates 30-100 scfm (0.8-2.8 m^3/min) • VOC conc > 1000 ppm • auxiliary fuel required • SVE off-gas: gummy reactive fuel • NO_x production

From: Buck and Seider (1991); Eklund *et al.*, (1992); USEPA (1992).

Emerging technologies that may be applicable for the treatment of SVE off-gas include:

- condensers,
- packed bed thermal processors, and
- biofilters.

Biofilters are an attractive control technology due to their low operating cost and ability to remove contaminants without the generation of residual waste streams. The use of biofilters will be discussed in greater detail later in this chapter.

2.3 Properties of BTEX

The physicochemical properties of each of the BTEX components are summarized in Table 2.6.

Table 2.6. Summary of Physical-Chemical Properties of BTEX

Compound	MW g/mol	BP ^{0}C	VP Pa	Water Solubility g/m^3	log K_{ow}	H_c Pa*m^3 /mol
Benzene	78.11	80.1	12700	1780	2.13	557
Toluene	92.13	110.6	3800	515	2.69	680
Ethyl-benzene	106.2	136.2	1270	152	3.13	887
o-Xylene	106.2	144	1170	220	3.15	565
m-Xylene	106.2	139	1100	160	3.20	730
p-Xylene	106.2	138	1170	215	3.18	578

MW = molecular weight, BP = boiling point (at 1 atm); VP = vapour pressure; H_c = Henry's Law Coefficient.
VP, Water Solubility, log K_{ow}, and H_c at 25 ^{0}C.
From Mackay *et al.*, 1992.

Biodegradation of BTEX

The biochemical pathways responsible for the aerobic degradation and utilization of BTEX compounds as a carbon source have been developed for each of the BTEX compounds and are presented in reviews by Smith (1990), and Gibson and Subramanian (1984). In both reviews it was noted that there have been very few reports of degradation of *o*-xylene as a sole carbon source. Smith (1990) reported that bacteria capable of degrading *meta* or *para*-xylene could not degrade the *ortho* isomer and vice versa. Arvin *et al.* (1989) found that *o*-xylene and toluene degrading bacteria were also capable of degrading benzene.

Similar trends were observed in a study by Ridgeway *et al.* (1990), in which 300 different strains of gasoline degrading bacteria were isolated from a gasoline-contaminated aquifer. Each isolate was tested for hydrocarbon degradation with each of fifteen test hydrocarbons. It was found that many of the strains could degrade several of the test hydrocarbons individually as a sole carbon source. Approximately 75% of the isolates could degrade toluene as a sole carbon source where as *o*-xylene was the least frequently degraded of the BTEX compounds. Marked differences in hydrocarbon preference were observed among closely related bacterial strains.

The effect of mixtures of hydrocarbons on degradation are of greater interest to researchers involved in biofilter or bioremediation studies. There have been several studies examining the degradation of various mixtures of BTEX compounds in liquid batch cultures (Alvarez and Vogel, 1991; Arvin *et al.*, 1989; Chang *et al.*, 1993; Goldsmith and Balderson, 1988; Haigler *et al.*, 1992; Lee *et al.*, 1994; Oh *et al.*, 1994). Degradation patterns observed included: diauxie, simultaneous utilization, co-metabolism, enhanced removal and competitive inhibition. The degradation patterns varied between different substrate combinations and differed greatly between different bacterial strains.

Several of the studies reported the co-metabolism of *p*-xylene in the presence of benzene and/or toluene (Alvarez and Vogel, 1991; Chang *et al.*, 1994; Oh *et al.*, 1994). Oh *et al.* (1994) discovered the accumulation of intermediates of *p*-xylene degradation indicating that *p*-xylene was not being utilized as a growth substrate in their cultures.

Haigler *et al.* (1992) presented the theory that there exists a nonspecific enzyme sequence that can be induced by one component of a hydrocarbon mixture allowing an organism to derive carbon from a second compound that cannot serve as a primary growth substrate. Lee *et al.* (1994) discovered a broad substrate enzyme capable of degrading metabolic intermediates of benzene, toluene and *p*-xylene degradation. They were able to create a hybrid *Pseudomonas* strain capable of simultaneous degradation of mixtures of benzene, toluene and *p*-xylene.

Biokinetic parameters have been developed for toluene degradation in biofilms (Arcangeli and Arvin, 1992) and the degradation of benzene, toluene and *p*-xylene individually in batch systems (Goldsmith and Balderson, 1988; Chang *et al.*, 1993). Mathematical expressions have been developed describing competitive inhibition and co-metabolism of BTX mixtures (Chang *et al.*, 1993; Oh *et al.*, 1994).

In summary, the degradation of mixtures of hydrocarbons is complex and no clear trends are apparent. The response of the microorganisms appears to be species specific.

2.4 Biofiltration

Biological Air Treatment

Biological air treatment technologies can be classified as: bioscrubbers, biotrickling filters and biofilters. In bioscrubbing, the contaminants in the off-gas are absorbed into a liquid stream (generally water) in a spraying tower. The contaminants in a liquid phase are then degraded in an activated sludge bioreactor prior to liquid discharge or reuse.

Bioscrubbing is generally restricted to soluble compounds with Henry's law coefficients less than 0.01 m^3-liquid/m^3-gas (Groenestijn and Hesselink, 1993).

Biotrickling filters and biofilters both utilize microorganisms immobilized on a packing material or bed substrate. In biotrickling filters a biologically inert packing material is used and a liquid stream is continuously recirculated through the bed. In biofilters a natural media such as compost is used for microbial support. The natural media supplies nutrients to the microorganisms and water is only added to maintain moisture levels.

Biofilters are less complex and are the least expensive of the biological air treatment options. Biofiltration is rapidly becoming an accepted and mature technique for air pollution control. The following discussion will focus primarily on biofiltration.

General Biofiltration Principles

Figure 2.1 illustrates a schematic of a typical biofilter. Microbial activity occurs in a thin liquid layer or biofilm which surrounds the organic particles in the biofilter bed. Microbial uptake creates a concentration gradient within the biofilm which promotes the diffusion of nutrients from both the gas/liquid and solid/liquid interfaces. The uptake and degradation of organic constituents from waste gases can occur by:

(1) absorption into the wet biofilm and transport by diffusion to microorganisms,

(2) absorption into the liquid layer, adsorption on the support media followed by cell uptake,

(3) absorption into the wet boundary layer, adsorption on the support media followed by exoenzymatic degradation, and

(4) direct adsorption onto the surface of an exposed microorganism (Hodge *et al.*, 1991).

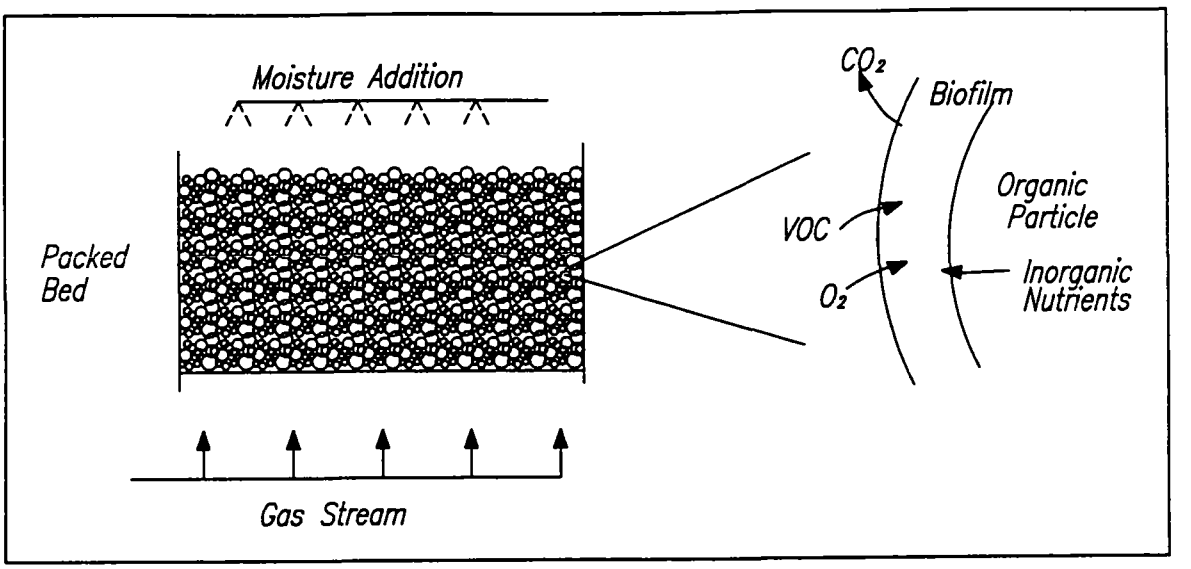

Figure 2.1. Biofilter Schematic

Inorganic nutrients are transported by diffusion from the bed material to the microorganisms and cell death will recycle some of the nutrients back to the bed.

Some contaminants can be utilized as primary substrate by microorganisms, but other compounds may require the presence of an additional carbon source. For example, aerobic degradation of trichloroethylene was found to occur by co-metabolism with propane as the primary organic source (Kampbell *et al.*, 1987).

Design Parameters

Some recommended design parameters are summarized in Table 2.7; the effect of bed

characteristics and loading rates will be discussed in the sections that follow. The list of design parameters were summarized from biofilter applications concerned primarily with the control of odorous waste gas.

Table 2.7: Design Parameters

PARAMETER	RECOMMENDED RANGE
Retention Time	> 15 s, 30-60 s typical
Filter Bed Temperature	15-45 ^{0}C, 37 ^{0}C optimum
Filter Bed pH	7-8
Filter Bed Moisture Content	50%-70% by weight, wet basis
Influent Gas Relative Humidity	80%-100%
Filter Media Porosity	60-90%
Surface Loading	Range 20-500 m^3/m^2h, 55-180 m^3/m^2h typical
Pressure Drop	< 0.25 kPa
Oxygen Content of Inlet Stream	5-15% by volume minimum
Maximum Pollutant Concentration	1 g/m^3 (total carbon) 765 ppm pure methanol 530 ppm pure ethanol 400 ppm pure acetone
Maximum Filter Elimination Capacity	200 g Carbon/m^3/h
Filter Media Loss on Ignition	60-80%
Filter Media Dry Density	0.40-0.45 g/mL
Filter Bed Depth	0.5-2.5 meters, 1 meter average
Organic Matter Content	25-35%

Summarized from: Dharmavaram (1991); International Process Systems (1990); Neff (undated); Williams and Miller (1992).

Bed Characteristics

The filter bed provides both a nutrient source and a method of attachment for the microorganisms. For maximum compound removal the bed material should have the following characteristics:

- high moisture retention capacity to prevent drying of the filter bed,
- high porosity to reduce head loss and to ensure an even distribution of incoming gases,
- available nutrients for optimal microbial growth, and
- diverse microbial population.

Compost, peat and soil have been observed to be effective bed materials with compost fulfilling most of the above requirements. Compost filters usually require bed replacement every 2 to 5 years compared with soil filter beds which can last indefinitely (Bohn 1993). However, compost filters exhibit higher removal rates and lower headloss per volume of packing than soil beds. Also, compost-based filters typically have higher microbial activity than soil or peat-based filters (Leson and Winer, 1991).

Nutrients. Compost-based filters usually contain sufficient inorganic nutrients to support microbial activity and nutrient supplementation is considered unnecessary (Leson and Winer, 1993; Bohn, 1993). A carbon/nitrogen/phosphorus ratio of between 20:1:0.2 to 10:1:0.1 in the bed material is recommended for optimum biofilter performance (Brauer, 1986; Tinari, 1994). Don (1986) found enhanced degradation of toluene after the addition of inorganic nutrients to a compost-based filter, however, the composition and amount of nutrients was not given.

Bed Structure. Natural packing, such as compost, usually requires the addition of inert material to prevent compaction and crack formation which creates an uneven flow distribution. Ottengraf (1986) recommended the addition of polystyrene spheres (3 to 5 mm in diameter) to compost filters to reduce head loss and prevent bed deterioration. It is also advisable to remove the smaller particle fractions from compost; Allen and Yang (1991) found that pressure drop increased significantly in filter beds with compost particles of less than 1.2 mm effective diameter. Williams and Miller (1992) recommended that 60% (by weight) of particles in a filter bed should have effective diameters of greater than 4 mm. Filter material consisting of sieved compost fractions of 4 to 6 mm and greater than 10 mm in a 1:1 mixture with wood bark has been used successfully with low headloss (Groenestijn and Hesselink, 1993).

Peters *et al.* (1993) found that it was necessary to add gypsum and perlite to their compost filter in order to prevent the formation of hard aggregates.

Shareefden *et al.* (1993) tested pressure drop and methanol removal using various mixtures of peat, perlite, vermiculite, and polyurethane. A mixture of perlite and peat (40:60 by volume) provided the best removal with the lowest pressure drop.

Microorganisms. The presence of microorganisms capable of degrading toxic contaminants is necessary for effective biofiltration. The degradation of poorly biodegradable compounds may require inoculation of the bed material with microorganisms that have been exposed to the contaminants. Activated sludge

suspensions, soil from a petroleum landfarm and specially cultivated microorganism have been used as inocula to enhance degradation of resistant compounds and reduce acclimation periods (Ottengraf *et al.*, 1986; Hodge *et al.*, 1991; Groenestijn and Hesselink, 1993). For example, Ottengraf *et al.* (1986) found that the degradation of dichloromethane was achieved only after inoculation of the bed with a culture of *Hyphomicrobium sp.*

Acclimation periods of 10 days have been reported for easily biodegradable compounds (Leson and Winer, 1991). Ottengraf and van den Oever (1983) found that their filter bed reached steady state in 10 days while treating a mixture of ethylacetate, toluene, butylacetate and butanol. Once acclimated, the beds could last 2 weeks between waste gas loadings without a reduction in removal efficiency. Ergas *et al.* (1993) required an acclimation period of three weeks for toluene removal in a compost filter.

Peters *et al.* (1993) noted an acclimation period of one week for the treatment of a VOC gas stream consisting of a mixture of kerosene and gasoline. They found that the biofilter bed required 2 days to adapt to moderate loading increases and large shock loads required 5 days for bed recovery.

Filter Bed pH. The degradation of some compounds, particularly chlorinated hydrocarbons, can produce acid intermediates which lower bed pH and subsequently inhibit microbial activity. Chalk, marl and oyster shells have been used to buffer acid production (Ergas *et al.*, 1993; Ottengraf and van den Oever, 1983). Reduction in pH is

generally not a problem for BTEX degradation unless chlorinated compounds are also present in the gas stream.

Moisture Control. Biofilters require a moisture content of 40 to 60% (by weight). Therefore, moisture control is crucial for maintaining optimal biofilter performance. Drying will reduce microbial activity and an excessively wet filter will lead to the formation of anaerobic zones.

Humidification of incoming air is the preferred method to prevent bed drying. Williams and Miller (1992) recommended a degree of saturation of the waste gas of greater than 95%, but stated that drying can still occur due to exothermic microbial activity unless the humidity is raised to above 99%.

Additional moisture is often added to a biofilter bed by surface spraying, but the application rate must suit the physical properties of a filter material. A water addition rate that is too high can cause flooding, bed compaction and leaching of bed nutrients. van Lith (1987) suggested a maximum water droplet size of 1 mm for direct humidification, and a maximum water addition rate of 20 to 30 $L/m^2/h$.

Elimination Rates and Loading Rates

Off-gas flow rates vary depending upon the particular biofilter application. Flow rates of up to 200,000 m^3/h have been successfully treated and volumetric loads between 100 to 200 m^3/m^3*h are typically encountered in biofilter applications (Groenestijn and

Hesselink, 1993).

Table 2.7 presented some typical design superficial velocities, but the bed velocity must be considered in conjunction with the mass loading rate to the filter. Don (1986) required a superficial bed velocity of less than 25 m/h to achieve 90% removal of toluene.

The elimination capacity of a filter bed is defined as the maximum amount of compound (or carbon) degraded per unit volume of bed material per unit time. The contaminant loading rate to the filter (mass/filter volume/time) and the elimination capacity will determine the biofilter size requirements for a waste gas application. A maximum pollutant gas phase concentration of 1 g carbon/m^3 has been recommended (Dharmavaram 1991), however, higher concentrations can be tolerated as long as the elimination capacity of the bed is not exceeded. A maximum BTEX gas phase concentration of 500 mg/m^3 and a maximum VOC concentration of 2500 mg/m^3 have been recommended by Yavorsky (1993).

Degradation rates vary widely depending on the compounds in the waste gas and the filter substrate. Typical degradation rates for VOCs range from 50 to 100 g/m^3/h (Leson *et al.*, 1991), however, Dharmavaram (1991) stated that some patented biofilters are capable of removing 100 to 200 g carbon/h/m^3 of material. Table 2.8 summarizes elimination capacities that were observed in various laboratory and pilot studies.

Table 2.8. Elimination Capacities for VOCs

Compound(s)	Media and Bed Volume	Inlet Concentration	Retention Time or Superficial Velocity	Removal Efficiency or Elimination Rate	Reference
Mixture: Ethylacetate Toluene Butylacetate Butanol	compost + inert particles V = 53 L	Toluene: 5.06-0.308 g/m^3	30-500 m/h EBRT: 6.0-0.41 min	Toluene: 21 g/m^3*h Mixture: 75 g Carbon/m^3*h	Ottengraf and van den Oever 1983
JP-5 Jet Fuel	diatomaceous earth + activated carbon V = 0.12 L	?	2.5 m/h EBRT: 22 min	5.0 g HC/m^3*h Methane Equivalent	Hodge *et al.*, 1991
SVE Off-Gas	bark + peat + perlite + CSS + enriched culture V = 1500 L	470 & 870 ppm total petroleum hydrocarbon	?	TPH: 32 g/m_3*h benzene: 0.8 toluene: 6.0 g/m_3*h	Zurlinden *et al.* 1993
85% kerosene 15% gasoline	CL + CSS + perlite + gypsum + activated sludge V = 16.7 L	25-1000 $ppm*m^3/m^2*min$	EBRT: 1-3 min	>95% @ 152 $ppm*m^3/m^2*min$ >99% BTEX removal	Peters *et al.*, 1993
BTEX	compost V = 8 L	300 ppm total BTEX	EBRT: 1.2 min	70-90% BTEX 20-30 $g/m^3/h$	Kamarthi and Willingham, 1994

Table 2.8 continued

Compound(s)	Media and Bed Volume	Inlet Concentration	Retention Time or Superficial Velocity	Removal Efficiency or Elimination Rate	Reference
BTEX	Trickling Filter: carbon-coated polyurethane foam V = 2.0 L	B: 0.136 mg/L T: 0.820 mg/L E: 0.194 mg/L m/p-X: 0.137 mg/L o-X: 0.023 mg/L	EBRT: 40 min	97% total BTEX @ 57 g/m^3*h	DeFelippi *et al.* 1993
BTX	pelletized biologically active media V = 10.5 L	600 ug/L total BTX in a ratio of 1.1:1.03:1.0	EBRT: 42 s	82-84% BTX @ 55 g/m^3*h	Severin *et al.*, 1993
BTX	peat moss + chicken manure	300 - 3300 mg/m^3 BTX	9.6, 24.1 and 36.1 m/h EBRT: 6.25 - 1.7 min	>95% BTX 5.8 - 63.6 g/m^3*h	Tahraoui *et al.*, 1994

EBRT = Empty Bed Retention Time; CSS = Composted Sewage Sludge; CL = Composted Leaf and yard wastes.

2.5 Biofilter Cost Estimates

Capital and operating costs for biofiltration vary depending on the waste gas stream being treated. Generally speaking biofilters are less expensive in both capital and operating costs than traditional physical/chemical methods for the treatment of dilute gas streams (Yavorsky, 1993). Fouhy (1992) estimated a range of biofilter capital costs of $5.50 to $30.00 (U.S.) per m^3/h of gas cleaned. Operating cost estimates varied from $0.03 to $2.00 per 1000 m^3/h gas cleaned.

Waste gas pretreatment, such as heating or cooling will have an impact on capital and operating costs. Grease droplets and dust particles can plug biofilters and must be removed. The main energy requirement during biofiltration filter operation is for blower operation which will be a function of system head loss.

Combined Technologies

It may be more cost effective to combine biofiltration with traditional air pollution control technologies. For example, a small regenerative activated carbon adsorber combined with a biofilter was found to be economically feasible for the treatment of contaminant concentrations of 10 g/m^3 (Fouhy, 1992). Activated carbon reduces the contaminant concentrations prior to entry into the biofilter; the net effect would be a decrease in activated carbon requirement. A conventional scrubber combined with a biofilter has been used to treat ethanol and aldehyde emissions (Fouhy, 1992). Since the waste gas usually requires humidification, the use of a conventional scrubber or bioscrubber in combination with a biofilter makes sense for the treatment of complex contaminant mixtures.

2.6 Theoretical Biofilter Models

Theoretical model development was not a research objective, hence, only some principle equations related to steady-state modelling will be presented. The modelling approach and equations are from Ottengraf (1986).

The biofilter equations are based on the following assumptions:

1) uniform biofilm thickness, which is much less than the particle radius
2) the bed consists of homogeneous spherical particles,
3) biofilms exist entirely on the exterior surface of packed-media particles,
4) nutrients in the biofilm are transported by molecular diffusion only,
5) biomass density is homogeneous throughout the bed,
6) interfacial resistance between the bulk gas and the liquid biofilm is negligible,
7) an equilibrium defined by Henry's law exists at the gas-biofilm interface,
8) gas flow through the packed bed is characterized by ideal plug flow, and
9) contaminant removal proceeds at steady-state.

Figure 2.2 provides an illustration of a biofilter particle surrounded by a wet biofilm with a thickness δ.

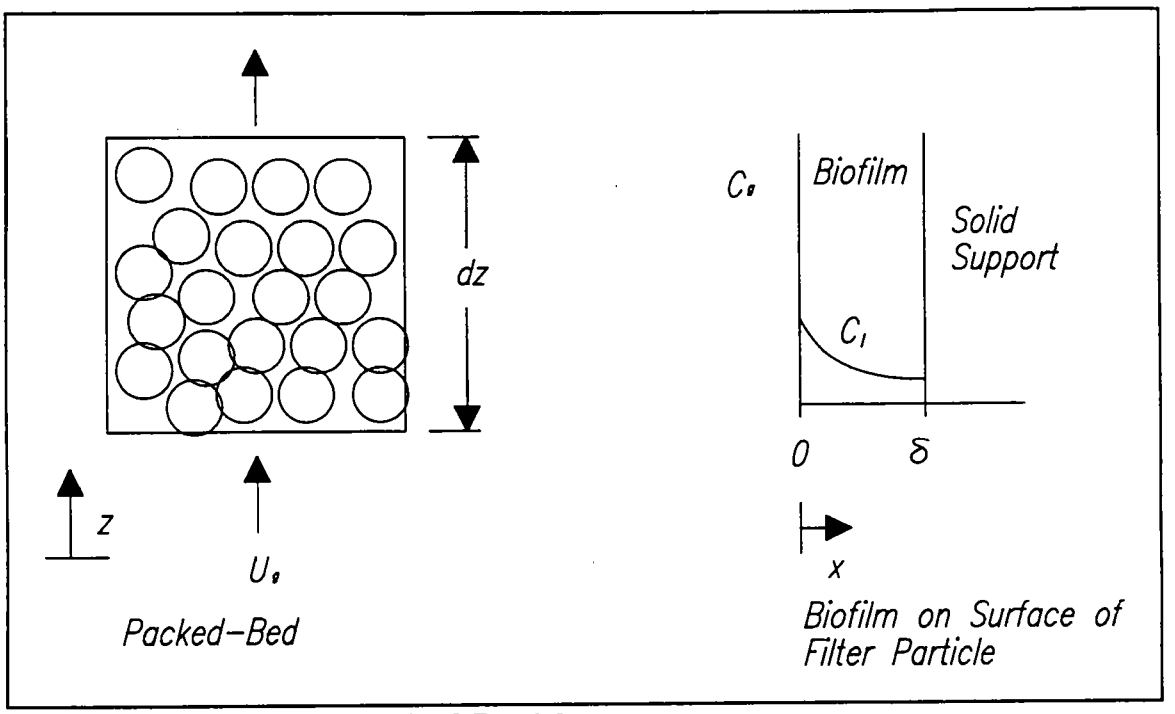

Figure 2.2. Sketch of Filter Bed Particle

At steady state, the equation describing the concentration of contaminant at a point in the biofilm is

$$D_e \frac{d^2 C_l}{dx^2} - R = 0 \qquad (1)$$

Where: C_l contaminant liquid phase concentration (g/m^3)
D_e effective diffusion coefficient (m^2/s)
R rate of contaminant biodegradation in the biofilm (g/m^3*s)
x distance in the biofilm (m)

A one-dimensional mass balance on contaminant in the gas phase of the biofilter as a function of distance, z, in the filter bed is given by:

$$-U_g \frac{dC_g}{dz} = Na \qquad (2)$$

where:
- a specific area for a fixed bed (m^2-particles/m^3-bed)
- C_g gas phase concentration (g/m^3)
- N substrate flux into the biolayer (g/m^2*s)
- U_g superficial velocity (m/s)
- z vertical distance in the filter bed (m)

The boundary conditions are:

$$at\ x=0 \quad C_l = \frac{C_g}{H_c};$$

$$at\ x=\delta \quad \frac{dC_l}{dx} = 0;$$

$$at\ z=0 \quad C_g = C_{go};$$

Also, flux, N, into the biolayer is

$$N = -D_E \left(\frac{dC_l}{dx}\right)_{x=0}$$

First Order Kinetics

If first order degradation kinetics are assumed in the biolayer, then

$$R = k_l C_l$$

where k_l is the first-order biodegradation rate constant (1/s).

Equations 1 and 2 can be solved with the above boundary conditions for a biofilter of height, h, to give

$$\frac{C_{ge}}{C_{go}} = \exp\left[\left(-\frac{haD_E}{H_c U_g \delta}\right)\phi_1 \tanh\phi_1\right] \quad (3)$$

where H_c is the Henry's Law Coefficient (m^3-liquid/m^3-gas) and

$$\phi_1 = \delta\sqrt{\frac{k_1}{D_E}} \quad (4)$$

Equation 3 can be rewritten as:

$$\frac{C_{ge}}{C_{go}} = \exp\left(-\frac{hK_1}{H_c U_g}\right), \quad where \ K_1 = \frac{aD_E}{\delta}\phi_1 \tanh\phi_1 \quad (5)$$

The parameter, K_1, is referred to as the apparent first-order reaction rate constant with units of s^{-1}.

Ergas *et al.* (1993) presented a similar analytical solution for first-order degradation kinetics. Model results compared favourably with experimental data for toluene removal.

Zero Order Kinetics

In the case of zero order degradation kinetics the equations must be solved for two conditions. In the first case it is assumed that there is no diffusion limitation in the biolayer and substrate conversion is limited by reaction rate. In the second case diffusion limitation occurs, therefore, the depth of penetration, λ, of the contaminant in the biolayer is less than the biofilm thickness, δ.

Assuming zero order degradation kinetics

$$R = k_0$$

where k_0 is the zero-order biodegradation rate constant (g/m^3*s). For case 1, reaction limitation, equations 1 and 2 along with the previously-described boundary conditions can be solved resulting in

$$\frac{C_{g_e}}{C_{go}} = 1 - \frac{k_0 a \delta h}{U_g C_{go}} = 1 - \frac{K_0 H}{U_g C_{go}} \qquad (6)$$

In the diffusion limited regime the second boundary condition becomes

$$at\ x=\lambda\ \frac{dC_l}{dx}=0$$

The solution of equations 1 and 2 then yields

$$\frac{C_{g_e}}{C_{go}} = \left(1 - \frac{ha}{U_g}\sqrt{\frac{k_0 D_E}{2H_c C_{go}}}\right)^2 = \left(1 - \frac{h}{U_g}\sqrt{\frac{K_O D_e a}{2H_c C_{go}\delta}}\right)^2 \qquad (7)$$

Ottengraf (1986) found good agreement with model predictions and experimental results using solutions to the zero order model.

Baltzis and Shareefdeen (1994) developed a more complex model including kinetic expressions for oxygen as a substrate and competitive inhibition between benzene and toluene. Modelling results indicated that oxygen limitation was not a problem for the benzene and toluene.

2.7 Summary

The choice of an appropriate method for the treatment of SVE off-gas depends upon on a variety of factors, such as off-gas flow rate and pollutant concentration. Biofiltration has been shown to be effective for the treatment of low concentrations of contaminants in off-gas. Furthermore, BTEX compounds have been found to be biodegradable under suitable conditions. Biofilters therefore have the potential to be used in place of or in conjunction with current technologies for the treatment of SVE off-gas, particularly when remediating small contaminated sites.

Studies of BTEX degradation in biofilters have been limited to a few recent studies. Further research is required in order to gain a better understanding of the processes involved. Also, realistic performance estimates are required to further assess the potential of biofilters for the treatment of SVE.

3.0 MATERIALS AND METHODS

3.1 Experimental Apparatus

Biofiltration System

Figure 3.1 presents an illustration of the experimental biofiltration system, which includes three parallel biofilter beds. The system consisted of the following components: 1) pre-humidification system, 2) sample injection system and 3) biofilter columns.

Each biofilter column consisted of three biofilter stages and an air distribution section. Each stage was constructed from sections of 6" schedule 40 stainless steel pipe (inside diameter of 15.4 cm) with a length of 34 cm. The filter bed was supported by a stainless steel perforated plate (3 mm diameter holes on 5 mm centres) welded to the bottom of each filter stage. Each biofilter stage was packed with filter material to a depth of 30 cm providing an overall bed depth for the biofilter of 90 cm, and an overall filter volume of 16.3 L. A plenum of approximately 3.5 cm wide existed between each stage to allow for gas sampling. Figure 3.2 illustrates sampling port placement for a biofilter stage.

Compressed air was passed through a 5 μm filter followed by a 0.3 μm filter in order to remove oil aerosols. Delivery air pressure was controlled with a two-stage regulator. The air stream was pre-humidified in a counter-current packed tower prior to chemical dosing. The humidification column consisted of a 80 cm length of plexiglass tubing, with an inside diameter of 15 cm, filled to a depth of 54 cm with #2 Tri-Pak packing. Water was circulated through the column from a constant temperature water bath (Lauda model RC

20).

The air stream was directed to the biofilter columns using 1/2 inch teflon® tubing. In the initial design, branch lines to each column (1/4 inch teflon tubing) were connected by tee junctions to the main supply line. The system was modified by the addition of a header constructed from 1 1/2 inch stainless steel tubing with a length of 60 cm. Air flow from the main line was fed into the header and lines from the header were connected to the column.

Contaminant Introduction

A Harvard model 22 programmable syringe pump, equipped with 50 mL gas-tight syringes, was used for chemical introduction into the air stream. Pure liquid contaminants were loaded into the syringes and fed into the gas stream at one of two possible locations depending on the experiment. The first contaminant introduction location was after the humidification column and prior to flow distribution to the columns as illustrated in Figure 3.1. In some experiments contaminants were introduced into the individual branch lines supplying each column. In both cases pure liquid compound was introduced into a tee junction in the supply line where the contaminants volatilized into the air stream. In later experiments, a wick which protruded into the air supply line was placed in the tee junction .

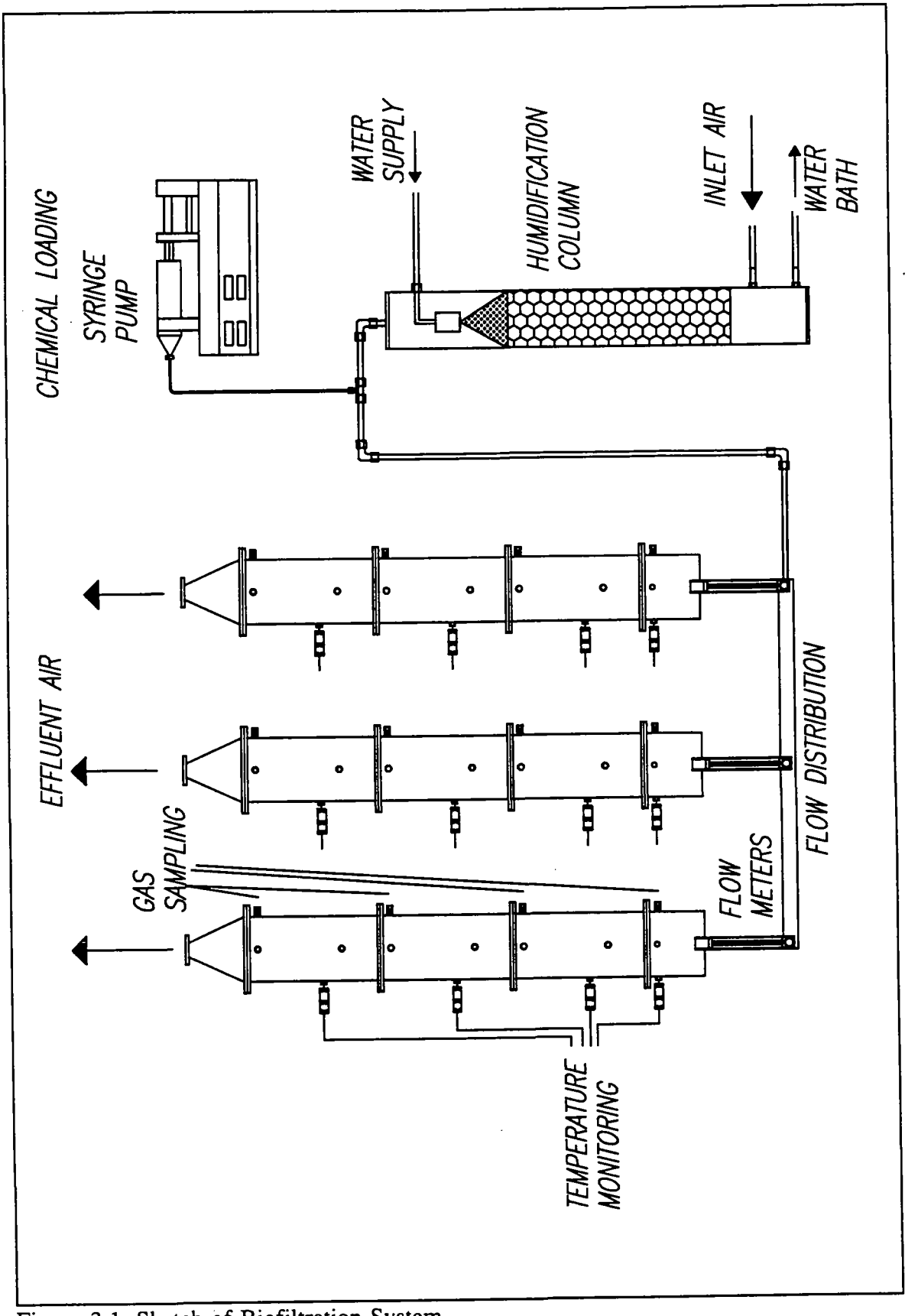

Figure 3.1. Sketch of Biofiltration System

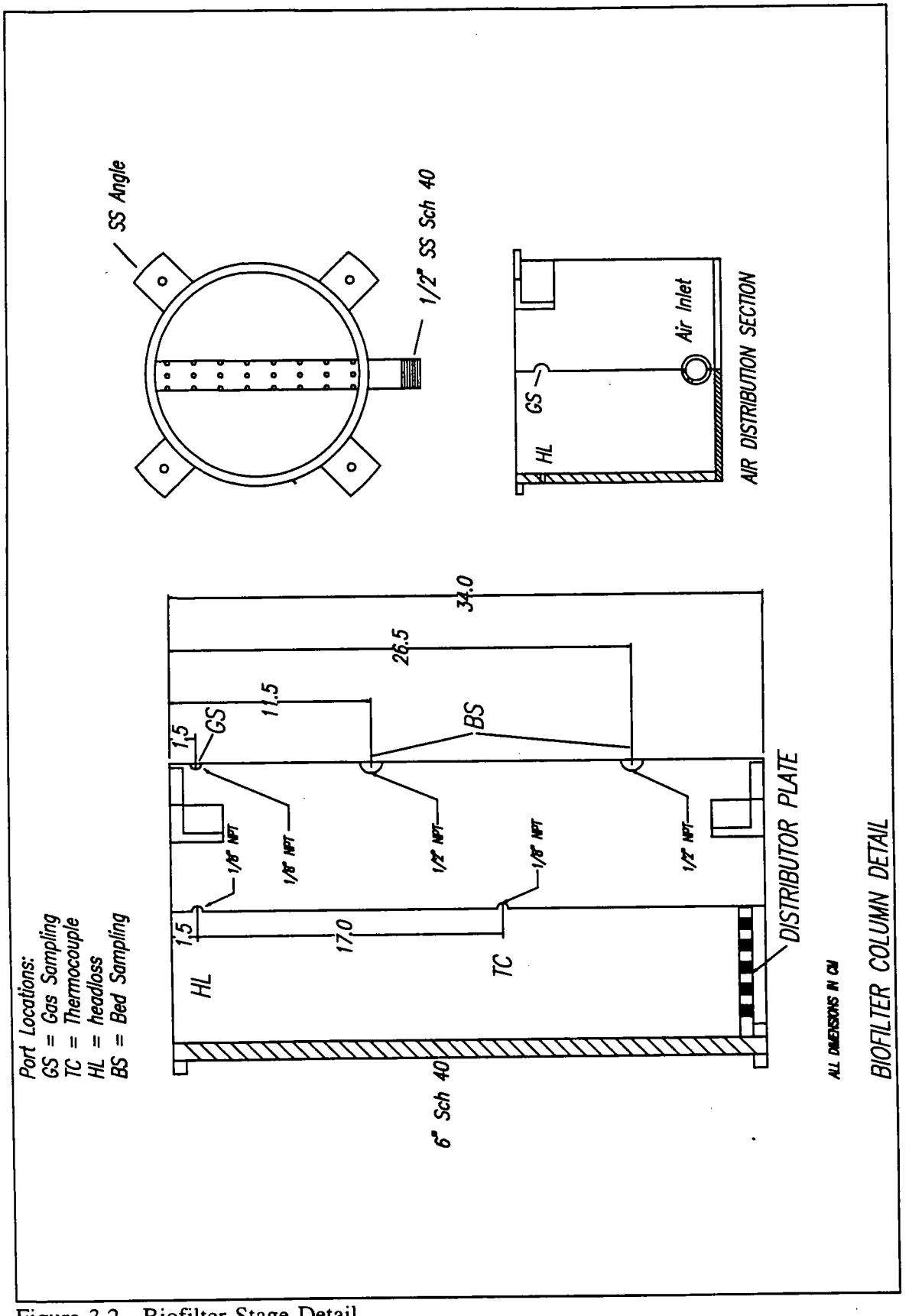

Figure 3.2. Biofilter Stage Detail

Temperature Measurement

Filter bed temperatures and inlet gas temperatures were monitored using type T thermocouples (Cole-Parmer); 10 cm in length by 3 mm in diameter. Thermocouple locations for the biofilter stages and the inlet are illustrated in Figure 3.2. When installed, the tip of the thermocouples protruded 7 cm into the reactor. Temperature measurements were recorded either automatically using a datalogger (Fluke 2240B) or manually using a thermocouple thermometer (Cole-Parmer, Digi-Sense).

Flow Measurement

In-line rotameters (Cole-Parmer, 150 mm stainless steel) were used to measure and control the flow rate to the biofilters. Factory supplied calibration curves, adjusted for a relative humidity of 96%, were used for flow calculations. Rotameters were located immediately prior to entry into the air distribution section of each biofilter, as indicated by Figure 3.1.

Humidity Measurement

Humidity levels in the biofilter influent and effluent gas streams were measured using a thermistor hygrometer (Cole-Parmer model number A21295).

Headloss Measurement

Pressure drop through the bed was measure using an oil-filled manometer (Dwyer model MM400). Pressure taps were located in the air distribution section, between each stage and at the exit of the biofilter columns.

Moisture Control

Once the biofilters were in operation additional moisture was added manually to the beds. Deionized water was introduced using perforated teflon® tubing (1/8 ") inserted into the gas sampling ports between the biofilter stages. The amount of supplemental water which was required was estimated based on the inlet gas and bed temperatures assuming an inlet gas relative humidity of 96% and saturated pore air in the bed.

3.2 Biofilter Media

Sources of Organic Media

The types of compost that were used in the studies are summarized in Table 3.1.

Table 3.1. Sources of Media

	Type of Material	Source
CMSW	composted source separated municipal solid waste	City of Guelph landfill
CL&Y	composted leaf and yard waste	Alltreat Farms Ltd., Arthur, Ont.
CB	composted bark fines	Alltreat Farms Ltd.
CF&Y	composted food (industrial and commercial) and yard waste	Scott Farms Ltd., Mississauga, Ont.
CSS	composted sewage sludge	City of Guelph wastewater treatment plant

Amendment

Horticultural grade perlite (Vil Vermiculite Incorporated) was added to the composted media in order to increase bed porosity. Screened composted wood pieces obtained from

CL&Y and retained on a 6.3 mm diameter screen, were also used in some mixtures.

Inoculum

In some studies an inoculum consisting of mixed liquor volatile suspended solids (MLVSS) from the activated sludge process from the City of Guelph wastewater treatment plant was used.

Nutrients

Lawn fertilizer (Home Hardware, 21-7-7) was used as a nutrient source during some experiments. The fertilizer contained 21% total nitrogen with 5.25% of the nitrogen derived from sulphur coated urea.

Media Preparation

The desired amount of each substrate including compost, inert material, inoculum and nutrients were placed in a cement mixer and tumbled until completely mixed. Deionized water was added as required to increase the moisture content of the mixture to an appropriate level. The amount of each media component used in filter mixtures for individual experiments is provided in subsequent chapters.

3.3 Analytical Methods

3.3.1 Gas Sampling

Sampling ports, fitted with 1/4" Swaglok fittings, were located at the inlet, outlet and between each stage of the biofilter columns. Gas samples could be withdrawn from the

middle of the plenum using a stainless steel probe or from the edge of the plenum.

3.3.2 Total Hydrocarbon Levels

A portable photoionization detector (HNU model DL-101) equipped with a 10.2 eV lamp was used to measure total hydrocarbon levels for mixed gas streams and toluene concentrations when present as a single gas stream contaminant. The total hydrocarbon (THC) detector was connected to a sampling port using 1/4" teflon® tubing, allowing direct on-line measurements. Readings were recorded after a stabilization period of 20 seconds.

The detector had a reported detection limit of 0.1 ppm benzene and accuracy of 1% of reading (HNU 1991).

Calibration

Multiple-point calibrations were performed, using toluene, according to the procedure described in the operator's manual (HNU 1991). Two methods were employed for the generation of toluene gas standards. In the first method a calibration gas standard of 1000 ppm toluene in an air balance (Scott Specialty Gases) was diluted with hydrocarbon-free air in 3 litre tedlar® bags. One and two litre volumes of gas standards were created using this method. This method was used during initial trials and only as a method for the generation of low concentration gas standards during later trials due to cost factors.

An alternative method of generating gas standards utilizing a purging system was employed. The required amount of pure toluene was injected into 10 mL of deionized water contained a needle purge sampler (Supelco). Hydrocarbon-free air was passed through the purge sampler into a 20 L tedlar® bag. A purging time of approximately 25 minutes was used resulting in calibration volumes of 15 L. This method was used to generate gas standards of 50, 100 and 200 ppm. The previously described method was used to generate gas standards of 1 and 10 ppm with the modification that the dilution air was also passed through the sparger containing only deionized water.

QA/QC

On several occasions during the experiments readings provided by the portable THC detector were compared with readings obtained from gas chromatographic analysis for toluene concentrations.

3.3.3 BTX Measurement

A gas chromatograph (GC), HNU model 311, with a photoionization detector (PID) and a 200 µL injection loop was used for the determination of benzene, toluene and *o*-xylene levels in the gas stream. Teflon® tubing (1/8 ") was used to connect a sampling port to the sample loop inlet on the GC. Table 3.2 provides the GC-PID parameters used in the analysis.

The chromatogram peaks were analyzed using software supplied with the GC. The baseline projection option was chosen for area response analysis of the resultant peaks.

Table 3.2. GC-PID settings

Parameter	Setting
Column Type	Supelco, VOCOL 1 μm phase length: 10 m dia: 0.32 mm id
Column Flow	carrier gas: UHP Helium flow: 3 mL/min
Column Temperature	65 ^{0}C
Injector Temperature	100 ^{0}C
Detector Temperature	100 ^{0}C

Calibration

Gas standards were generated using 3 L tedlar® bags. Pure BTX compounds were diluted in 20 mL vials with HPLC grade methanol. Ten microlitres of the mixture was injected into a tedlar® bag containing 2 L of ultra-pure nitrogen. The bags were warmed to 40 ^{0}C for 30 minutes. Gas standards were not stored and were produced immediately prior to use with the GC.

QA/QC

Three replicate bags of a gas standard were prepared. Four samples were withdrawn from each bag and subsequently analyzed using the GC.

Predicted contaminant concentrations at the biofilter inlet were calculated based on the liquid loading rate of the syringe pump and the measured airflow rate. Contaminant concentrations measured with the GC were compared against the predicted values.

3.3.4 CO_2 Analysis

CO_2 Detector

In the early experiments a portable infra-red detector (Nova Systems) was used to measure CO_2 levels in the biofilter gas stream. The detector had an operating range of 0 to 2% CO_2, a precision to 100 ppm and an accuracy of +/- 100 ppm. The detector was calibrated using a calibration gas of 800 ppm and a zero concentration standard. The detector was connected on-line when required to the desired sampling port.

GC-TCD Analysis

In order to obtain more precise measurements of CO_2 levels a GOW MAC series 550 GC equipped with a thermal conductivity detector (TCD) was used. Grab samples were collected using 10 mL polyethylene syringes fitted with stop-cock valves. A ten mL sample was manually injected into the GC; Table 3.3 presents the GC settings that were used.

Calibration Procedure

Calibration standards were prepared using 3.0 L tedlar® bags filled with 1.5 L of nitrogen. An appropriate amount of a CO_2 gas standard (82,700 ppm, Matheson) was injected into each bag through the septum.

QA/QC Procedure

Four replicate bags were created for each standard; one sample was injected from each bag and the resultant area response was plotted as a function of concentration.

Table 3.3. GC-TCD Settings

Parameter	Setting
Column Type	6', 0.25" SS Chromosorb 60/80 packed column length: 6' (1.83 m) dia: 1/4" (6.4 mm)
Column Flow	carrier gas: Helium flow: 28 mL/min
Column Temperature	60 ^{0}C
Injector Temperature	50 ^{0}C
Detector Temperature	150 ^{0}C
Bridge Current	160 mA
Integrator	Waters 745 data module

3.4 Media Analysis

3.4.1 Toluene Sorption

Sampling

Biofilter media was manually sampled from the filter beds during filter operation using bed sampling ports (illustrated in Figure 3.2).

Extraction Method

One gram biofilter media samples were placed into a 40 mL glass vial containing 20 mL of HPLC grade methylene chloride. The vials were refrigerated at 4 ^{0}C for approximately 5 hours and then shaken with a wrist shaker for 15 minutes. A 1 mL sample of the liquid was then placed in a 2 mL sample vial for GC analysis.

GC-FID Analysis

The samples were analyzed using a GC with a flame ionization detector (FID) equipped with an autosampler and automatic injector (Hewlett-Packard 5890 series II). A sample volume of 1 μL was injected automatically for the analysis. The GC method and settings are listed in Table 3.4.

Liquid toluene standards were prepared by diluting pure toluene with methylene chloride in 2 mL autosampler vials.

Table 3.4. GC-FID Settings

Parameter	Setting
Column Type	J&W Scientific, DB5 phase 1 μm thick length: 30 m dia: 0.32 mm id
Column Flow	carrier gas: helium flow: 3.2 mL/min aux gas flow: 37 mL/min hydrogen flow: 32 mL/min air flow: 376 mL/min
Column Temperature	program: 31 ^{0}C for 4 min; ramp 10.0 ^{0}C/min to 150 ^{0}C
Injector Temperature	250 ^{0}C
Detector Temperature	250 ^{0}C

3.4.2 Media Properties

Bulk Density

Bulk density of the filter media was estimated on a wet basis. A one litre sample contained in a 2 L beaker was weighed using an analytical balance. Moisture content of

a sub-sample was determined. In addition, the contents of some biofilter stages were weighed at the completion of the experiment.

Moisture Content

The moisture content of biofilter media was determined by drying a known mass of sample in an oven at a temperature of 103 ^{0}C for 24 hours.

Particle Size Distribution

The particle size distribution of the media was determined on a wet weight basis. Approximately 1 kg of media was introduced into a soil screener (BM&M) and shaken for approximately 15 minutes. The recovered fractions, four in total, were then weighed. The soil shaker was equipped with three screens with opening sizes of:

- 6.4 mm,
- 3.18 mm, and
- 1.7 mm.

3.4.3 Nutrients

The analysis of nutrient levels and pH levels in filter media was performed by Analytical Services, Land Resource Science, Ontario Agricultural College, University of Guelph.

pH

The determination of pH was performed on a saturated paste of composted material.

Total Nitrogen, Phosphorous, and Potassium

Total nitrogen, phosphorus and potassium levels were determined on a sub-sample (0.25 to 0.5 g) of oven-dried ground compost using sulphuric acid digestion. Concentrations of nitrogen and phosphorus were measured using a Technicon Auto Analyzer. Potassium levels were determined using an atomic absorption spectrophotometer.

Ammonium (NH_4-N) and Nitrate (NO_3-N) Nitrogen

A sub-sample (5.00 g) of composted material was placed into a 2 M solution of KCl and shaken for 30 minutes. The solutions were then filtered through Whatman filter paper (number 42). Ammonium and nitrate levels in the filtrate were determined using a Braun and Lubbe Traacs 800 autoanalyzer.

Total Organic Carbon (TOC)

The Leco SC-444 method of carbon determination was used to measure percent carbon. Percent organic carbon was determined by first ashing a known mass of dried compost at 475 ^{0}C followed by carbon measurement of the residue. Percent organic carbon is defined as the difference between total carbon and inorganic carbon.

3.5 Statistical Analysis

Non-linear regressions and analysis of variance were performed using the SAS statistical package. The Marquardt method was chosen for non-linear regression analysis.

3.6 Outline of Experiments

Biofilter experiments were organized into three main phases: i) media effects, ii) effects of airflow rate, and iii) biofiltration of mixtures. Toluene was used as a single gas stream contaminant in group i) and ii) experiments; mixtures of benzene, toluene and *o*-xylene were used as contaminant sources during biofiltration of VOC mixtures.

Additional detail regarding filter material characteristics and experimental conditions are provided in chapters 4 to 8.

3.6.1 Media Effects

Table 3.5 lists the experiments conducted to assess the impact of media on the removal of toluene and the date each experiment was conducted. Experiments 1B to 1F utilized two or three filters which were operated in parallel. Experiments number 1A and 1G were conducted using single biofilters. In all experiments the THC detector was used to measure toluene levels in the air stream. Carbon dioxide levels in experiment 1A were measured using the portable infra-red detector.

In experiments 1A to 1D, three-stage biofilters were employed during each experiment. Single-stage biofilters, consisting of the first section of the filter (volume of 5.43 L), were used in experiments number 1E, 1F and 1G.

Table 3.5. Experimental Outline: Media Effects

Experiment Number	Media	Supplement	Date Conducted
1A	CMSW+p	-	Aug 17 - Sept 1, 1993
1B	CL&Y+p CL&Y+CB CB+p	- - -	Oct 15 - Oct 28, 1993
1C	CMSW+p CL&Y+p CB+p	- MLVSS MLVSS	Oct 31 - Nov 17, 1993
1D	CMSW+p CF&Y+p	- -	Dec 9 - Dec 20, 1993
1E	CL&Y+p CL&Y+p CSS+p	CMSW slurry fertilizer -	Jan 23 - Feb 3, 1994
1F	CL&Y+p CL&Y+p	fertilizer -	May 25 - May 31, 1994
1G	CMSW+p	-	Sept 24, 1994

3.6.2 Effects of Airflow Rate

The impact of airflow rate on the removal of toluene was assessed in three filters containing the same media that were operated in parallel, each with a different flow rate. The THC detector, GC-PID and GC-TCD were used to quantify toluene removal during air sample analysis. Table 3.6 summarizes experiment type and date.

Table 3.6. Experimental Outline: Effects of Airflow

Experiment Number	Media	Approximate Superficial Velocity (m/h)	Date Conducted
3	CMSW+CSS+p	30 60 90	Aug 31 - Sept 9, 1993

3.6.3 Biofiltration of VOC Mixtures

Table 3.7 summarizes experiments involved with the biofiltration of mixtures of benzene, toluene, and *o*-xylene.

Table 3.7. Experimental Outline: Biofiltration of BTX Mixtures

Experiment Number	Media	Contaminant	Comments	Date Conducted
2A	CMSW+CSS+p	T B+T B+T+X	same mass load	Apr 30 - May 20, 1994
2B	CMSW+CSS+p	X T+X	same xylene mass load	Jul 26 - Jul 31, 1994

4.0 PRELIMINARY TESTING

4.1 Objective

Preliminary studies were conducted to test the experimental system and provide background information that was used in the planning of future experiments. Toluene profiles in the biofilter bed and CO_2 formation were evaluated to assess toluene biodegradation kinetics.

4.2 Experimental Conditions

A single, three-stage biofilter packed with a mixture of CMSW and perlite was used in the experiment; the packing material characteristics are summarized in Table 4.1.

Table 4.1. Filter Material: Exp. 1A

Filter Media	Filter Volume	Initial MC (% wt)[1]	pH
CMSW + p (60:40 by volume)	16.3 L	48.0	7.76

[1]Wet basis
where: p = perlite
MC = moisture content

The details of filter operation are presented in Table 4.2. The filter was operated at a constant inlet load until day 8. On day 8 the inlet concentration was increased by approximately 40%, and was then held constant for the remainder of the experiment.

The portable THC detector was used to measure toluene levels in the gas stream and the infra-red detector was used to measure CO_2 levels.

Table 4.2. Experimental Conditions: Exp 1A

Parameter	Setting	
	Day 1 - 8	Day 8 - 12
Inlet Concentration (ppm)		
average	69	108
sd	14.1	10.7
Flow Rate (L/min)		
average	8.27	8.20
sd	0.8	0.2
EBRT (min)	1.97	1.99
Superficial Velocity (m/h)	27.4	27.1
Loading Rate ($g/m^3/h$)		
average	8.04	12.2
predicted	9.29	12.4
difference (%)	-14	-1.6
Average Inlet Gas Temperature (^0C)	22.8	22.8

where: sd = standard deviation
EBRT = empty bed retention time

The filter was shut down for approximately four hours on day 6 due to water accumulation in the supply line and rotameter. Inlet concentrations fluctuated slightly but the measured inlet concentrations were generally within 15% of predicted values. The predicted loading rate was calculated based on the syringe pump liquid delivery rate.

4.3 Filter Performance

4.3.1 Acclimation

Figure 4.1 illustrates toluene removal at three sampling ports as a function of time. The filter exhibited rapid acclimation, achieving 98% removal in approximately 2 days. An acclimation period of 4 days was reported by Martin (1994) for toluene degradation in a compost biofilter. Longer acclimation periods have been reported (Ergas *et al.*, 1993; Ottengraf and van den Oever, 1987) indicating that acclimation periods can differ depending on the source of biofilter media.

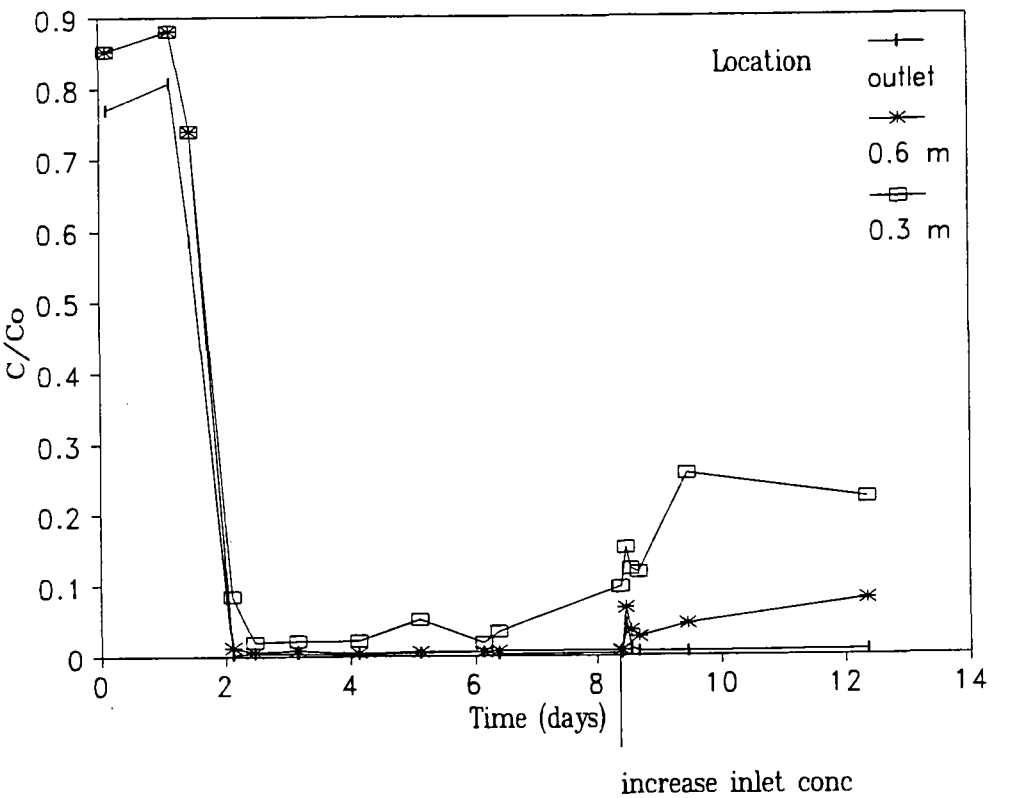

Figure 4.1. Biofilter Acclimation

It is apparent from Figure 4.1 that once the filter was acclimated most of the contaminant was removed in the first stage. Removal efficiency in the first stage decreased to approximately 80% after the inlet concentration was increased but the toluene mass removal rate in the first section increased from 22 $g/m^3/h$ to 34 $g/m^3/h$. The increase in

inlet concentration had little effect on the overall removal efficiency for the filter which indicated that the maximum removal capacity for the filter was not exceeded at the higher loading rate.

The temperature of the first stage was consistently 2 ^{0}C warmer than the inlet gas temperature at the higher loading rate. Bed temperatures in the second and third stage were close to that of the inlet gas stream. The temperature profile suggested that microbial activity occurred in the bed.

4.3.2 Model Fitting

Figure 4.2 illustrates biofilter profiles for four inlet concentrations recorded at the same gas flow rate, and a best fit non-linear regression. The form of the model used in the regression was:

$$C/Co = \exp(-A*h)$$

where h is height in the biofilter and A is a constant with units of m^{-1}.

The regression yielded a value of 5.76 m^{-1} for A with a 95% confidence interval of 5.06 to 6.45 m^{-1}.

From the solution of the first order model, equation 5 in chapter 2.6, a value for K_1 can be calculated. Using:

- flow = 8.11 L/min; corresponding to U = 0.447 m/min and
- H_c = 0.240 m^3-liq/m^3-gas,

results in K_l/H_c = 2.6 min^{-1} and K_l = 0.62 min^{-1}.

Martin (1994) calculated a range of first-order reaction coefficients for toluene degradation using a similar equation and found values ranging from 4.0 to 1.0 min^{-1} at inlet concentrations of 60 to 120 ppm. The first order reaction coefficient calculated in the Martin (1994) study is equivalent to K_l divided by H_c, which in this case was found to be 2.6 min^{-1}.

Ergas *et al.* (1993) observed a first-order degradation pattern for toluene at an inlet concentration of 50 ppm. However, kinetic parameters for toluene degradation were not provided in the study.

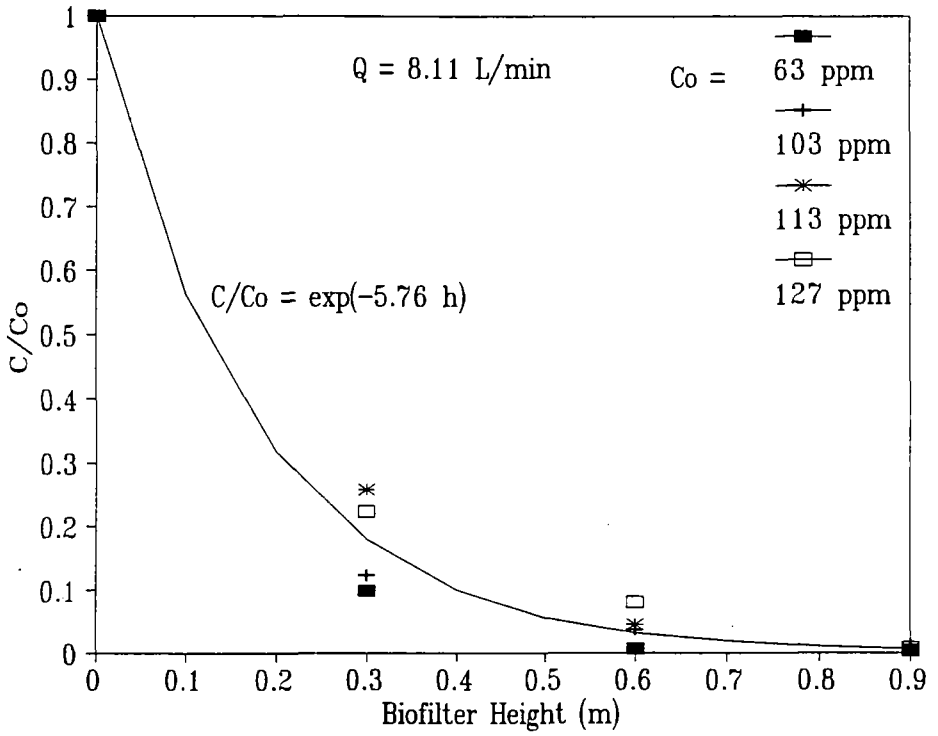

Figure 4.2. Toluene Removal Profiles

4.3.3 CO_2 Balance

The complete mineralization of toluene, assuming no net gain in cell mass, can be represented by the following equation:

$$C_7H_8 + 9 \cdot O_2 \rightarrow 7 \cdot CO_2 + 4 \cdot H_2O$$

Therefore, 3.34 grams of CO_2 are produced for every gram of toluene degraded.

Figures 4.3 and 4.4 present profiles of CO_2 production, both predicted and measured, and toluene degradation as a function of height in the filter bed. Initial filter effluent CO_2 concentrations of 500 to 600 ppm were recorded prior to toluene introduction. A basal CO_2 production rate of 16.4 g/m^3-bed/h was estimated assuming uniform CO_2 production

in the bed. Predicted CO_2 profiles at steady state were produced using the following mass balance:

$$Q \cdot C_{CO2\text{-}IN} - Q \cdot C_{CO2\text{-}OUT} + [\text{generation: basal + toluene degradation}] = 0$$

The predicted CO_2 profiles are within 20% of the measured CO_2 levels which is considered reasonable given the accuracy of the CO_2 analyzer. The profiles confirm that biodegradation was responsible for toluene removal in the bed.

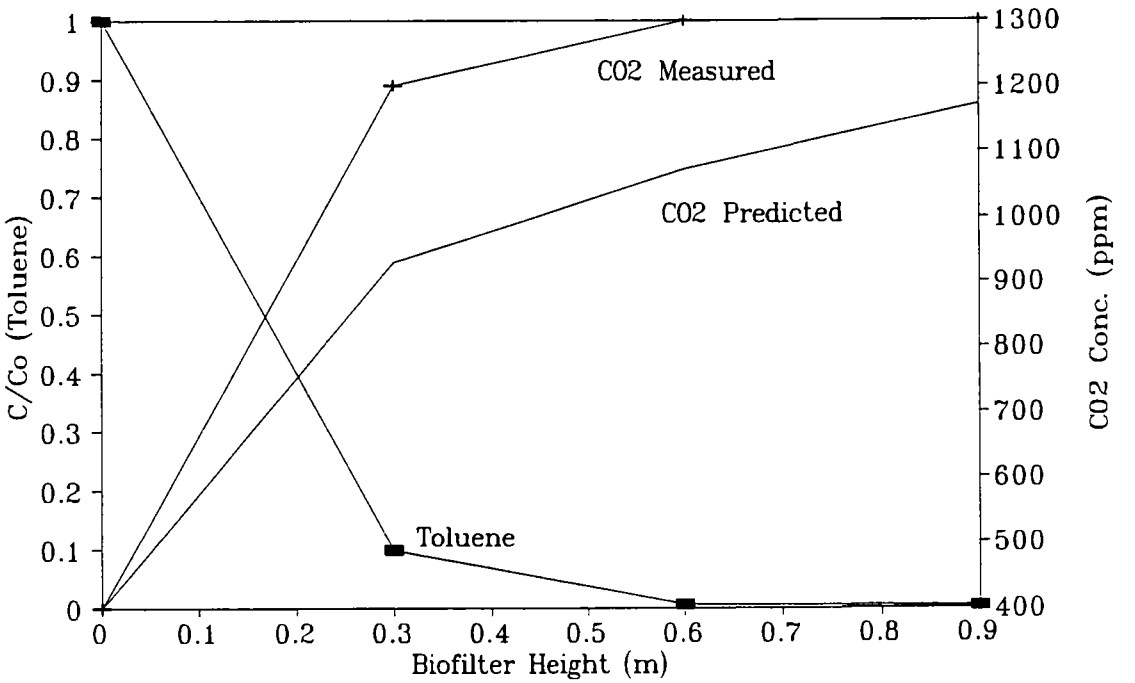

Figure 4.3. Toluene Removal and CO_2 Profile (C_o = 63 ppm)

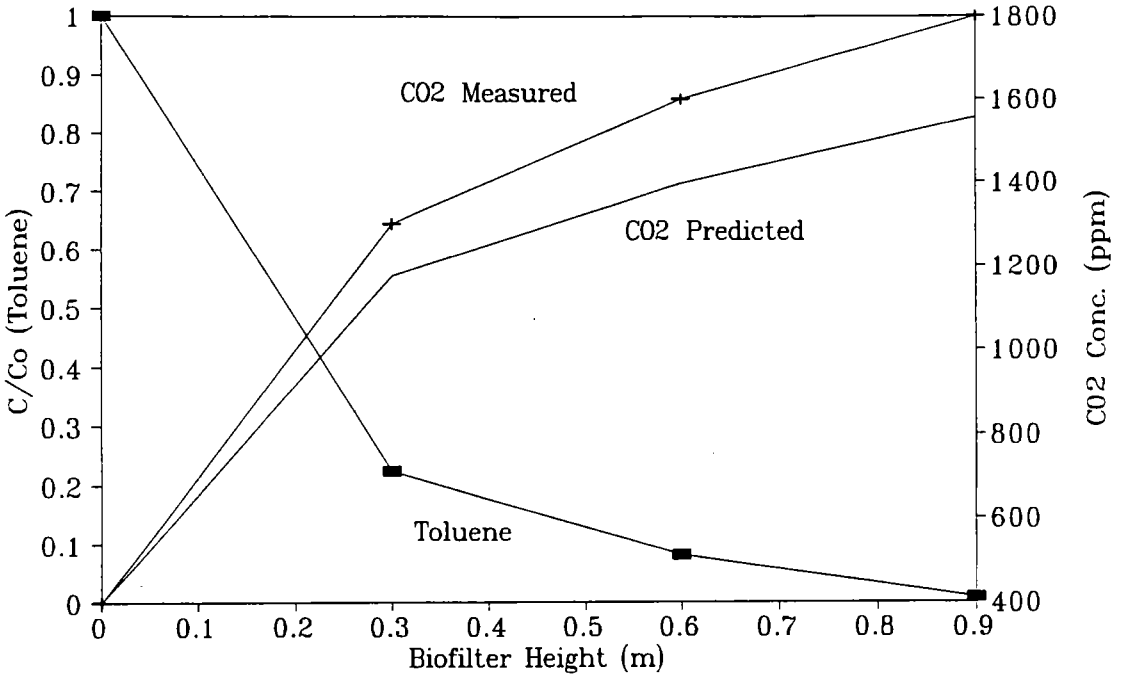

Figure 4.4. Toluene Removal and CO_2 Profile (C_o = 127 ppm)

5.0 COMPARISON OF PACKING MATERIAL

5.1 Objectives

The objectives of this series of experiments were to identify characteristics of effective biofilter media. The effects of inoculum addition and nutrient supplementation on biofilter performance were evaluated.

5.2 Experiment 1B: CL&Y and CB

5.2.1 Experimental Conditions

Three, three-stage biofilters were packed with different types of compost and operated in parallel. The packing material characteristics are summarized in Table 5.1.

Table 5.1. Filter Material: Exp. 1B

Filter Number	Filter Media	Initial MC (% wt)	pH
1	CL&Y + p (60:40 by volume)	58.0	7.32
2	CL&Y + CB (60:40 by volume)	58.3	7.49
3	CB + p (60:40 by volume)	53.6	7.76

Each filter was operated at a constant inlet toluene load for 12 days. The details of filter operation are presented in Table 5.2.

Table 5.2. Experimental Conditions: Exp 1B

Parameter	Measured Reading		
	Filter 1	Filter 2	Filter 3
Inlet Concentration (ppm)			
average	50	83	86.5
sd	11.3	18.4	14.7
Flow Rate (L/min)			
average	8.69	8.79	8.55
sd	0.90	0.79	0.86
EBRT (min)	1.88	1.85	1.91
Superficial Velocity (m/h)	28.7	29.2	28.3
Average Inlet Gas Temperature (^{0}C)	22.8	22.8	22.8

A head loss of approximately 1 mm water column was recorded for each filter. Inlet gas humidity was consistently greater than 96% relative humidity.

5.2.3 Filter Performance

Operational Problems. On day 4 the filters were shut down for approximately three hours due to moisture accumulation in the flow meter for filter number 3. Problems maintaining constant inlet concentrations and flow rates were encountered. Also, the goal of obtaining a similar inlet concentration for each filter was not achieved which led to system modifications for future experiments as discussed in Chapter 3.

Removal Efficiencies. Figure 5.1 illustrates the response to toluene in the three filters during the experimental period. Variability in the data, which may have been due to fluctuations in inlet loading, made comparisons between media difficult, but none of the filters displayed a removal efficiency greater than 40% during the trial period.

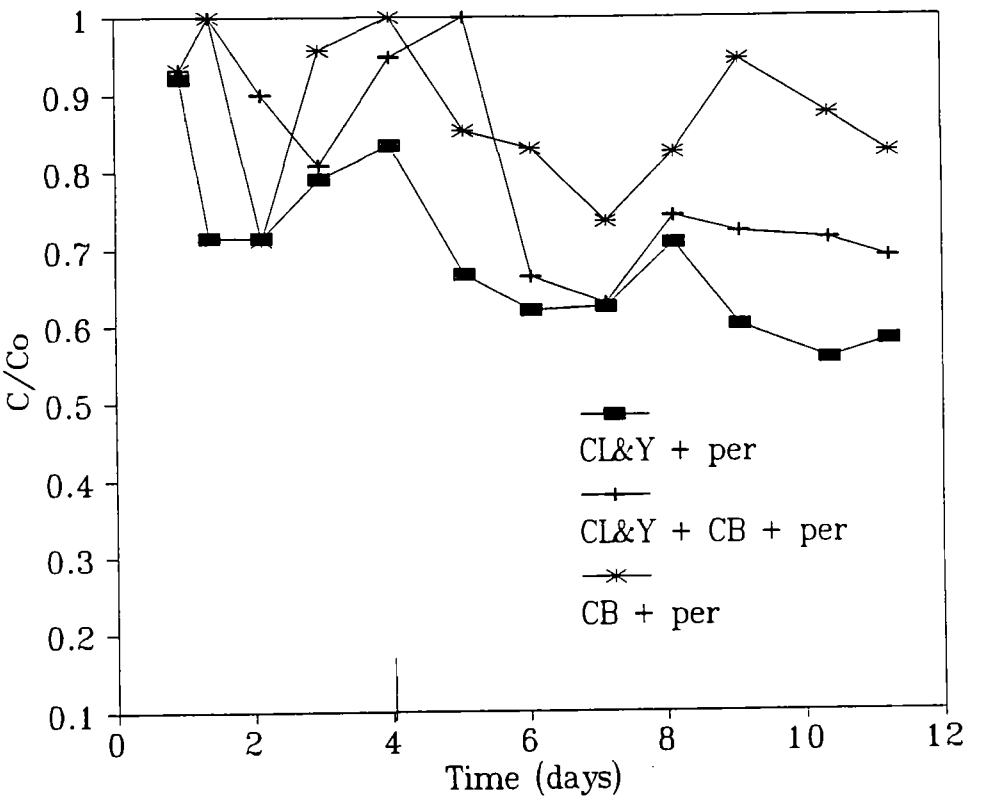

Figure 5.1. Toluene Removal for CL&Y and CB Filters

Moisture content of the filters was measured at the end of the experimental period (Table 5.3). Since the measured values were within the accepted operating range, it was assumed that drying was not the cause of poor performance. Nutrient availability or a lack of toluene-degrading microorganisms may have been factors which contributed to low toluene removal efficiencies. Further experiments were conducted to identify factors responsible for poor filter performance.

Table 5.3. EXP 1B: Final Moisture Content

Filter	MC (% wt)
1. CL&Y + p	55.6
2. CL&Y + CB	58.9
3. CB + p	53.3

5.3 Experiment 1C: CMSW, CL&Y and CB (+MLVSS)

5.3.1 Experimental Conditions

System Modifications. A header, as described in chapter 3, was added to the biofiltration system in order to distribute the flow evenly to each biofilter.

Three, three-stage biofilters were packed with different compost mixtures and operated in parallel. An inoculum consisting of 250 mL of mixed liquor volatile suspended solids (MLVSS), diluted in one litre of water, was added to filters 2 and 3. The packing material characteristics are summarized in Table 5.4.

Table 5.4. Filter Material (Exp. 1C)

Filter Number	Filter Media	Inoculum	Initial MC (% wt)	pH
1	CMSW + p (60:40)	none	54	7.32
2	CL&Y + p (60:40)	250 ml MLVSS	60	7.59
3	CB + p (60:40)	250 ml MLVSS	63	7.09

The filters were operated at a constant inlet toluene load for 11 days. On day 11 the inlet load to all three filters was doubled and then kept constant for the remainder of the experiments. The details of filter operation are presented in Tables 5.5 and 5.6. Nominal loading rate is defined as average inlet concentration multiplied by average flow rate.

Table 5.5. Experimental Conditions: Exp 1C

Parameter	Measured Reading					
	Filter 1		Filter 2		Filter 3	
Day	1-11	11-15	1-11	11-15	1-11	11-15
Inlet Conc. (ppm)						
average	35.1	56.9	33.8	50.9	33.5	50.0
sd	4.5	2.7	4.4	3.9	4.8	4.8
Flow Rate (L/min)						
average	8.52	8.45	8.71	8.33	8.59	8.97
sd	0.44	0.18	0.60	0.51	0.40	0.46
EBRT (min)	1.91	1.93	1.87	1.96	1.90	1.82
Superficial Velocity (m/h)	28.3	28.0	28.9	27.6	28.4	29.7
Nominal Loading Rate ($g/m^3/h$)	4.22	6.78	4.15	5.98	4.06	6.33
Average Inlet Gas Temperature ^0C	20.8 (all filters)					

Table 5.6. Inlet Mass Balance: Exp 1C

	Average Inlet Load; Three Filters Combined		
	Measured (g/h)	Predicted (g/h)	Difference (%)
Day 1 - 11	0.20	0.21	-3
Day 11 - 15	0.31	0.38	-19

5.3.2 Filter Performance

Mass balances performed at the inlet of the biofilters (Table 5.6) confirmed that sampling and analytical procedures provided a reasonable degree of accuracy for quantification of contaminant levels.

Figure 5.2 presents the response of the three filters with time after biofilter start-up. Filter 1, containing CMSW, displayed rapid acclimation reaching 99% removal in 4 days. This acclimation period was similar to the one observed during experiment 1A. Despite the use of an inoculum the other two filters exhibited poor removals throughout the experimental period. The marked differences in toluene removal observed in this experiment led to further experimental trials which were designed to evaluate the issue of nutrient availability on filter performance.

The increase in inlet load resulted in a slight initial decrease in removal efficiency for filter 1. However, within 5 hours the removal efficiency increased to over 90%.

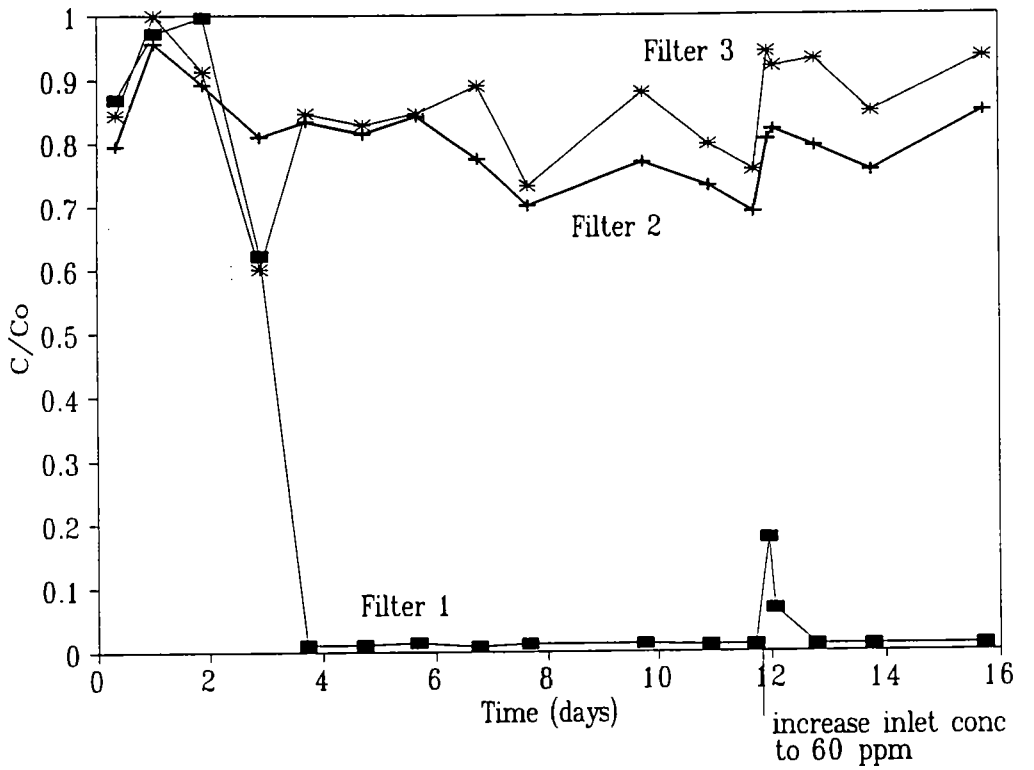

Figure 5.2. Comparison of CMSW and Inoculated CL&Y and CB Filters

5.4 Experiment 1D: CMSW and CF&Y

5.4.1 Experimental Conditions

Two, three-stage biofilters were packed with different compost material and were operated for 9 days. Filter 1 was packed with a CMSW and perlite mixture which had been used previously in experiment 1C. Filter 2 was packed with a mixture of CF&Y and perlite; filter material characteristics are summarized in Table 5.7. Inlet concentrations and flow rates are presented in Table 5.8.

Table 5.7. Filter Material: Exp. 1D

Filter Number	Filter Media	Initial MC (% wt)	pH
1	CMSW + p; remixed from Exp 1C	-	-
2	CF&Y + p (60:40)	50.2	7.4

Table 5.8. Experimental Conditions: Exp 1D

Parameter	Measured Reading	
	Filter 1	Filter 2
Inlet Concentration (ppm)		
average	79.0	73.5
sd	12.6	12.5
Flow Rate (L/min)		
average	9.71	9.27
sd	0.43	0.87
EBRT (min)	1.68	1.76
Superficial Velocity (m/h)	32.1	30.7
Average Loading Rate ($g/m^3/h$)	10.8	9.6
Inlet Mass Balance		
average loading (g/h)	0.333 (total)	
predicted loading (g/h)	0.296	
difference (%)	+6.9	

5.4.2 Filter Performance

The filter containing the CF&Y mixture exhibited no greater than 30% toluene removal efficiency during 9 days of filter operation. By comparison, the CMSW filter toluene removal efficiency was found to be consistently higher than 98%. Composted food and yard waste was tested for use as a filter material because CF&Y was assumed to be similar in composition to CMSW.

5.5 Experiments 1E and 1F: Nutrient Addition

5.5.1 Experimental Conditions

In these two experiments, single-stage reactors (filter volume of 5.43 L), consisting of the bottom section of each filter, were used to assess the impact of nutrient addition on biofilter performance. The filters were packed with a separate material and operated in parallel. In experiment 1E an inoculum consisting of a slurry of pre-acclimated CMSW filter material from experiment 1C, mixed into 1 L of deionized water was added to filter 1.

Nutrient Addition. Fertilizer was added as a nutrient source to filter 2 in experiment 1E and filter 1 in experiment 1F. Approximately 8 g of fertilizer was added to 4 L of compost.

System Modifications. In experiment 1E, toluene was introduced into the branch lines supplying each biofilter, as described in chapter 2.

Tables 5.7 and 5.8 summarize filter media characteristics for the two experiments.

Table 5.9. Filter Material: Exp. 1E

Filter Number	Filter Media	Inoculum	Nutrient Addition	Initial MC (% wt)	pH
1	CL&Y + p (50:50)	43 g acclimated CMSW	NONE	54	7.48
2	CL&Y + p (50:50)	NONE	7.7 g fertilizer	59	7.86
3	CSS + p (50:50)	NONE	NONE	60	7.00

Table 5.10. Filter Material: Exp. 1F

Filter Number	Filter Media	Nutrient Addition	Initial MC (% wt)	pH
1	CL&Y + p (50:50)	7.7 g fertilizer	64	6.7
2	CL&Y + p (50:50)	NONE	65	7.7

The filters were operated at a constant loading rate for the experimental period. Filter operating conditions are summarized in Tables 5.11 and 5.12.

Table 5.11. Experimental Conditions: Exp 1E

Parameter	Measured Reading		
	Filter 1	Filter 2	Filter 3
Inlet Concentration (ppm)			
average	75.5	71.1	66.2
sd	37.0	38.0	32.8
Flow Rate (L/min)			
average	7.44	8.50	8.31
sd	0.86	0.70	0.90
EBRT (min)	0.73	0.64	0.65
Superficial Velocity (m/h)	24.7	28.1	27.7
Nominal Loading Rate ($g/m^3/h$)	23.8	25.6	23.3

Table 5.12. Experimental Conditions: Exp 1F

Parameter	Measured Reading	
	Filter 1	Filter 2
Inlet Concentration (ppm)		
average	52.7	51.2
sd	11.9	14.1
Flow Rate (L/min)		
average	8.52	8.58
sd	0.39	0.39
EBRT (min)	0.64	0.63
Superficial Velocity (m/h)	28.1	28.6
Loading Rate ($g/m^3/h$)		
average	19.7	19.1
predicted	19.1	19.1
difference (%)	+2.6	0

5.5.2 Filter Response

Operational Problems. Moisture build up in the supply lines and rotameters resulted in interruption of biofilter operation on day 2 for 30 min and again on day 4 for 1 hour

during experiment 1E. Mechanical problems with the air-line regulator resulted in fluctuating inlet flow rates during days 4 to 6.

Filter performance for experiments 1E and 1F are illustrated in Figures 5.4 and 5.5 respectively. A substantial change in biofilter performance was observed with nutrient addition to the CL&Y filters. Nutrient supplemented CL&Y filters and the CSS filter demonstrated rapid acclimation and mass removal rates of between 18 to 20 $g/m^3/h$. The CL&Y filter which received an inoculum consisting of CMSW did not show significant removal. The performance of filters 2 and 3 in experiment 1E appeared to deteriorate after 4 days of operation. The reduction in filter activity may have been due to flow channelling, since the moisture content of the filters did not change over the course of the experiments.

The results of these two experiments suggested that nutrient availability was responsible for poor biofilter performance in filters consisting on CL&Y. Furthermore, the results of experiments 1B to 1F indicated that nutrient availability was the main factor responsible for differences in filter performance between various compost-based media.

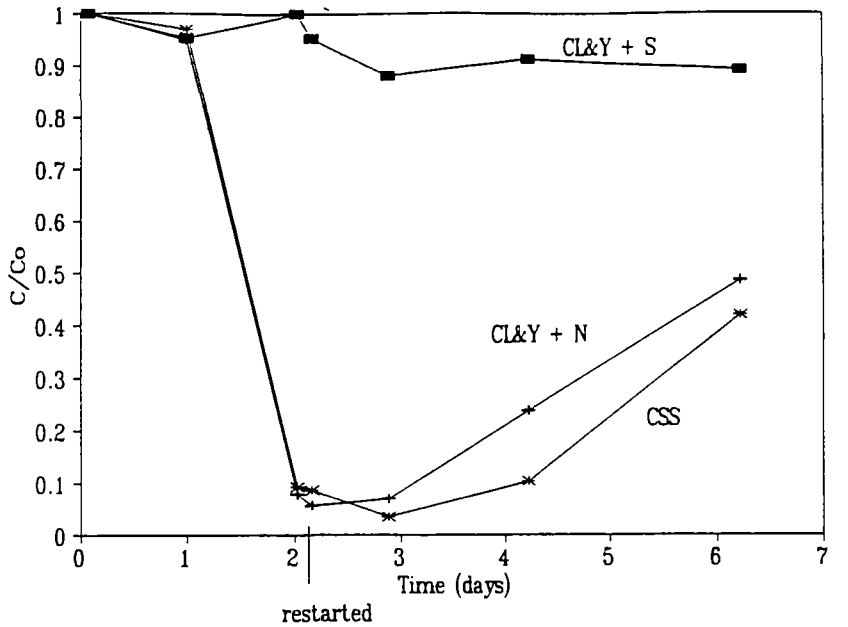

Figure 5.3. Response of CSS and Amended L&Y Filters: Experiment 1E

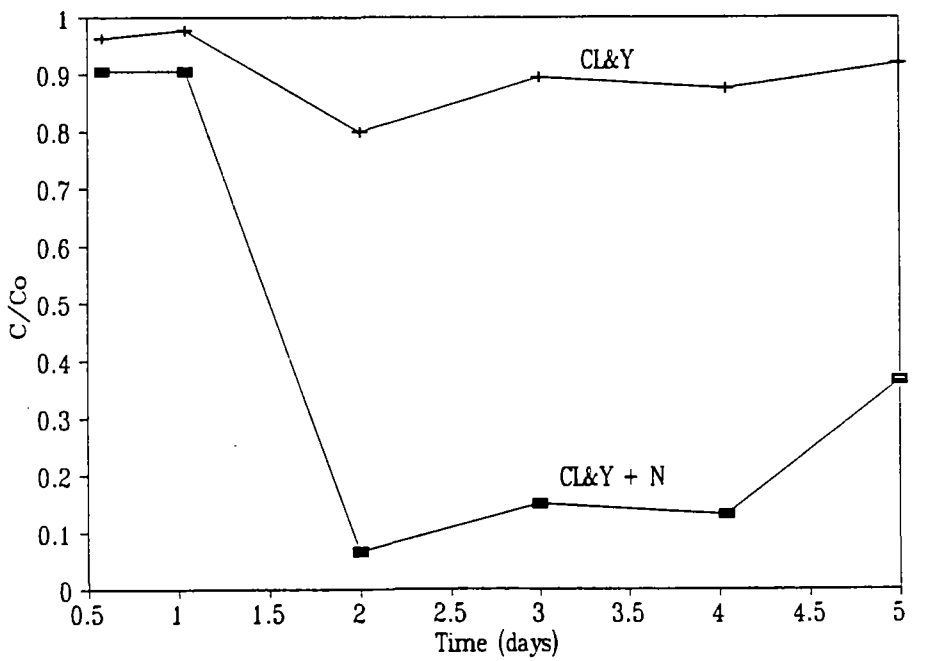

Figure 5.4. Effect of Nutrient Addition: Exp 1F

5.6 Media Characteristics

The following section presents and discusses results of analysis of physical and chemical properties of filter media. Differences in media properties, in particular nutrient levels, as related to toluene removal will be discussed.

5.6.1 Physical Properties

Particle size distributions and apparent densities for each type of media are summarized in Table 5.11.

The CB+p and CMSW+p filters have a greater proportion of particles in the lower size ranges, otherwise the filter material appear similar.

Table 5.13. Physical Characteristics of Media

			Particle Size Distribution (weight %)			
			Screen Size (mm)			
Filter Material (60:40)	Density (g/L)	MC[1] (% wt)	>6.4	6.4-3.2	3.2-1.7	<1.7
CL&Y+p	652	61.9	41.5	50.0	7.8	0.4
CB+p	592	55.7	35.0	49.8	13.0	2.3
CL&Y+CB	766	58.5	45.2	46.6	7.6	0.6
CF&Y+p	697	52.2	66.0	31.7	2.2	0.1
CMSW+p	709	54.5	30.4	53.1	13.4	3.1

[1]Wet basis, determined at time of analysis.

5.6.2 Nutrient Analysis

Tables 5.14 and 5.15 report nutrient levels for a variety of filter materials used in these experiments. Total organic carbon (TOC), nitrogen, phosphorus and potassium are expressed on a dry weight basis.

Table 5.14. Nutrient Levels

Filter Material	EF	TOC (%)	N (%)	P (%)	K(%)	C:N:P Ratio	% Dry Matter[2]
CB+p+MLVSS (exp 1C)	-	27.4	0.61	0.07	0.34	45:1:0.1	38.2
CL&Y+p+MLVSS (exp 1C)	-	22.1	1.00	0.23	0.92	22:1:0.2	42.2
CF&Y+p (exp 1D)	-	9.7	1.12	0.29	1.95	8.9:1:0.3	49.8
CL&Y+p+i (exp 1E)	-	19.3	0.86	0.21	0.87	22:1:0.2	38.9
CL&Y+p (exp 1F)	-	16.0	0.93	0.21	0.88	17:1:0.2	40.1
CL&Y+p+n (exp 1F)	+	14.7	0.99	0.25	0.90	15:1:0.3	39.9
CL&Y+p+n (exp 1E)	+	21.7	0.88	0.22	0.96	25:1:0.3	47.2
CSS+p (exp 1E)	+	13.3	0.74	0.42	0.45	18:1:0.6	42.8
CMSW+p (exp 1C)	+	16.4	1.03	0.21	0.72	16:1:0.2	47.3
CMSW+p (exp 1C)[1]	NA	15.1	0.91	0.2	0.76	17:1:0.2	39.9

All nutrients expressed on a percent dry matter basis.
[1] Sample taken from stage 1 at the end of experiment 1C.
[2] Determined at time of analysis.
EF = effective.

Table 5.15. Nitrogen Levels

Filter Material	EF	N (mg/kg)[2]	NH_4-N (mg/kg)	NO_3-N (mg/kg)	Total NH_4-N + NO_3-N (mg)[3]
CB+p+MLVSS (exp 1C)	-	2330	18	6	24
CL&Y+p+MLVSS (exp 1C)	-	4220	8	9	17
CF&Y+p (exp 1D)	-	5578	12	4.5	17
CL&Y+p+i (exp 1E)	-	3345	8	17	25
CL&Y+p (exp 1F)	-	3729	42	33	75
CL&Y+p+n (exp 1F)	+	3950	624	42	666
CL&Y+p+n (exp 1E)	+	4153	262	15	277
CSS+p (exp 1E)	+	3167	101	415	516
CMSW+p (exp 1C)	+	4872	54	293	347
CMSW+p (exp 1C)[1]	NA	3631	18	50	68

All results expressed on a wet weight basis.
[1] Sample taken from stage 1 at the end of experiment 1C.
[2] Calculated using percent dry matter from Table 5.14.
[3] Total per kg of filter material.

5.6.3 Discussion

As mentioned in chapter 2, required C:N:P ratios have been suggested in biofiltration literature but based on the previous tables, C:N:P ratios do not appear to be a useful measure of filter media potential. Aside from composted bark and composted food and yard waste, which were observed to have the lowest and highest C:N ratios respectively,

there were no definite trends. However, there appears to have been significant differences in available nitrogen. Filter material with higher combined ammonium and nitrate levels exhibited significantly higher toluene removal. Additional forms of available nitrogen were probably present but combined ammonium and nitrate-nitrogen were used as a surrogate measure of nitrogen availability. Depending on the species present, both ammonium and nitrate can be used as nutrient sources by microorganisms (Ottengraf and Diks 1992). Experimental biotrickling filters, in which nitrate was used as a nitrogen source, demonstrated superior performance with respect to toluene removal compared with filters supplied with ammonia (Smith *et al.*, 1994). Ammonia, when used as the sole source of nitrogen was found to promote proliferation of nitrifying bacteria in the biotrickling filter beds.

The issue of nutrient availability or nutrient supplementation has not been addressed sufficiently in biofilter literature. Bohn (1993) suggested that natural packing materials contain sufficient inorganic nutrients. However, nutrient levels in composted material can vary widely depending on the source of raw materials and method of processing (Bugbee, 1994). Also, Bugbee (1994) observed that nitrogen leaching rates differed between composted materials. Leaching from biofilter beds due to moisture application may reduce nutrient levels over time.

Don and Feenstra (1984) found a twenty fold increase in toluene removal two days after the addition of inorganic nutrients to a compost filter. Neither the composition nor amount of nutrients that were added were reported.

It is interesting to note that available nitrogen appears to have decreased in the sample of CMSW taken at the end of experiment 1C. The overall level of nitrogen should remain the same in a filter over time unless leaching or denitrification occurs. At steady state, cell death will recycle nutrients back to the bed, however, nutrients incorporated into cell mass will not be available.

At steady-state, a cell mass balance can be described by:

$$0 = YQ(C_o - C) - k_d M V_R \tag{8}$$

which simplifies to

$$M = \frac{Y}{k_d}(EC) \tag{9}$$

Where:

C = contaminant concentration (mass/volume)
C_o = inlet contaminant concentration (mass/volume)
EC = elimination capacity (mass/volume/time)
k_d = endogenous decay coefficient (1/time)
M = biomass concentration (mass/volume)
V_R = reactor volume (volume)
Y = yield coefficient (mass biomass/mass substrate metabolized)

With appropriate kinetic parameters this equation can be used to predict steady-state biomass levels in the filter. Kinetic parameters from biodegradation literature are summarized in Table 5.16.

Table 5.16. Kinetic Parameters

Parameter	Value		Source
Y (g/g)	0.71	- toluene degradation - consortium - batch liquid	Oh *et al.*, 1993
	1.22 - 0.99	- pure cultures - toluene degradation - batch liquid	Chang *et al.*, 1993
	0.88 - 1.15	- toluene degradation - fixed film reactor	Arcangeli and Arvin, 1992
	0.715	- theoretical - toluene	Martin, 1994
k_d (1/day)	0.3 - 0.4	- estimated from published data for toluene degradation in biofilm reactor	Arcangeli and Arvin, 1992
	0.41	- degradation of *p*-xylene - pure strain - batch	Chang *et al.*, 1993

Consider a sample calculation based on toluene removal in the first stage of a biofilter. Using an average Y of 0.97 g/g, a k_d of 0.4 day^{-1}, an EC of 30 $g/m^3/h$, and V_R of 5.43 L results in total biomass of 9.5 g. Initial biomass levels are unknown, but, using an EC of 1 $g/m^3/h$, results in 0.3 g of biomass. Therefore, a biomass increase of 9.2 g is required to increase toluene mass removal from 1 to 30 $g/m^3/h$. Since biomass composition can be represented by $C_5H_7O_2N$ (Arcangeli and Arvin, 1992), 0.12 g of nitrogen are required for 1 g of biomass. An available nitrogen concentration of 0.2 g/L or 290 mg/kg (using a density of 700 g/L) is necessary to achieve the required increase in cell mass.

The above analysis, although simplified, yields reasonable numbers when compared with

values from Table 5.14. Additional research is needed in order to evaluate the efficacy of this approach. The availability of nutrients could affect biofilter response to dynamic load changes. During periods of rapid cell growth the amount of nutrients recycled to the bed by cell death will be minimal. Dynamic response studies may be an additional method of evaluating biofilter nutrient requirements.

6.0 TOLUENE SORPTION

6.1 Objective

The objective of these experiments were to evaluate the significance of toluene sorption in biofilters and to test for residual toluene contamination in used biofilter media.

6.2 Experimental Conditions

Two sorption trials were conducted; both trials utilized a single stage reactor packed with fresh CMSW mixed with perlite (60:40). The filters were subjected to a step input and monitored using the portable PID. In trial 1, two bed samples were obtained at heights of 10 and 20 cm and analyzed for toluene contamination. Table 6.1 summarizes the experimental conditions.

Table 6.1. Experimental Conditions: Exp. 1G

Trial Number	Filter Weight (g)	MC (% wt)	Average Inlet Conc. (ppm)	Flow Rate (L/min)	Inlet Air Temp (^{0}C)	Bed Temp (^{0}C)
1	3682	63.6	110	10.4	22.6	21.7
2	3767	62.8	138	11.0	21.4	22.0

The relative humidity of the inlet gas stream was maintained at greater than 97%.

6.3 Results and Discussion

Figures 6.1 and 6.2 illustrate normalized toluene concentration for the two trials. In trial 1, the inlet concentration increased from 94 to 124 ppm over the course of the

experiment. Inlet concentration, C_o, was estimated by taking the average concentration over the time period between measurements.

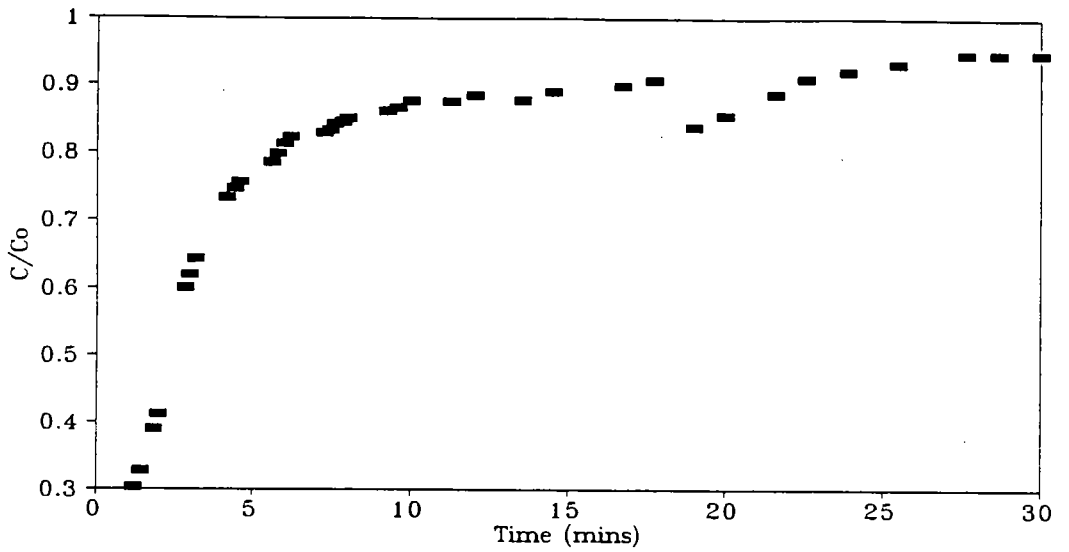

Figure 6.1. Toluene Sorption: Trial 1

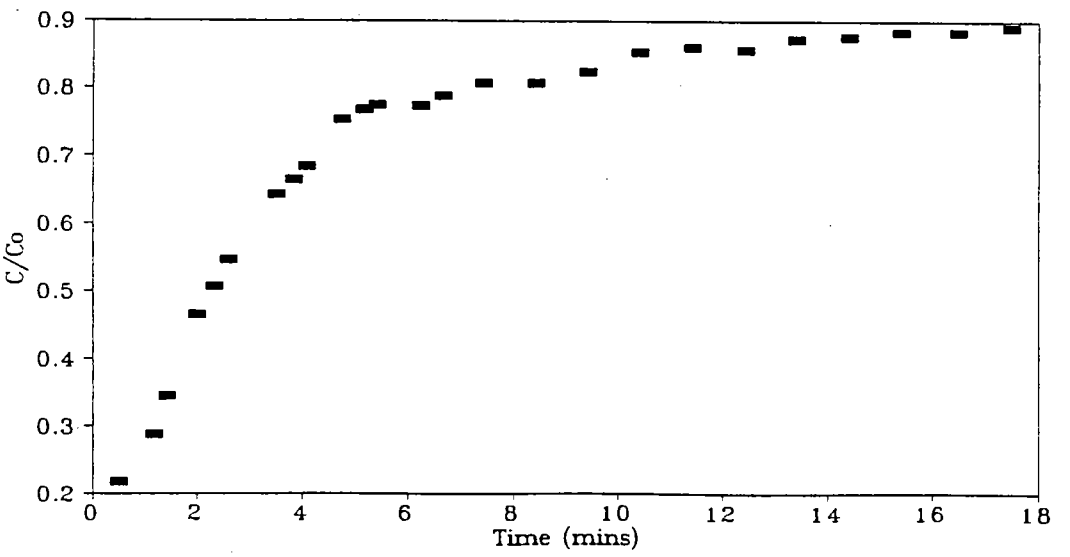

Figure 6.2. Toluene Sorption: Trial 2

Sorption capacity was estimated using a procedure outlined by Gong and Keener (1993) where:

$$q_t = \frac{C_O A Q(MW)}{24.2 * 10^6 W} \quad (10)$$

where:

q_t = adsorption capacity, (g toluene adsorbed/g of filter material)
C_o = toluene inlet concentration (ppm)
A = area integrated from the y axis to the breakthrough curve (min)
Q = gas flow rate in (L/min)
W = mass of filter material in bed (g)
MW = molecular weight of toluene (g/mole)

The results of experimental sorption capacity calculations are presented in Table 6.2.

Table 6.2. Sorption Capacity of CMSW + Perlite

Trial Number	Sorption Capacity (g/g)
Trial # 1	$5.9*10^{-6}$
Trial # 2	$4.3*10^{-6}$

Toluene was not detected in filter bed samples; the lowest toluene standard used was 8.7 mg/L (in methylene chloride). Based on the previous analysis a lower detection limit would be required in order to detect the amount of toluene sorbed in this experiment.

Complete breakthrough was not exhibited in the experimental trials. Instead, a prolonged tailing period was observed at approximately 90% breakthrough. It is possible that there was limited biodegradation, even though the material was not acclimated, thus preventing

attainment of 100% breakthrough. Alternatively, diffusion limitations due to the formation of aggregates in the bed may have hindered toluene uptake.

Based on these results, adsorption is not a significant removal mechanism for toluene in compost-based biofilters. The calculated adsorption capacities are approximately five orders of magnitude less than sorption by activated carbon in humid gas streams (Gong and Keener, 1993).

6.4 Residual Contamination

Filter material from the first stage of a biofilter (5.43 L) which had received a total toluene load of approximately 225 g was analyzed for toluene contamination. No toluene was detected in the samples. Martin (1994) tested used biofilter material for the presence of VOCs and detected no residual contamination.

Yavorsky (1993) obtained approval to dispose of used biofilter material in a municipal landfill. He suggested operating the filter with clean air for a day in order to metabolize residual contaminants.

7.0 EFFECTS OF AIRFLOW RATES

7.1 Objectives

The objective of this set of experiments was to examine the effects of airflow rate on toluene removal.

7.2 Experimental Conditions

7.2.1 System Modifications

Toluene was introduced into the branch lines supplying individual filters as described in chapter 3. A wick material was placed in the tee-junction at the point of contaminant introduction.

7.2.2 Filter Media

Three filters were packed with a mixture of CMSW, CSS and perlite and operated in parallel. The packing material had been used previously in experiments 2A and 2B. The filter material was remixed prior to loading the columns; media characteristics are summarized in Table 7.1. A layer of coarse composted wood particles, 2.5 cm thick, was placed at the bottom of each filter stage.

Table 7.1. Packing Material: Experiment 3

Composition	Nutrients	Initial MC (% weight)	pH
CMSW + CSS + p (25:25:50)	10 g fertilizer	58.9	7.14

7.2.3 Experimental Protocol

The three filters were initially operated at the same airflow rate and organic loading for three days. On day 3, the flow rates to filters 1 and 3 were changed to the desired setting and kept constant for the remainder of the experiment. The filters were operated at two different mass loadings during the course of the experiment. The progression of the experiment is presented in Table 7.2.

Table 7.2. Experimental Protocol

Experimental Day	Procedure
0	• pack columns • start air flow
1	• CO_2 measurement column 1 • start toluene loading- identical flow rates
3	• toluene measurement - GC-PID • CO_2 measurement column 1 • set flows columns 1 and 3 • head loss measurement
4	• toluene measurement - GC-PID • increase toluene load by 2X
6	• toluene measurement - GC-PID and portable THC detector • CO_2 measurement column 1 • decrease toluene loading by 2X
7	• channelling assessment - portable THC • moisture content

Carbon dioxide levels were measured using the GC-TCD as described in Chapter 3. Bed temperatures were recorded daily.

7.2.4 Flow Rates and Loading Rates

The loading and flow rates imposed during the experiment for the different experimental days are outlined in Table 7.3. On day 3 the average inlet concentrations for columns 1 and 2 were higher than predicted by syringe loading. In both cases the average concentration was affected by one of the measurements being substantially larger than the other two readings. If these measurements were rejected, or if the median number was used instead of the mean value, the inlet mass balance approached the predicted value. Technical problems with the GC resulted in the loss of data for filter 3 on experimental day 3. On day 4 some minor leaks were detected and repaired in the toluene loading system for columns 2 and 3.

Table 7.3. Loading Rates: Experiment 3

Day		Filter 1	Filter 2	Filter 3
3	Inlet Conc (g/m^3)[1]	1.56 (407 ppm)	1.42 (370 ppm)	-
	Flow Rate (L/min)	8.69	8.69	-
	EBRT (min)	1.88	1.88	-
	Superficial Velocity (m/h)	28.7	28.7	
	Loading Rate			
	average ($g/m^3/h$)	50.4	45.7	
	predicted ($g/m^3/h$)	38.3	38.3	
	difference (%)	+32	+19	
4	Inlet Conc (g/m_3)[1]	0.547 (143 ppm)	0.894 (233 ppm)	0.344 (90 ppm)
	Flow Rate (L/min)	17.24	8.95	25.80
	EBRT (min)	0.95	1.82	0.63
	Superficial Velocity (m/h)	57.1	29.7	85.5
	Loading Rate			
	average ($g/m^3/h$)	34.7	30.5	32.7
	predicted ($g/m^3/h$)	38.3	38.3	38.3
	difference (%)	-9.4	-20	-15
6	Inlet Conc (g/m_3)[1]	1.23 (321 ppm)	2.32 (605 ppm)	0.765 (200 ppm)
	Flow Rate (L/min)	17.10	8.69	26.09
	EBRT (min)	0.95	1.88	0.62
	Superficial Velocity (m/h)	56.8	28.7	87.1
	Loading Rate			
	average ($g/m^3/h$)	77.3	74.4	73.4
	predicted ($g/m^3/h$)	76.6	76.6	76.6
	difference (%)	+0.9	-2.9	-4.2

[1]Average of 3 measurements.

Head Loss Measurements

Head loss of 1.0 mm, 0.5 mm and 2.0 mm of water column were measured for filters 1, 2 and 3, respectively, on day 3 after airflow adjustment.

7.3 Biofilter Performance

7.3.1 Filter Profiles Prior to Flow Change

Figure 7.1 illustrates toluene removal profiles prior to the flow rate change. Filters 1 and 2 exhibited similar toluene removal efficiencies at each sampling port. The measured values divided by the average inlet concentration for each filter are presented. A best fit non-linear regression of the form

$$C/C_o = \exp(-A*ht)$$

is also displayed for the combined average values for filters 1 and 2.

The regression resulted in a value for *A* of 3.80 m^{-1} with a 95% confidence interval of 2.88 to 4.71 m^{-1}. Using equation 5 in chapter 2 and a superficial velocity of 28.7 m/h resulted in a value for K_l/H_c of 1.82 min^{-1} or a K_l of 0.44 min^{-1} (using an H_c of 0.24 (m^3-liquid/m^3-gas)).

The value for K_l was less than the coefficient calculated in experiment 1A (chapter 4). Also, the fit was poor for the first-order steady-state model. However, the inlet concentrations and loading rates were much higher than in previous experiments.

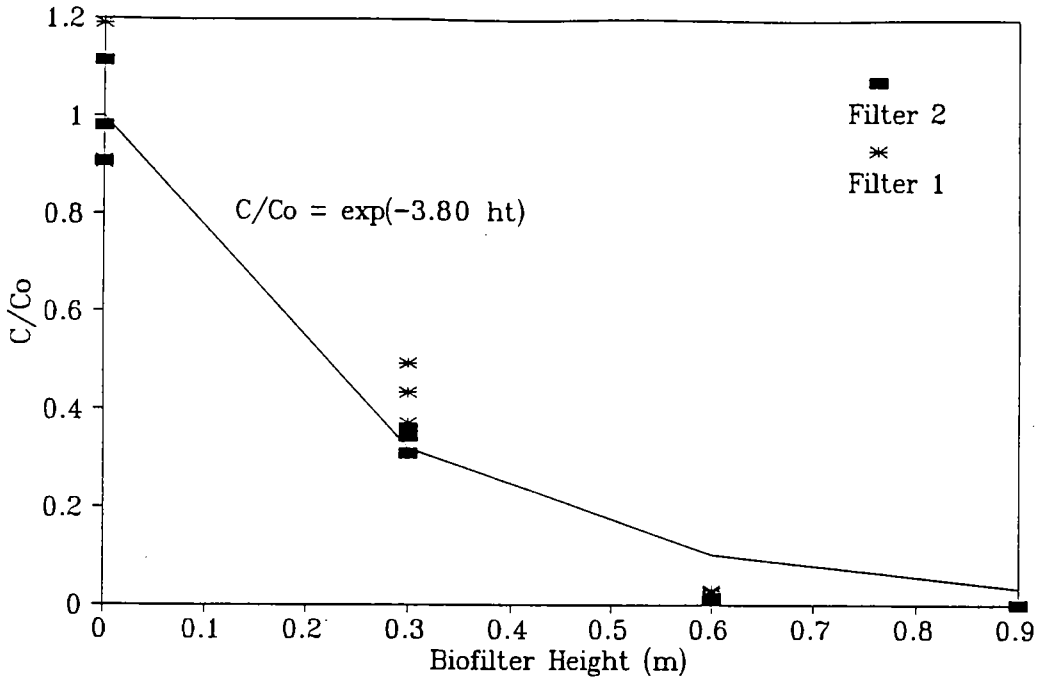

Figure 7.1. Biofilter Profiles: Day 3

The observed toluene profiles indicate that degradation rate may have been in a zero-order regime initially, changing to first-order after the first stage. Additional sampling ports would be required to fully evaluate the nature of degradation order. Arcangeli and Arvin (1992) observed zero-order kinetics for toluene liquid concentrations of 6 to 8 mg/L, and first-order kinetics below 0.14 mg/L in aerobic fixed film reactors. Equilibrium liquid concentrations at the inlet of the biofilters can be calculated using the Henry's law coefficient. For filters 1 and 2 the equilibrium inlet concentrations were 6.5 and 5.9 mg/L, respectively, indicating that degradation kinetics may have initially approached first-order.

7.3.2 Effects of Air Flow

Experimental Day 4

Figure 7.2 illustrates toluene removal profiles for the three filters one day after flow adjustment. Filters 1 and 3 exhibited removal profiles different from that of filter 2, however, overall removal efficiencies were similar. Removal profiles similar to filters 1 and 3 were encountered by Martin (1994) for toluene removal and Tahraoui *et al.* (1994) for BTX removal.

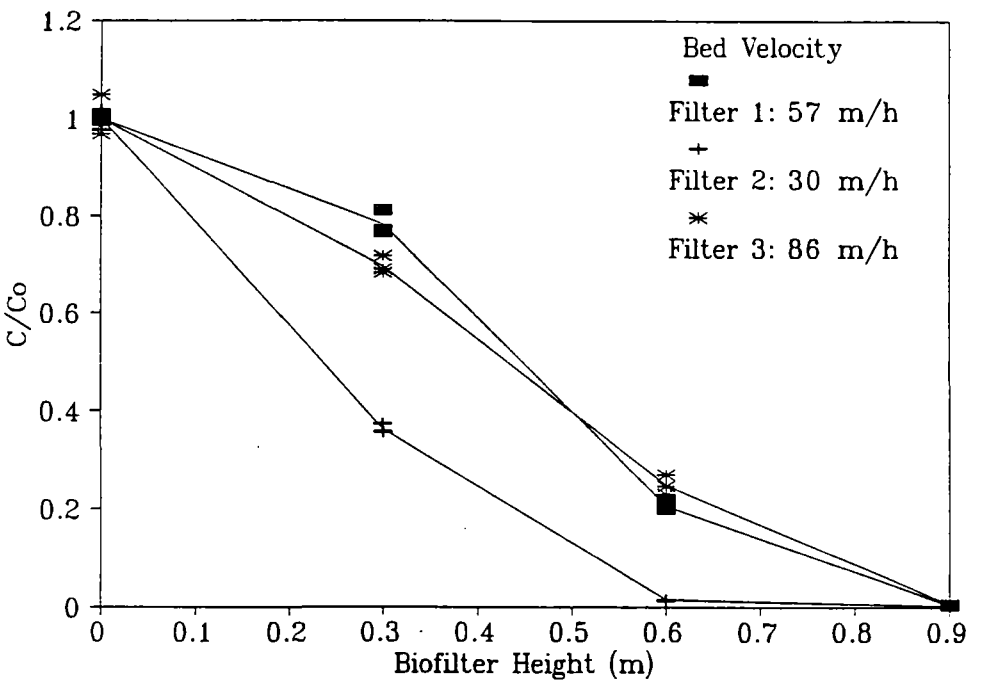

Figure 7.2. Biofilter Profiles After Flow Change: Day 4

A statistical analysis was performed in order to determine if there was a significant difference in performance between the three filters. The filters were compared with respect to mass load (mass/time) and filter height. Table 7.3 summarizes the results of a two-way analysis of variance (ANOVA) for the filters.

Table 7.3. ANOVA Results: Day 4

Source	DF	Anova SS	Mean Square	F Value	Pr > F
Treatments	11	1715331	1555939		
Filter	2	82468	41234	448	0.0001
Height	3	1569383	523127	5686	0.0001
Filter* Height	6	63480	10580	115	0.0001
Error	24	2208	92.0		
Corrected Total	35	1717538			

Where: DF = degrees of freedom
SS = sum of squares

ANOVA results indicated that the performance of the three filters was significantly different. Pair-wise comparison between filters using T Least Significant Difference (LSD), Tukey's Studentized Range (HSD) and Scheffe's test confirmed that the performance of the three filters was significantly different. However, the inlet load to filter 2 was found to be significantly lower than filters 1 and 3, which complicated comparisons. Complete results of the statistical analysis are included in Appendix C.

The nature of the difference between filters is best demonstrated by a comparison of removal rates for each biofilter section, as illustrated in Figure 7.3.

In filter 2, maximum toluene removal was observed in the first stage, consistent with results from earlier experiments. In filters 1 and 3, maximum toluene removal was found to occur in the middle stage of the biofilter indicating that some factor reduced removal

capacity in the first stage. Inhibition due to toxicity effects is not probable because filter 2 was operated at the highest inlet concentration. Reduced removal due to flow channelling or filter drying are hypothesized to be the most likely explanations for the reduced performance.

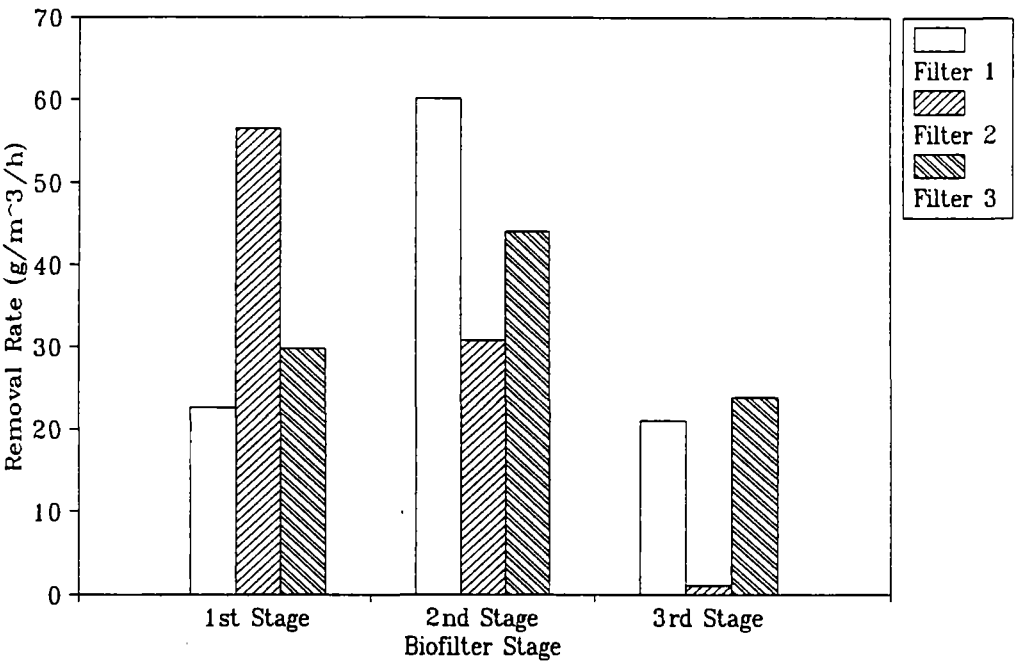

Figure 7.3. Mass Removal Rates: Day 4

Increased Inlet Loading

Figures 7.4 and 7.5 illustrate toluene profiles and removal rates for the biofilters two days after an increase in the inlet load. All three filters exhibited a decrease in removal efficiency. Also, maximum removal capacity was observed in the third stage of all filters. A statistical difference was observed between filter 2 and filters 1 and 3; filter 2, with the lowest flow rate, exhibited the best performance. The inlet mass load to the three filters was found to be statistically similar.

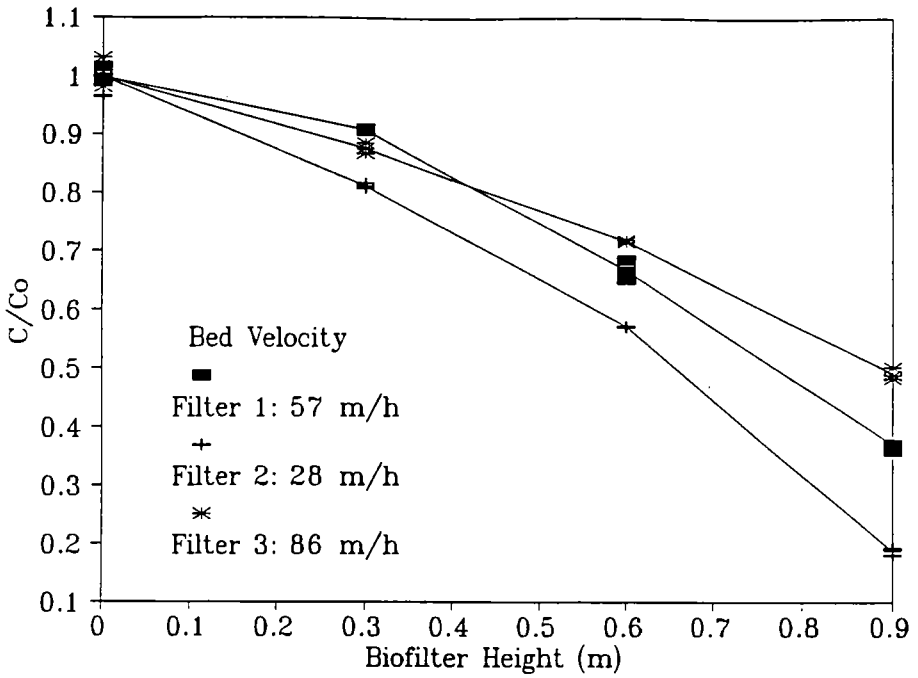

Figure 7.4. Toluene Profiles After Loading Increase: Day 6

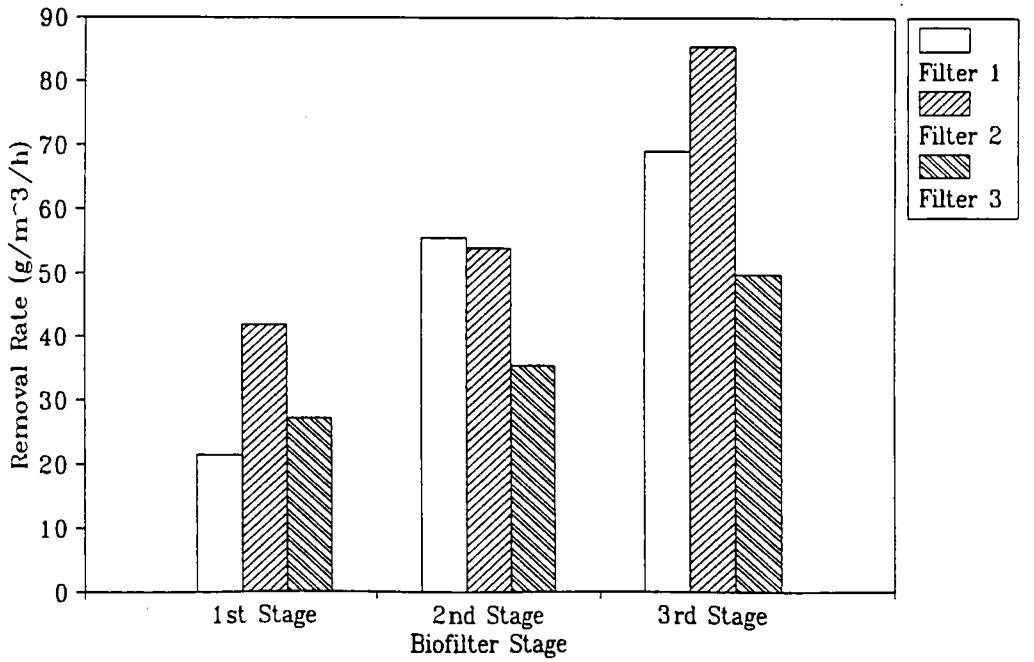

Figure 7.5. Removal Rates: Day 6

7.3.3 Assessment of Channelling

The performance of the filters was examined using the THC detector one day after reducing inlet loading back to the original level. Overall removal efficiency for each filter did not improve after the reduction in inlet load which indicated an irreversible loss of removal capacity. Concentration profiles across the diameter of the filter were examined by measuring toluene levels at 1.5 cm, 7.6 cm and 13.7 cm from the inside edge of the sampling port. The results of traverses are provided in Table 7.4.

Table 7.4. Biofilter Channelling

Height (m)	Concentration (ppm)								
	Filter 1 Flow = 17.1 L/min			Filter 2 Flow = 8.98 L/min			Filter 3 Flow = 26.1 L/min		
	Location (cm)			Location (cm)			Location (cm)		
	1.5	7.6	13.7	1.5	7.6	13.7	1.5	7.6	13.7
Inlet	172	168	174	245	244	242	106	105	105
0.3	152	118	134	234	225	253	75	62	79
0.6	92	70	100	168	48	168	62	46	55
0.9	52	31	58	47	8.4	8.4	35	14	39

It is evident that in some sections preferential flow along the sides of the reactor wall was occurring. It is interesting that significant channelling appears to have occurred in filter 2, which had the lowest flow rate.. Further research is required in order to assess hydrodynamic changes in biofilters during operation.

It should be noted that during sampling with the GC, samples were withdrawn from the

edge of the reactor, which in most cases would be measuring the highest concentration.

7.3.4 Summary of Mass Removal

Each biofilter column can be considered as three reactors in series, two reactors in series and each stage as an individual reactor. For example, each biofilter column represents six combinations of reactors. Toluene mass loadings and mass removal rates (per unit volume of bed) were calculated for individual stages and combinations of stages and are presented in Figure 7.6. Experimental data from GC measurements from day 4 and day 6 are included in the summary. The diagonal line represents the line of 100% removal (i.e. loading rate equals removal rate). The horizontal lines represent the average elimination capacity for each filter. Elimination capacity was defined as the average removal rate of the filter, calculated over the range of loading rates which corresponded to greater than 95% removal.

The scatter of the data make comparisons between filters difficult. However, filter 2 appears to have demonstrated the best overall performance with an average elimination capacity of 59 $g/m^3/h$. Average elimination capacities of 47 and 37 $g/m^3/h$ were calculated for filters 1 and 3, respectively. Removal efficiencies of 97% or greater were obtained for mass loading rates less than 40 $g/m^3/h$ regardless of airflow rate.

Maximum removal rates observed in this study are consistent with maximum removal rates reported in pilot studies which were summarized previously in Table 2.2.

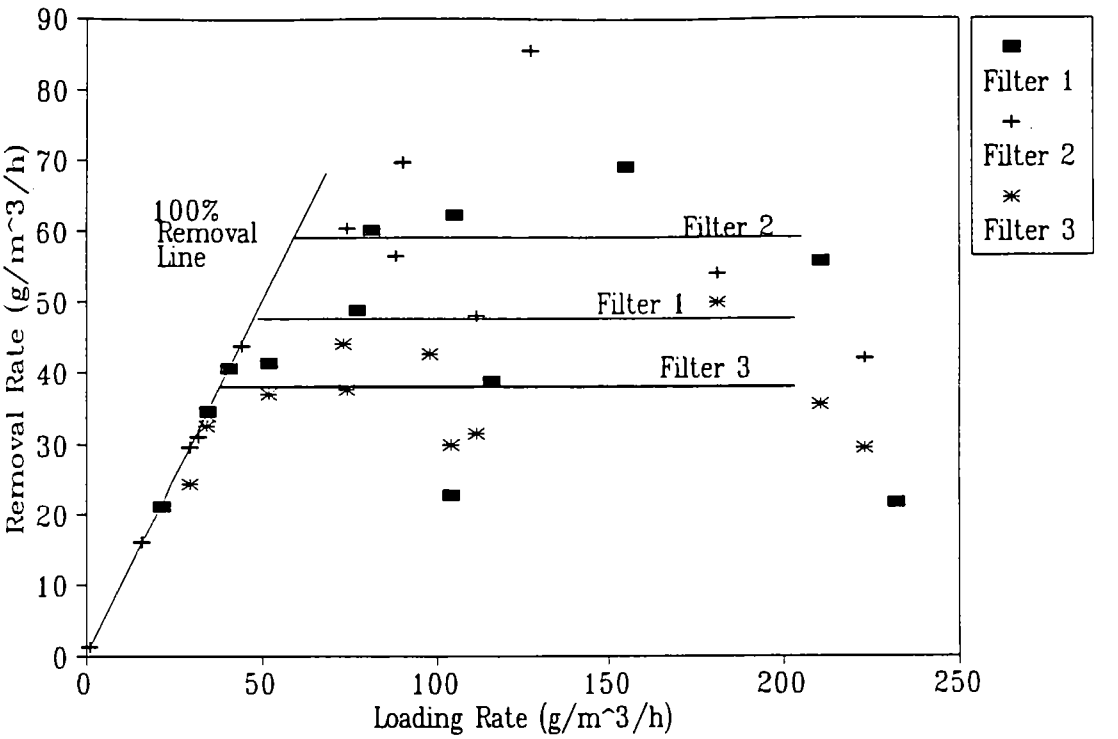

Figure 7.6. Removal Rate vs. Loading Rate

7.3.5 Temperature Profiles and Moisture Content

Temperature profiles for the three filters corresponding to toluene measurements for days 3, 4 and 6 are reported in Figures 7.7 to 7.9.

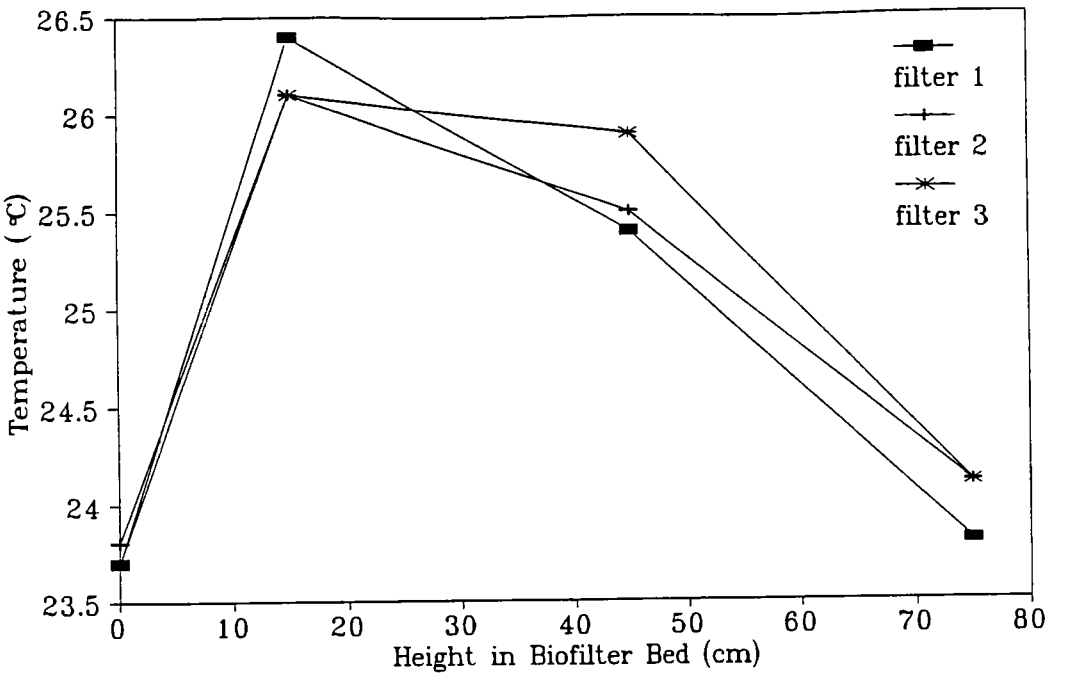

Figure 7.7. Temperature Profiles: Day 3

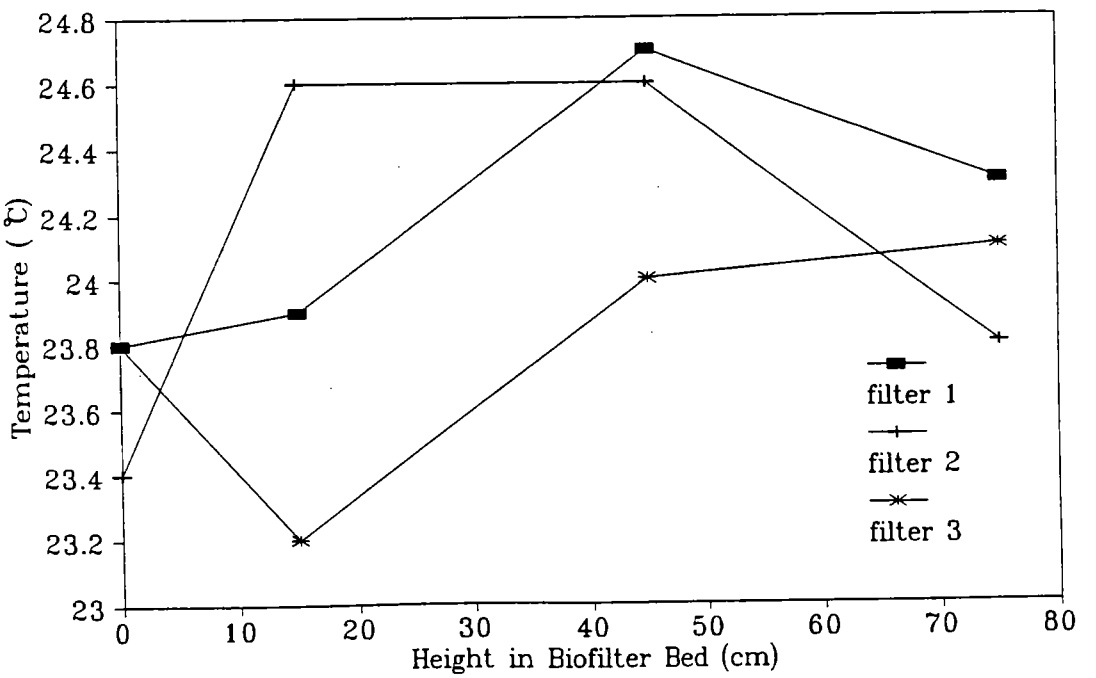

Figure 7.8. Temperature Profiles: Day 4

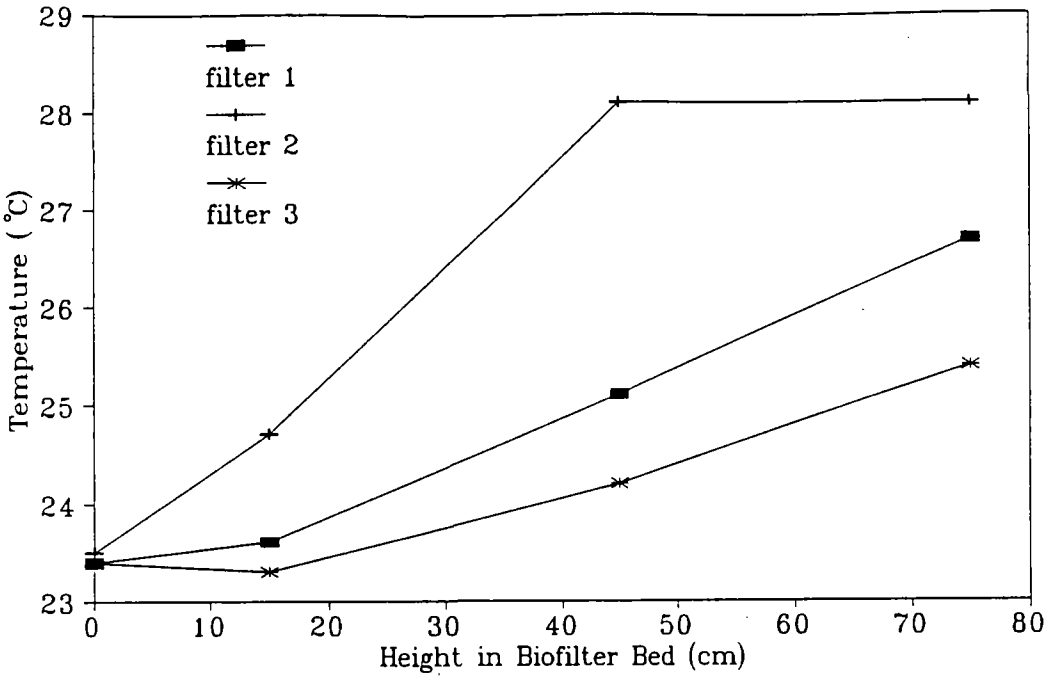

Figure 7.9. Temperature Profiles: Day 6

Some general trends are apparent; first, for each filter the maximum temperature measurement occurred in the stage with the highest removal rate. Also, as flow rate increased, the magnitude of temperature rise decreased. The temperature profiles indicated that potential problems with moisture control could occur. For example, even if the inlet gas stream is completely saturated, moisture loss will still occur as the temperature of the gas stream increases while passing through the filter bed. Therefore, additional moisture will be required. Also, as the gas stream cools, condensation may occur in the bed. At higher superficial velocities there is a greater potential for evaporative water loss.

Biological reactions are often autocatalytic; for example, as temperature increases due to

microbial activity, reaction rate will also increase. However, as temperature of the pore air increases the contaminant will have a higher affinity to the air stream. The net effect on removal rate will depend on the properties of the contaminants; the effect of this phenomenon on BTEX removal has not been investigated.

Moisture Content

Table 7.6 summarizes the moisture contents of the three biofilters at locations throughout the filter sampled on day 7.

Table 7.6. Moisture Profiles

Height (cm)	Moisture Content (% wt)		
	Filter 1	Filter 2	Filter 3
10	34.4	37.7	40.8
20	38.7	38.3	37.4
30	36.7	40.4	37.8
40	39.5	39.9	38.5
50	37.7	36.8	41.5
60	39.7	41.1	36.8

Moisture content measurements indicated that drying occurred in all three filters. Additional water was added daily to the filter sections but was insufficient in preventing moisture loss. There does not appear to be a difference in moisture content between filters measured at the end of the experiment. Due to a lack of on-line moisture measurement it is unknown when drying first occurred.

Commercial units have employed load cells for on-line moisture measurement (Ziminski and Yavorsky, 1994). However, this approach does not account for zonal variations in moisture contents. van Lith (1993) suggested down-flow operation of biofilters in order to facilitate moisture control. Tahraoui *et al.* (1994) encountered problems with drying when operating above a superficial velocity of 36 m/h in a biofilter degrading a BTX mixture.

The results suggest that the potential for drying increases as toluene mass loading to the biofilter increases. The development of efficient biofilters for the treatment of toluene requires further research in on-line moisture measurement and process control.

7.3.6 CO_2 Mass Balance

Figure 7.10 illustrates predicted and measured CO_2 concentration profiles for filter 1 on day 6 of operation. Predicted CO_2 concentrations were developed using the method described in chapter 4.3.3. Influent and effluent CO_2 concentrations from filter 1 prior to toluene introduction were found to be 321 and 633 ppm, respectively.

The measured and predicted CO_2 profiles are in good agreement except for the sample from a biofilter height of 60 cm. Predicted effluent CO_2 concentration (90 cm height) is within 10% of the measured value.

Samples were collected from filter 1 on day 4, however, syringe leakage resulted in the loss of some samples.

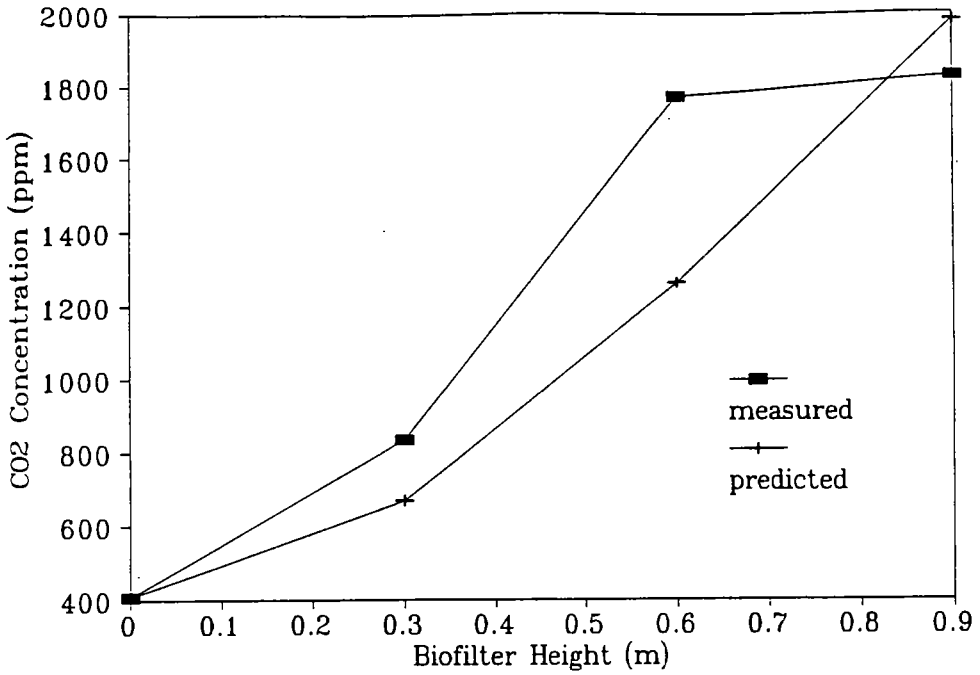

Figure 7.10. CO_2 Mass Balance: Filter 1, Day 6

8.0 REMOVAL OF BTX MIXTURES

8.1 Objectives

The objective of this set of experiments was to examine the degradation of mixtures of benzene, toluene and *o*-xylene. In experiment 2A toluene degradation was compared with the degradation of a mixture of benzene, toluene and xylene. The effect of toluene addition on the degradation of *o*-xylene was examined in experiment 2B.

8.2 Experimental Conditions

8.2.1 Experiment Number 2A

Filter Media

Three parallel filters were each packed with a mixture of CMSW, CSS and perlite. The CMSW material had been used previously in toluene biofiltration experiments (experiments 1C and 1D). Filter media characteristics are summarized in Table 8.1.

Table 8.1. Packing Material: Experiment 2A

Composition	Initial MC (% weight)	pH
20 L CMSW mix (60:40)[1] + 20 L CSS + 20 L perlite	58.3	7.5

[1]60% CMSW + 40% perlite (by volume)

Experimental Protocol

The three filters were operated at the same airflow rate and organic loading. The mass

loading to the filters was increased by a factor of two on day 9 and again on day 12. The performance of the biofilters during the acclimation period, day 1 to 9 was monitored using the THC detector. Biofilter contaminant profiles were measured on days 4, 12 and 19 using the GC-PID. The filters were shut down on day 13 and restarted on day 16 in order to repair problems with the contaminant loading system.

Each filter was subjected to a different contaminated air stream; mixtures of pure liquid compounds were loaded into syringes supplying each column. Table 8.2 summarizes contaminant sources for each filter.

Table 8.2. Contaminant Supply

Filter Number	Contaminant
Filter 1	Toluene
Filter 2	Benzene + Toluene 1:1 mixture by volume of liquid contaminant
Filter 3	Benzene + Toluene + *o*-Xylene 1:1:1 mixture by volume of liquid contaminant

8.2.2 Experiment Number 2B

Filter Media

Two parallel filters were packed with filter material which had been used previously in experiment 2A (Table 8.1). The filter material was remixed prior to being packed into the columns. The initial moisture of the material was found to be 59.6% by weight.

Experimental Protocol

The two filters were operated at the same airflow rate and *o*-xylene loading rate for 4 days. On day 4 an additional toluene load was added to filter number 2 while the original xylene loading was maintained. Contaminant levels in the air streams were quantified on day 4 and day 5 (24 hours after toluene introduction) using the GC-PID. Carbon dioxide levels were measured using the GC-TCD.

8.3 Experiment 2A: T vs BTX

8.3.1 Flow Rates and Loading Rates

Acclimation Period

The inlet concentrations and flow rates measured during the acclimation period for filters 1 and 3 are summarized in Table 8.3. Filter number 2 was shut-down after 3 days of operation due to a leak in the contaminant supply system.

Fluctuations in inlet airflow rates were observed during the acclimation period, which led to varying inlet concentrations.

Table 8.3. Loading Rates: Acclimation Period Exp 2A

Parameter	Measured Reading	
	Filter 1	Filter 3
Inlet Concentration[1] (ppm, toluene equivalents)		
average	73.6	87.4
sd	26.2	31.3
Flow Rate[1] (L/min)		
average	8.73	8.33
sd	1.47	0.98
EBRT (min)	1.87	1.96
Superficial Velocity (m/h)	28.9	27.6
Loading Rate ($g/m^3/h$)		
average	8.97	NA
predicted	9.57	
difference (%)	-5.2	

[1]Recorded daily.

Filter Profiles

The loading and flow rates measured during the experiment for the different experimental days are outlined in Table 8.4

Table 8.4 Loading Rates: Experiment 2A

Day		Filter 1	Filter 3
4	Inlet Conc (g/m^3)[1] (ppm)[2]		
	toluene	0.203 (53)	0.107 (29)
	benzene		0.095 (30)
	o-xylene		0.073 (17)
	Flow Rate (L/min)	9.89	9.60
	EBRT (min)	1.65	1.70
	Superficial Velocity (m/h)	32.7	31.8
	Loading Rate ($g/m^3/h$)[3]		
	average	7.40	9.72
	predicted	9.57	9.66
	difference (%)	-23	+0.6
12	Inlet Conc (g/m^3)[1] (ppm)[2]		
	toluene	0.678 (177)	0.271 (71)
	benzene		0.257 (79)
	o-xylene		0.292 (66)
	Flow Rate (L/min)	8.11	7.82
	EBRT (min)	2.01	2.08
	Superficial Velocity (m/h)	26.9	26.0
	Loading Rate ($g/m^3/h$)		
	average	20.3	23.6
	predicted	19.1	19.3
	difference (%)	+5.8	+22
19	Inlet Conc (g/m^3)[1] (ppm)[2]		
	toluene	1.027 (267)	0.429 (112)
	benzene		0.425 (131)
	o-xylene		0.428 (97)
	Flow Rate (L/min)	8.98	8.69
	EBRT (min)	1.82	1.88
	Superficial Velocity (m/h)	29.7	28.7
	Loading Rate ($g/m^3/h$)		
	average	33.9	38.6
	predicted	38.3	41.0
	difference (%)	-11	+6.1

[1]Average of two measurements.
[2]Number in brackets; 293 K used for conversion.
[3]Total mass loading of mixture.

8.3.2 Biofilter Performance: Acclimation Period

Figure 8.1 illustrates contaminant response for the filters during the acclimation period. Filter 1, which received the toluene load, exhibited rapid acclimation and achieved greater than 98% removal in less than one day after start-up. The short acclimation time was probably due to the presence of acclimated CMSW filter material in the media mixture. The use of pre-used filter material effectively acted as an inoculum by providing microorganisms which had previously been exposed to toluene.

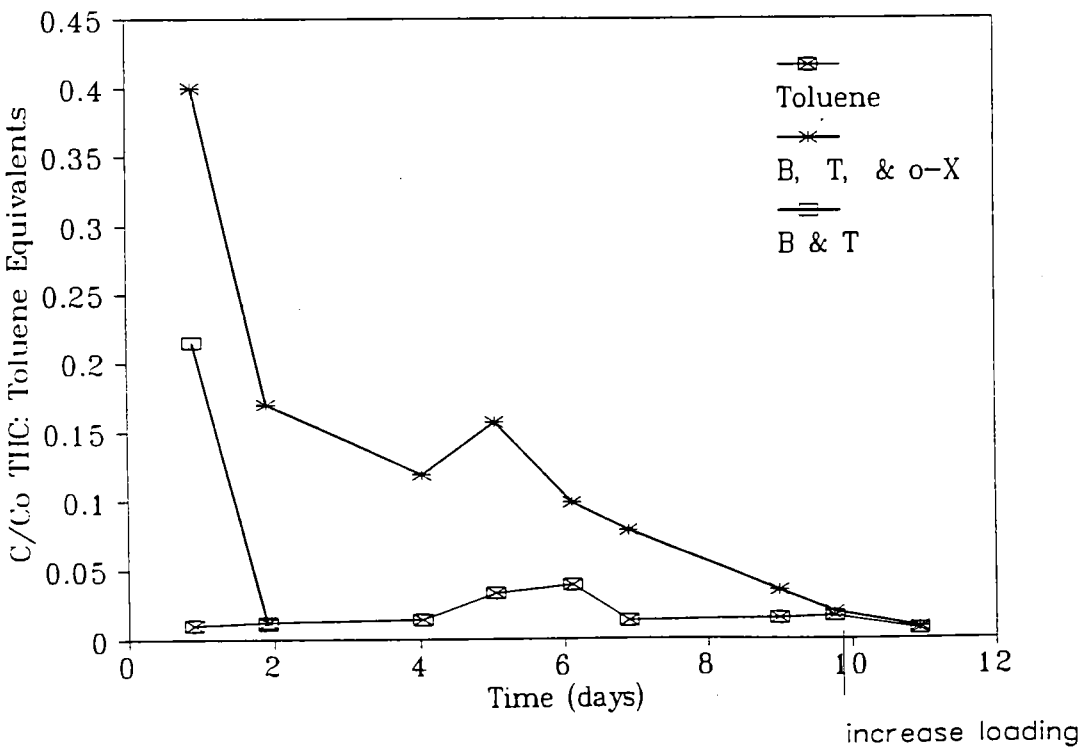

Figure 8.1. Biofilter Acclimation: Experiment 2A

Filter 2 was operated for only 3 days, but appeared to have reached a removal efficiency of 98% at approximately two days after start-up. Filter 3, which was subjected to a contaminated air stream consisting of benzene, toluene and *o*-xylene, required approximately 9 days to reach removal efficiencies similar to filter 1.

A profile of contaminant removal as a function of height for filter 3, recorded on day 4, is presented in Figure 8.2. The data points represent measured concentration divided by the average inlet concentration, and the lines correspond to the average values for each height. A low removal efficiency was observed for *o*-xylene, indicating that the longer acclimation period for filter 3 was due to the presence of *o*-xylene in the gas stream.

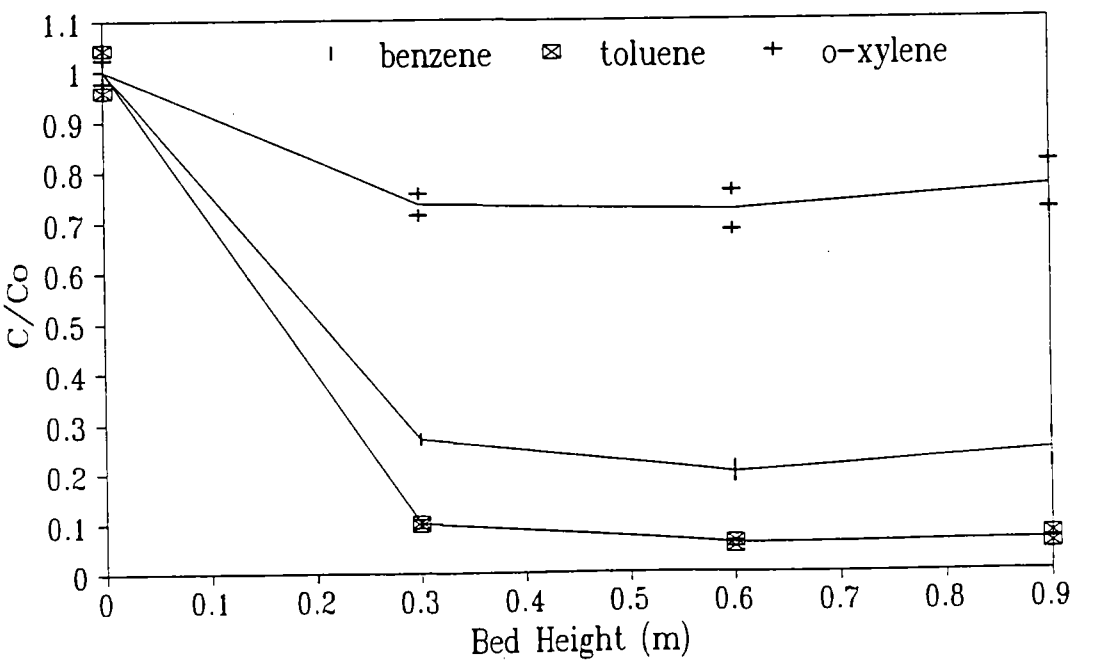

Figure 8.2. Biofilter Profile: Filter 3, Day 4

Similar trends have been observed in batch liquid reactors. For example, Alvarez and Vogel (1991) found that the lag period for degradation increased from 2 days for toluene alone to 6 days for a mixture of benzene, toluene and *p*-xylene as carbon sources.

It is possible that a longer acclimation period is required for xylene degradation to allow for the development of the required enzyme pathways or to allow for proliferation of *o*-xylene degrading organisms.

8.3.3 BTX Removal

Figure 8.3 illustrates removal profiles for benzene, toluene and *o*-xylene for filter 3 on day 12. Similar removal efficiencies were observed for each compound at the exit of the biofilter with individual outlet concentrations less than 1 ppm. Benzene and toluene appeared to be preferentially degraded compared to xylene in the first biofilter stage. However, a two-way analysis of variance (unequal replication) of removal efficiency and bed height indicated that there was not a significant difference in removal efficiency between the three compounds. Further sampling points and a greater number of replicates would be required in order to further evaluate preferential degradation.

The performance of filter 3 was compared with filter 1 on the basis of average carbon removal efficiency and biofilter height (Figure 8.4). The fraction of carbon removed with respect to height was defined as stage effluent carbon load (g/h) divided by the inlet carbon load (g/h). The two filters were not found to be significantly different with respect to carbon removal efficiency based on a two-way ANOVA (unequal replication).

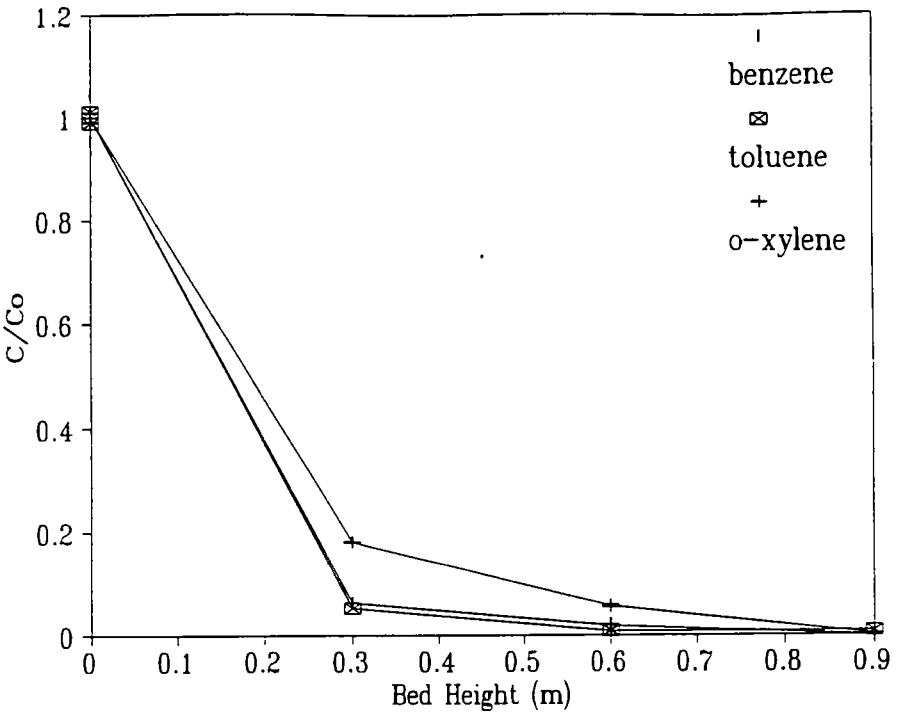

Figure 8.3. Biofilter Profile: Filter 3, Day 12

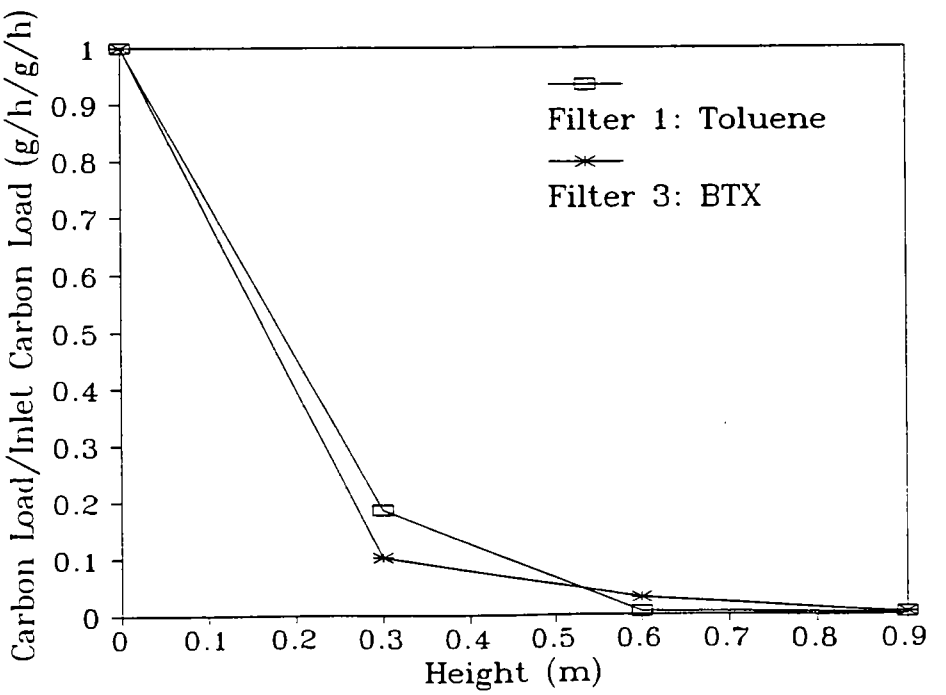

Figure 8.4. Carbon Removal Efficiency, Day 12

Figures 8.5 and 8.6 illustrate biofilter performance 19 days after filter start-up, approximately a week after an increase in mass loading. Both filters exhibited a reduction in removal efficiency in the first biofilter section indicating potential performance problems. In filter 3 the difference in removal efficiency of individual compounds is more obvious than observations at the lower loading rate, and was found to be statistically significant. The degradation profile displayed in Figure 8.4 exhibits a pattern consistent with competitive inhibition in which toluene is preferentially degraded. It appears that the complete removal of *o*-xylene first requires a significant reduction in toluene and benzene levels. Goldsmith and Balderson (1988) found preferential degradation occurred in the order of toluene, benzene, *p*-xylene and *o*-xylene in batch liquid culture experiments.

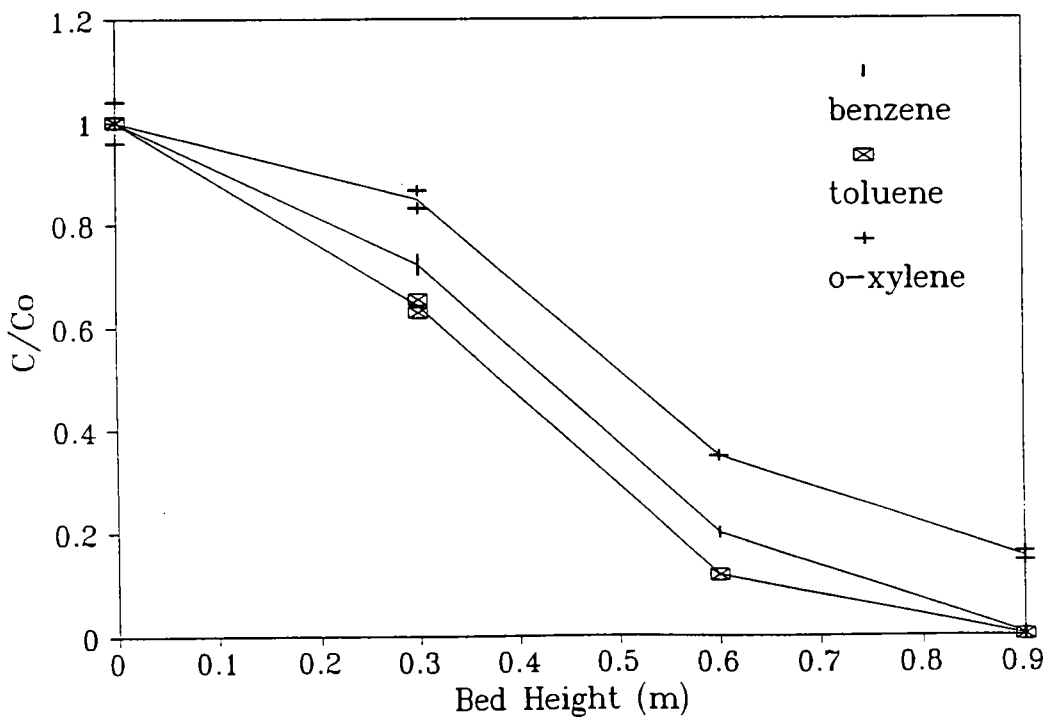

Figure 8.5. BTX removal: Filter 3, Day 19

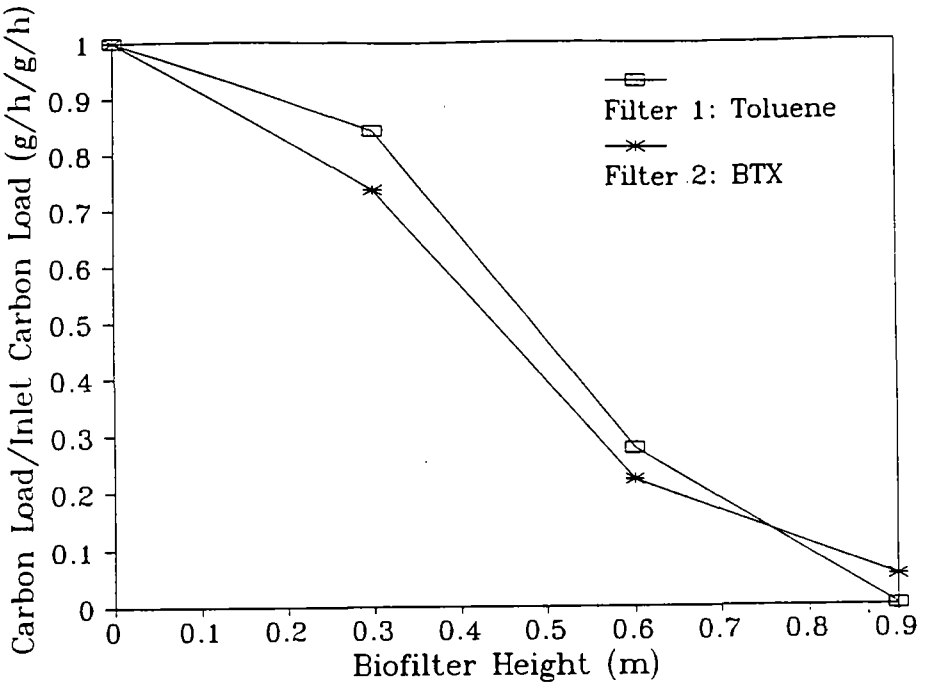

Figure 8.6. Carbon Removal, Day 19

Carbon removal efficiency, illustrated in Figure 8.6, was found to be similar for the two filters. Filter 3 exhibited a slightly lower overall carbon removal efficiency due to the effluent xylene concentration. Xylene effluent levels may be the limiting factor for overall biofilter performance at high inlet BTX concentrations.

8.3.3 Moisture Content

The filter material was analyzed for moisture content at the termination of the experiment. Table 8.5 presents moisture contents of composite bed samples for each filter stage.

Table 8.5 Moisture Content: Experiment 2A

	Moisture Content (% weight, wet basis)	
Section	Filter 1	Filter 2
1st	61.5	62.2
2nd	61.7	61.6
3rd	65.4	64.5

Moisture contents indicated that filter drying did not occur and was not responsible for the reduction of removal capacity in the first stage. However, visual inspection of the first stage from each filter revealed the formation of a wet 'mucky' zone at the base of the filter sections. Water addition to the first stage of the biofilters during filter operation could have resulted in transport and settling of fine particles or degraded bed material at the filter base which may have plugged the filter inlet. The net result would have been the formation of flow channels and short-circuiting in the filter stage.

Ensuring appropriate moisture levels while maintaining bed porosity appears to be a limiting factor for efficient performance of biofilters at higher loading rates.

8.3.4 Summary of Mass Removal Rates

A summary of removal rates corresponding to various carbon mass loading rates for the two filters is presented in Figure 8.7. The data presented were calculated using the procedure described in Chapter 7 and represents data from day 12 and day 19 of operation. The diagonal line represents the line of 100% removal (i.e. carbon removal rate equals loading rate). Carbon mass removal rates for the BTX mixture were observed

to be similar to carbon removal rates for toluene. The two data points furthest to the right in the graph represent loadings to the bottom sections of both filters on day 19. Both filter sections exhibited reduced removal rates after 19 days of operation, as indicated previously by Figure 8.5.

The removal rate data appeared to follow a pattern consistent with earlier observations (Figure 7.6, filter 2). Although, the range of loading rates was not sufficient for the calculation of a maximum elimination capacity for the filters.

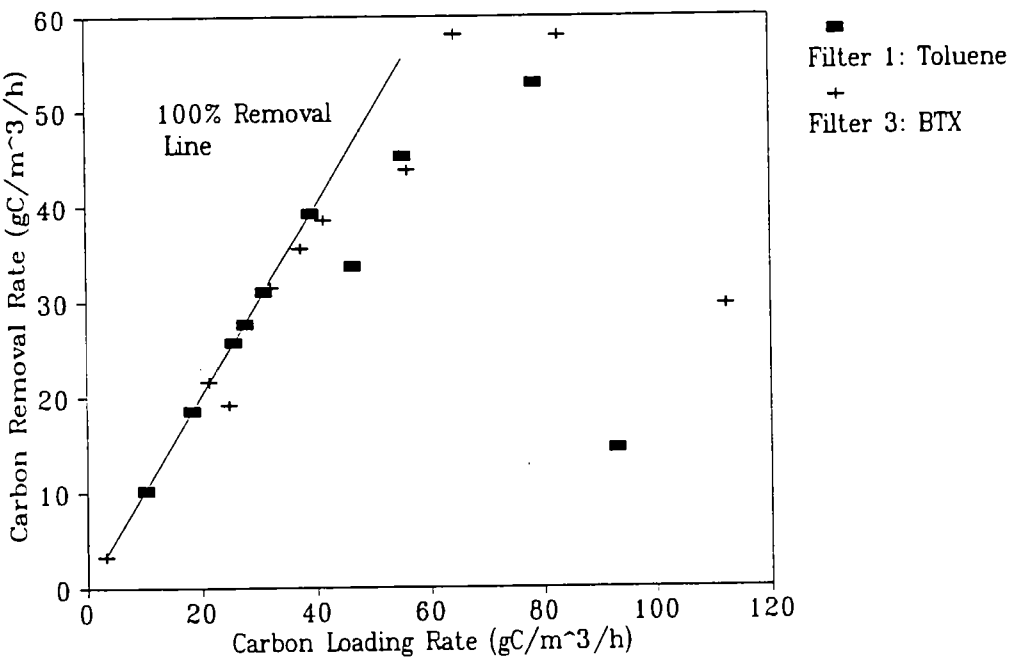

Figure 8.7. Carbon Removal Rate vs Loading Rate

8.4 Experiment 2B: Effect of Toluene Introduction on Xylene Removal

8.4.1 Flow Rates and Loading Rates

The loading and flow rates measured during the experiment for days 4 and 5 are listed

in Table 8.6.

Table 8.6 Loading Rates: Experiment 2B

Day		Filter 1	Filter 2	
4	Inlet Conc (g/m^3)[1] (ppm)[2]			
	o-xylene	-	0.274 (62)	
	Flow Rate (L/min)	-	9.27	
	EBRT (min)	-	1.76	
	Superficial Velocity (m/h)	-	30.7	
	Loading Rate ($g/m^3/h$)			
	average	-	9.33	
	predicted		9.72	
	difference (%)		-3.9	
5	Inlet Conc (g/m_3)[1] (ppm)[2]			
	toluene		0.281 (73)	
	o-xylene	0.269 (61)	0.281 (64)	
	Flow Rate (L/min)	9.27	9.27	
	EBRT (min)	1.76	1.76	
	Superficial Velocity (m/h)	30.7	30.7	
	Loading Rate ($g/m^3/h$)		*o*-xylene	toluene
	average	9.16	9.58	9.61
	predicted	9.72	9.72	9.58
	difference (%)	-5.7	-1.4	+0.4

[1]Average of 2 measurements.
[2]Number in brackets.

The operation of filter 1 was interrupted for 45 minutes on day 4 due to condensation in the rotameter. As a result, concentration data were not recorded for filter 1 on that day.

8.4.2 Contaminant Profiles

Figure 8.8 illustrates *o*-xylene and toluene removal for filter 1, 24 hours after the addition of the toluene load. Toluene and *o*-xylene removal efficiencies were found to be 89% and 72%, respectively, at a bed height of 0.30 m. Contaminant removal at each sampling location indicated preferential degradation of toluene, which is consistent with results from experiment 2A.

Figure 8.9 illustrates a comparison of *o*-xylene removal for filter 2 before and after toluene addition and for filter 1 on day 5. The profiles indicated a slight reduction in *o*-xylene removal from 80% to 72% after toluene addition to filter 2. Filter 1 exhibited identical performance to filter 2 prior to toluene addition. In general, toluene addition had little effect on filter performance. Carbon mass removal efficiency in filter 2 remained the same at 80% at a filter height of 0.30 m, even though the organic load to the filter had been doubled.

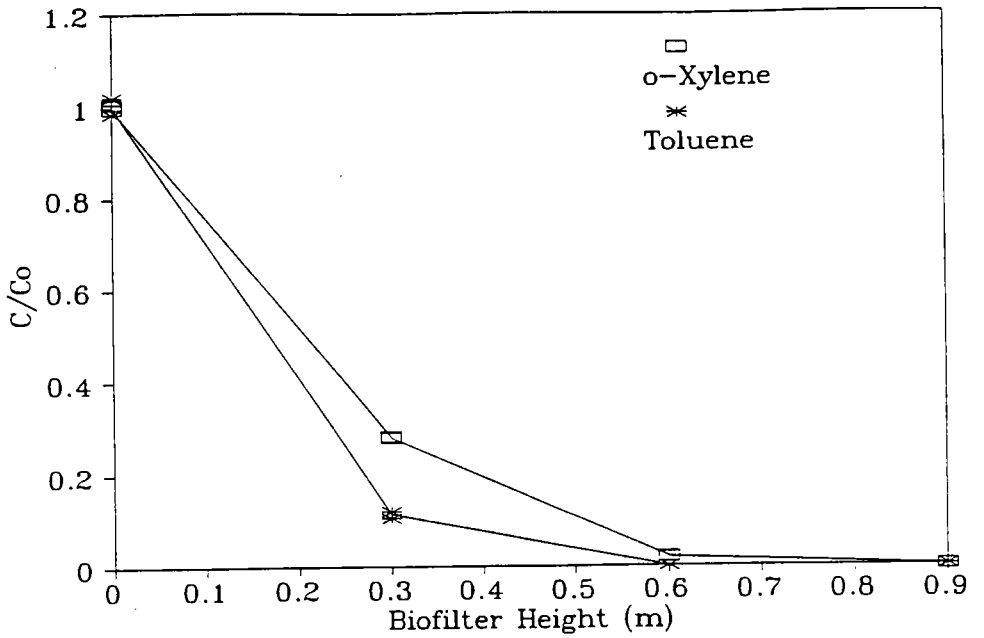

Figure 8.8. TX Profiles: Filter 2, Day 5

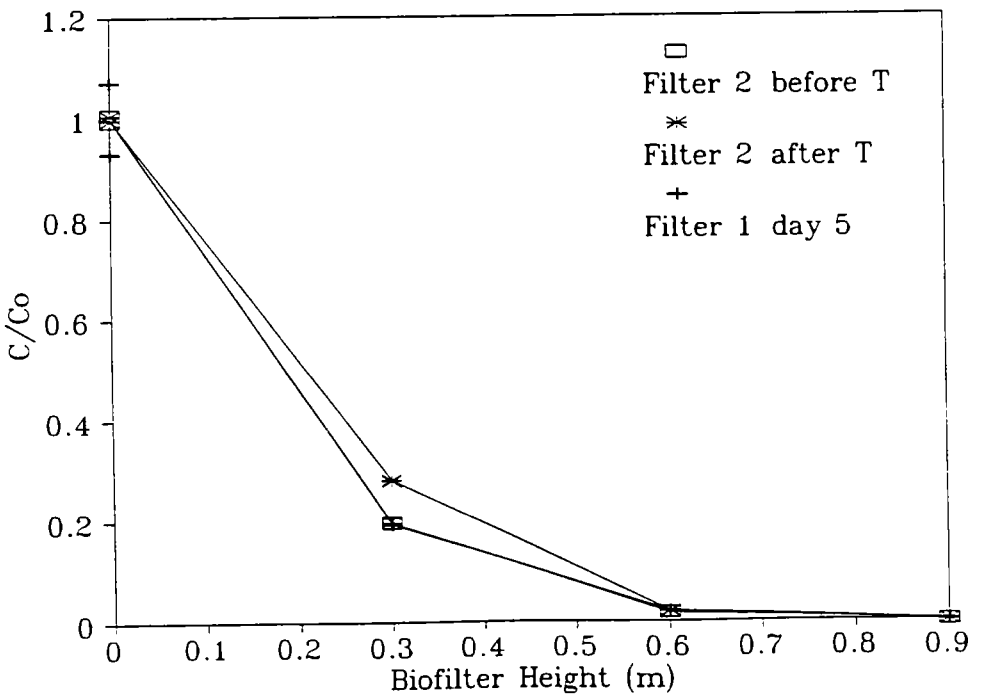

Figure 8.9. Xylene Removal: Filters 1 and 2

8.4.3 CO_2 Mass Balance

Carbon dioxide production as a function of toluene degradation has been previously presented in chapter 4. Assuming steady-state performance, complete *o*-xylene mineralization can be represented by:

$$C_8H_{10} + 7.5 \cdot O_2 \rightarrow 8 \cdot CO_2 + 5 \cdot H_2O$$

Therefore, 3.32 grams of CO_2 are produced for 1 gram of xylene degraded.

Both measured and predicted carbon dioxide profiles for filters 1 and 2 from day 5 are presented in Figure 8.10. The lines represent predicted values and the data points correspond to measured values. Effluent CO_2 concentration from filter 2 prior to toluene introduction (day 4) was found to be approximately 900 ppm but loss of one sample prevented the display of a concentration profile. A basal CO_2 generation rate of 15 g/m^3-bed/h was used in the development of predicted CO_2 profiles. The increase in CO_2 concentration in the air stream from filter 2 can be directly attributed to the additional toluene load. The CO_2 measurements confirmed that *o*-xylene was degraded as a sole carbon source prior to toluene introduction.

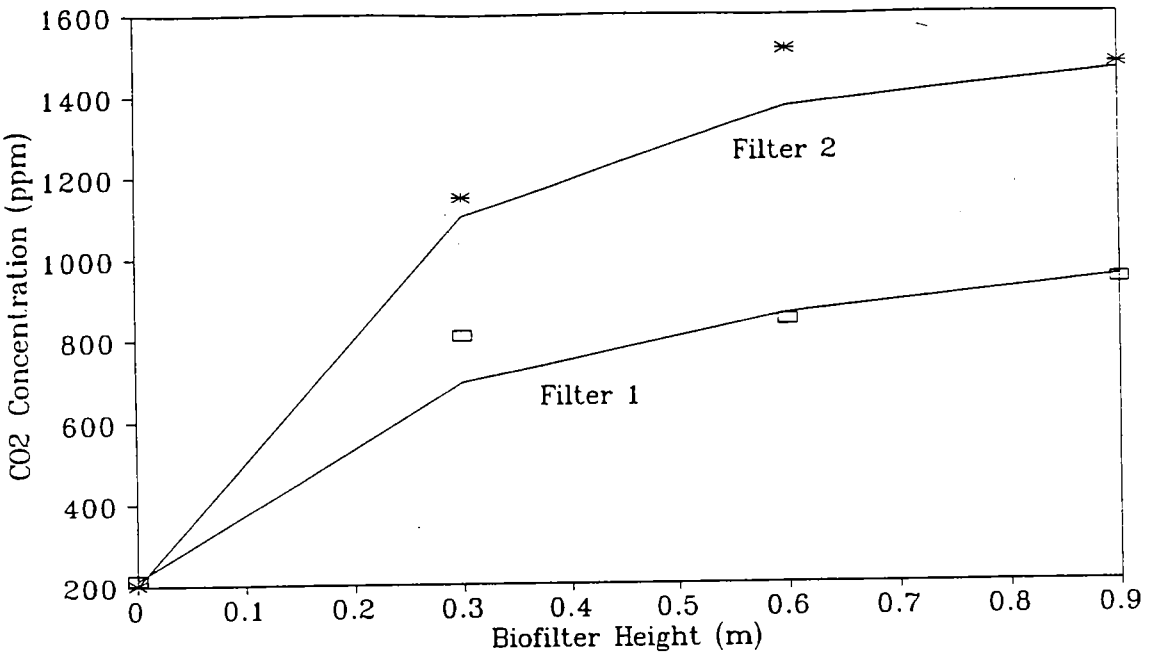

Figure 8.10. CO_2 Profiles, Day 5

8.5 Chapter Summary

The biofiltration of mixtures of VOCs is a complex issue and the experiments conducted in this study represent preliminary investigations into this issue. Mixtures containing the *ortho* isomer of xylene were chosen because *o*-xylene has been reported to be the least readily degradable of the BTEX group of compounds.

The results of experiments 2A and 2B indicated preferential degradation of toluene in BTX and TX mixtures. Also, *o*-xylene was found to be degraded when present as a single contaminant.

The presence of *o*-xylene in the contaminant load resulted in an increased acclimation period compared to toluene alone. However, once acclimated the filters exhibited similar carbon removal efficiencies.

9.0 CONCLUSIONS

The removal of toluene, *o*-xylene and mixtures of BTX and TX from gas streams using biofilters was investigated using an experimental lab-scale system. The results of laboratory studies led to the following conclusions.

Benzene, toluene and o-xylene can be readily degraded in gas phase biofilters. Removal efficiencies of 97% or greater were observed for toluene and BTX mass loading rates of 40 $g/m^3/h$ or less. Carbon dioxide mass balances confirmed that biodegradation was responsible for contaminant removal.

Nutrient availability is a limiting factor for effective biofiltration in some compost-based filter media. Composted leaf and yard waste and composted bark filter media exhibited poor toluene removal due to a lack of available nitrogen. Composted municipal solid waste and composted sewage sludge were found to be effective filter material, with acclimation periods of 2 to 4 days.

Increase in airflow rates results in reduced filter elimination capacity. Average toluene removal rate was found to be highest (59 $g/m^3/h$) at the lowest superficial velocity (30 m/h) tested in the experiment. The reasons for performance differences between filters were unclear. Comparisons were complicated by the fact that all three filters exhibited a reduction in removal capacity in first and second filter stages over the time period of the experiment (10 days).

Filter performance was also observed to degrade over time (19 days) in filters treating BTX and toluene gas streams. *Although toluene and BTX carbon mass removal rates of 60 g/m^3/h or greater are possible, maintaining high removal rates is difficult.* Reduced removal rates were attributed to filter channelling or media drying. The potential for filter drying increased as loading rate and airflow rate were increased.

Longer acclimation periods are required for the removal BTX mixtures compared with toluene as a single gas-phase contaminant. The increase in acclimation period appeared to be due to the presence of *o*-xylene in the gas stream. For this study, similar carbon mass removal efficiencies were observed between acclimated filters which received toluene as a contaminant compared with a mixture of benzene, toluene and *o*-xylene.

Preferential degradation in the order of toluene, benzene and o-xylene occurs in compost-based biofilters which treat BTX.

Biofilters appear to be suitable for the treatment of off-gas containing low concentrations (less than 600 ppm) of VOCs. Experimental results indicated that biofiltration may be feasible for the treatment of SVE off-gas but would be restricted for use with low BTEX (less than 600 ppm) concentrations. These off-gas concentrations may be encountered during remediation of a small site or following pre-treatment with other control technologies.

10.0 RECOMMENDATIONS

The issue of nutrient availability has not been sufficiently addressed in biofilter research. Further research is required to identify appropriate type, amount and frequency of nutrient supplementation.

While maintaining appropriate moisture levels and adequate porosity during filter operation is recognized as being necessary to maintain efficient operation, hydrodynamic changes during filter operation has not been studied. Such studies would aid in the assessment of filter performance and lead to the further development of process control strategies for biofilter operation.

The effect of mixtures of VOCs on biofilter performance requires further study. In the case of SVE off-gas treatment a wide range of contaminants may be present which could affect BTEX removal. The effect of these contaminants on biofilter removal efficiency should be investigated.

The behaviour of biofilters when subjected to a dynamic inlet load was not investigated in this study. Fluctuating inlet loads may be encountered in many potential biofilter applications. However, experimental data and biofilter modelling related to filter response during such conditions are scarce.

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APPENDIX A

EXPERIMENTAL RESULTS: BTX CONCENTRATION DATA

Experiment 1A, CMSW mix: Aug 17 - Sept 1, 1993

[1]injection stopped for 2 hours.

Time (h)	Flow Read	Flow (L/min)	Inlet (ppm)	1st	C/Co	2nd	C/Co	Outlet	C/Co	(g/min)
3	25	6.66	6.1	5.2	0.85	5.2	0.85	4.7	0.770	
27.25	26	6.95	83	73	0.88	73	0.88	67	0.807	0.002212
35.17	26	6.95	92	68	0.74	68	0.74	54	0.587	0.002452
50.72	31	8.40	61	5.2	0.09	0.7	0.01	0.1	0.002	0.001965
58.89	32	8.69	54	1.1	0.02	0.3	0.01	0.2	0.004	0.001799
75.5	32	8.69	74	1.6	0.02	0.6	0.01	0.3	0.004	0.002466
99.08	33	8.98	77	1.6	0.02	0.3	0.00	0.2	0.003	0.002651
123.08[1]	32	8.69	79	4.1	0.05	0.4	0.01	0.3	0.004	0.002632
147.08	32	8.69	39	0.7	0.02	0.2	0.01	0.2	0.005	
153.08	32	8.69	72	2.5	0.03	0.5	0.01	0.2	0.003	0.002399
201.08	30	8.11	63	6.1	0.10	0.4	0.01	0.2	0.003	0.001959
201.41	30	8.11	63	6.1	0.10	0.4	0.01	0.2	0.003	0.001959
203.243	30	8.11	102	15.6	0.15	6.8	0.07	4.5	0.044	0.003172
205.16	30	8.11	103	12.6	0.12	3.7	0.04	1.1	0.011	0.003203
208.16	32	8.69	97	11.4	0.12	2.5	0.03	0.5	0.005	0.003232
226.993	30	8.11	113	29	0.26	5	0.04	0.6	0.005	0.003514
296.493	30	8.11	127	28.1	0.22	10.1	0.08	1	0.008	0.00395

Experiment 1B: Oct 15 - Oct 28

	Filter 1: CL&Y				Filter 2: CL&Y + CB				Filter 3: CB			
Time (days)	Flow (L/min)	inlet (ppm)	outlet (ppm)	C/Co	Flow (L/min)	inlet	outlet	C/Co	Flow (L/min)	inlet	outlet	C/Co
0.9	8.693	39	35.9	0.92	8.69	93	86.6	0.93	8.69	100	93.1	0.93
1.4	8.693	58.5	41.8	0.71	8.69	81	81	1.00	8.69	73	73	1.00
2.1	11.01	35	25	0.71	10.4	70	63	0.90	10.7	97	69	0.71
3.0	7.533	43	34	0.79	7.53	125	101	0.81	7.24	114	109	0.96
4.0[1]	9.273	36	30	0.83	9.85	56	53	0.95	9.56	56	56	1.00
5.1	8.403	54	36	0.67	8.98	60	60	1.00	8.11	81	69	0.85
6.1[2]	7.823	63	39	0.62	8.4	95	63	0.66	8.11	93	77	0.83
7.1	7.823	69	43	0.62	8.11	94	59	0.63	8.11	98	72	0.73
8.1	8.113	65	46	0.71	8.11	66	49	0.74	8.11	74	61	0.82
9.1	8.403	42	25.2	0.60	8.11	97	70	0.72	7.82	89	84	0.94
10.4	9.273	45	25	0.56	9.27	80	57	0.71	8.69	80	70	0.88
11.2	9.273	50	29	0.58	9.27	80	55	0.69	8.69	83	68.4	0.82

[1]Condensation in rotameters; toluene shut off for 3 hours.
[2]Refill syringes, shut down for 1 hour

Experiment 1C: Oct. 31 - Nov 17

Days	Filter 1: CMSW				Filter 2: CL&Y + MLVSS				Filter 3: CB + MLVSS				M.Load (g/min)
	flow (L/min)	Inlet (ppm)	Outlet (ppm)	C/Co	flow	Inlet	Outlet	C/Co	flow	Inlet	Outlet	C/Co	
0.35	8.74	34.6	30	0.87	8.45	35.8	28.4	0.79	8.45	33.7	28.4	0.84	
1.02	7.87	47	45.6	0.97	8.45	42.1	40.2	0.95	8.45	41.9	41.9	1.00	0.0041
1.90	8.16	39.9	39.7	0.99	8.74	39	34.7	0.89	8.74	39.6	36.1	0.91	0.0039
2.90	7.87	37.9	23.5	0.62	7.87	40	32.3	0.81	8.16	41.7	25	0.60	0.0037
3.73	9.32	32.2	0.3	0.01	9.90	31.2	26	0.83	9.03	29.6	25	0.84	0.0034
4.74	8.16	30.4	0.3	0.01	8.45	29.5	24	0.81	8.16	29	24	0.83	0.0028
5.70	9.03	31.7	0.4	0.01	9.61	30.2	25.4	0.84	9.03	31.6	26.7	0.84	0.0033
6.77	8.74	35.1	0.3	0.01	8.74	33	25.5	0.77	8.74	30.5	27.1	0.89	0.0033
7.67	8.16	35.6	0.4	0.01	7.87	35	24.5	0.70	7.87	35.6	26	0.73	****
9.75	8.74	33.2	0.4	0.01	9.32	28	21.5	0.77	9.32	27.2	23.9	0.88	0.0031
10.93	8.74	33	0.3	0.01	8.74	32	23.4	0.73	8.74	31.4	25	0.80	0.0032
11.7[1]	8.74	30.6	0.3	0.01	8.45	29.9	20.6	0.69	8.45	30.6	23.1	0.75	0.0030
11.9	8.45	58	10.2	0.18	8.74	50	40.1	0.80	9.03	45.6	42.9	0.94	
12.06	8.45	60.5	4	0.07	8.74	49	40.1	0.82	9.03	49	45	0.92	0.0053
12.79	8.74	56.6	0.5	0.01	8.74	55.3	43.8	0.79	9.03	54.5	50.6	0.93	0.0056
13.79	8.16	57.5	0.6	0.01	7.87	55.1	41.5	0.75	8.16	56.5	47.8	0.85	0.0052
15.74	8.45	52.1	0.5	0.01	7.58	45	38.1	0.85	9.61	44.4	41.4	0.93	0.0046

Syringes refilled on day 8, no measurements taken; [1]increase injection rate

Experiment 1D: Dec 9 - Dec 20, 1993

Time (h)	Filter 1: CMSW from exp. 1C				Filter 2: CF&Y (Scott's Farm)			
	flow (L/min)	inlet (ppm)	outlet (ppm)	C/Co	flow (L/min)	in	out	C/Co
48[1]	10.14	91.6	1.6	0.02	10.14	84	52.6	0.63
72						78	68	0.87
120						52.1	50.6	0.97
192	9.27	66.4	1.1	0.02	8.40	79.9	56.1	0.70

[1]Power failure previous day.
Problems with rotameters on day 4.

Experiment 1E: Jan 23 - Feb 3, 1994

Days	Filter 1: CL&Y + innoc				Filter 2: CL&Y + fert				Filter 3: CSS			
	flow (L/min)	inlet (ppm)	outlet (ppm)	C/Co	flow (L/min)	inlet	outlet	C/Co	flow (L/min)	inlet	outlet	C/Co
0.07	8.69	10.2	10.2	1.00	9.56	10.2	10.2	1.00	9.56	10.2	10.2	1.00
1	7.82	63.3	60.3	0.95	8.11	60.1	57	0.95	7.82	55.1	53.4	0.97
2.03[1]	7.53	11.2	11.2	1.00	8.69	8.9	0.7	0.08	8.69	12	1.1	0.09
2.17	7.53	19	18.1	0.95	8.69	20	1.1	0.06	8.69	24.9	2.1	0.08
2.88	7.24	35.7	31.4	0.88	8.69	23.1	1.6	0.07	8.40	23	0.8	0.03
4.23		66.9	61	0.91		72	17.1	0.24		72.5	7.4	0.10
6.22	5.79	136	121	0.89	7.24	129	62.9	0.49	6.66	114	48	0.42

[1]Condensation in supply lines resulted in 1/2 hour shut down 3 hours prior to recording of readings.
PID recalibrated on day 5.

Experiment 1F: May 25 - May 32, 1994

Days	Column 1: CL&Y + fert					Column 2: CL&Y				
	flow (L/min)	inlet (ppm)	outlet (ppm)	C/Co	M.load (g/min)	flow (L/min)	inlet	outlet	C/Co	M.Load (g/min)
0.58	8.11	52	47	0.90	0.00162	8.11	53	51	0.96	0.0016
1.04		42	38	0.90			41	40	0.98	
2	8.11	78	5.1	0.07	0.00243	8.11	80	64	0.80	0.0025
3	8.98	48	7.2	0.15	0.00165	8.98	47	42	0.89	0.0016
4.04	8.40	48	6.3	0.13	0.00155	8.69	44	38.5	0.88	0.0015
5	8.98	48	17.6	0.37	0.00165	8.98	42	38.6	0.92	0.0014

Experiment 2A: Acclimation Period

Started April 30, 1994.

	Filter 1: Toluene					Filter 3: BTX				Filter 2: BT			
Time (days)	Flow (L/min)	Inlet (ppm)	outlet (ppm)	C/Co	M-Load (g/min)	Flow (L/min)	in	out	C/Co	Flow	in	out	C/Co
0.92	5.21	137	1.4	0.01	0.00274	6.66	150	60	0.40	6.66	155	33.3	0.22
1.92	8.40	80	1	0.01	0.00258	8.98	94	16	0.17		96	1	0.01
4.04	9.85	65	0.9	0.01	0.00246	6.95	118	14	0.12		3.7	1.1	0.31
5.06	8.69	67	2.2	0.03	0.00224	9.27	58	9.1	0.16				
6.13	10.14	56	2.2	0.04	0.00218	9.27	65	6.4	0.10				
6.91	8.40	77	1	0.01	0.00248	7.82	94	7.4	0.08				
9.00[1]	9.85	63	0.9	0.01	0.00238	8.69	63	2.2	0.03				
9.77[2]	9.27	44	0.7	0.02	0.00157	8.98	57	1.1	0.02				
10.94		134	0.9	0.01			128	1.1	0.01				

[1]Contaminant flow stopped for 1 hour.
[2]Contaminant flow rate increased by factor of 2.
All concentrations in toluene equivalents.

Experiment 2A: May 4, 1994

Note: Concentrations less than 0.004 g/m^3 are extrapolated from the calibration curves

Filter 3
Flow = 9.60

Concentration (g/m^3)	(ppm)	Compound	Height (m)
0.0256	7.9	benzene	0.9
0.0076	2.0	toluene	0.9
0.0596	13.5	o-xylene	0.9
0.0203	6.2	benzene	0.9
0.0054	1.4	toluene	0.9
0.0528	11.9	o-xylene	0.9
0.0201	6.2	benzene	0.6
0.0065	1.7	toluene	0.6
0.0501	11.3	o-xylene	0.6
0.0180	5.5	benzene	0.6
0.0053	1.4	toluene	0.6
0.0557	12.6	o-xylene	0.6
0.0254	7.8	benzene	0.3
0.0107	2.8	toluene	0.3
0.0554	12.5	o-xylene	0.3
0.0255	7.8	benzene	0.3
0.0100	2.6	toluene	0.3
0.0523	11.8	o-xylene	0.3
0.0903	27.8	benzene	inlet
0.1026	26.7	toluene	inlet
0.0716	16.2	o-xylene	inlet
0.0987	30.3	benzene	inlet
0.1121	29.2	toluene	inlet
0.0749	16.9	o-xylene	inlet

Experiment 2A: May 4, 1994

Filter 1
Flow = 9.89
Toluene Concentrations

Concentration (g/m^3)	(ppm)	Height (m)
ND	0	0.9
ND	0	0.9
0.0086	2.2	0.6
0.0070	1.8	0.6
0.0028	0.7	0.3
0.0031	0.8	0.3
0.2096	54.6	inlet
0.1968	51.3	inlet

Experiment 2A: May 12, 1994

Filter 1
Flow = 8.11
Toluene Concentrations

Port	Conc (g/m^3)	(ppm)	Carbon Load (g/h)
out	0.0029	0.7	
out	0.0016	0.4	0.0010
0.6	0.0026	0.7	0.0011
0.3	0.1363	35.5	
0.3	0.1165	30.4	0.0561
inlet	0.6700	174.5	
inlet	0.6870	178.9	0.301

Experiment 2A: May 12, 1994

Filter 3
Flow = 7.82

CMPD	Port	Conc (g/m^3)	(ppm)	Ave Conc (g/m^3)	Carbon Load[1] (gC/h)
b	out	0.0000	0.0	0.0000	
t	out	0.0018	0.5	0.0018	
x	out	0.0004	0.1	0.0004	0.0009
b	0.6	0.0059	1.8		
t	0.6	0.0024	0.6		
x	0.6	0.0176	4.0		
b	0.6	0.0032	1.0	0.00454	
t	0.6	0.0020	0.5	0.00224	0.0072
x	0.6	0.0161	3.6	0.01685	
b	0.3	0.0159	4.9	0.0159	
t	0.3	0.0139	3.6	0.0139	0.0357
x	0.3	0.0538	12.2	0.0538	
b	in	0.2451	75.3		
t	in	0.2679	69.8		
x	in	0.2891	65.4		
b	in	0.2686	82.5	0.2568	
t	in	0.2737	71.3	0.2708	0.351
x	in	0.2952	66.7	0.2922	

[1]Carbon loading to each filter stage.

Experiment 2A: May 19, 1994

Filter 3
Flow = 8.69 L/min

CMPD	Port	Conc (g/m^3)	(ppm)	Ave Conc (g/m^3)	Carbon Load (g/h)
b	out	0.0006	0.2		
t		0.0003	0.1		
x		0.0621	14.0		
b	out	0.0019	0.6	0.0012	
t		0.0001	0.0	0.0002	
x		0.0695	15.7	0.0659	0.032
b	0.6	0.0854	26.2	0.0854	
t		0.0502	13.1	0.0502	
x		0.149	33.7	0.149	0.135
b	0.3	0.302	92.8		
t		0.281	73.1		
x		0.370	83.7		
b	0.3	0.311	95.6	0.307	
t		0.270	70.3	0.275	
x		0.356	80.5	0.363	0.450
b	in	0.423	130		
t		0.429	112		
x		0.445	101		
b	in	0.426	131	0.425	
t		0.428	112	0.429	
x		0.411	93	0.428	0.610

Experiment 2A: May 19, 1994

Filter 1
Flow = 8.98 L/min
Toluene Concentrations

Port	Conc. (g/m^3)	Ave	Carbon Load (g/h)
inlet	0.9601		
	1.0933	1.027	0.505
0.3	0.8843		
	0.8498	0.867	0.426
0.6	0.2699		
	0.2971	0.284	0.139
outlet	0.0003		
	0.0001	0.0002	0.0001

Experiment 2B

July 29th and 30th
Xylene concentrations
Flow = 9.27 L/min

Port	Concentration (g/m^3)	Average
Filter 2, Before Toluene Addition (July 29,1994)		
outlet		
outlet		
0.6	0.0043	
0.6	0.0047	0.0045
0.3	0.0532	
0.3	0.0537	0.0535
inlet	0.2754	
inlet	0.2715	0.274
Filter 1: July 30 1994		
outlet		
outlet		
0.6	0.0056	
0.6	0.0054	0.0055
0.3	0.0523	
0.3	0.0510	0.0516
inlet	0.2495	
inlet	0.2874	0.269

Experiment 2B

Toluene and Xylene Concentrations
Filter 2, After Toluene Addition, July 30, 1994.
Flow = 9.27 L/min

Cmpd	Port	Concentration (g/m^3)	Average
t	0.6		
x	0.6	0.0052	
t	0.6		
x	0.6	0.0058	0.0055
t	0.3	0.02943	
x	0.3	0.0784	
t	0.3	0.033544	0.0315
x	0.3	0.0790	0.0787
t	inlet	0.276448	
x	inlet	0.2791	
t	inlet	0.286524	0.282
x	inlet	0.2823	0.281

Experiment 3

Sept 5, 1994

Port	Concentration (g/m^3)	Average
Filter 2: Flow = 8.69 L/min		
outlet	0	
outlet	0	
outlet	0	0
0.6	0.017312	
0.6	0.01343	
0.6	0.015461	0.0154
0.3	0.508605	
0.3	0.488349	
0.3	0.439061	0.479
inlet	1.29471	
inlet	1.400208	
inlet	1.589915	1.428
Filter 1: Flow = 8.69		
outlet	0	
outlet	0.000066	
outlet	0.000059	0.00004
0.6	0.038263	
0.6	0.044832	
0.6	0.046005	0.0430
0.3	0.583377	
0.3	0.681654	
0.3	0.775864	0.680
inlet	1.42047	
inlet	1.870343	
inlet	1.434485	1.575

Experiment 3

Sept 6, 1994

Port	Concentration (g/m^3)	Mass Load (mg/h)	Average Conc
Filter 2: Flow = 8.95			
outlet	0.000109	0.06	
outlet	0.000107	0.06	
outlet	0.000078	0.04	0.0001
0.6	0.011726	6.52	
0.6	0.011347	6.31	
0.6	0.010969	6.10	0.0113
0.3	0.3193	178	
0.3	0.317705	177	
0.3	0.332545	185	0.323
0.0	0.91032	506	
0.0	0.900753	501	
0.0	0.872293	485	0.894
Filter 1 : Flow = 17.24			
outlet	0.002466	2.55	
outlet	0.002166	2.24	
outlet	0.001561	1.61	0.002
0.6	0.108804	113	
0.6	0.109742	114	
0.6	0.118775	123	0.1124
0.3	0.444177	459	
0.3	0.421217	436	
0.3	0.418321	433	0.428
0.0	0.546539	565	
0.0	0.543785	562	
0.0	0.550455	569	0.547

Filter 3: Flow = 25.8			
outlet	0.001684	2.61	
outlet	0.001543	2.39	
outlet	0.001558	2.41	0.00160
0.6	0.092648	143	
0.6	0.079546	123	
0.6	0.084053	130	0.0854
0.3	0.234899	364	
0.3	0.246539	382	
0.3	0.237021	367	0.239
0.0	0.33302	516	
0.0	0.36046	558	
0.0	0.338544	524	0.344

Experiment 3

Sept 8, 1994.

Port	Concentration (g/m^3)	Loading Rate (g/h)	Average Conc
Filter 1: Flow = 17.1			
outlet	0.460725	0.473	
outlet	0.452795	0.465	
outlet	0.447591	0.459	0.454
0.6	0.799174	0.820	
0.6	0.841311	0.863	
0.6	0.817838	0.839	0.819
0.3	1.112756	1.142	
0.3	1.111429	1.140	
0.3	1.116788	1.146	1.114
0.0	1.215869	1.247	
0.0	1.244933	1.277	
0.0	1.222232	1.254	1.228
Filter 2: Flow = 8.69			
outlet	0.446068	0.233	
outlet	0.43773	0.228	
outlet	0.419861	0.219	0.435
0.6	1.327557	0.692	
0.6	1.324243	0.690	
0.6	1.325223	0.691	1.326
0.3	1.876164	0.978	
0.3	1.900129	0.991	
0.3	1.885988	0.983	1.887
0.0	2.240558	1.168	
0.0	2.376719	1.239	
0.0	2.356915	1.229	2.32

Filter 3: Flow = 26.1			
outlet	0.383336	0.600	
outlet	0.372399	0.583	
outlet	0.367976	0.576	0.374
0.6	0.546233	0.855	
0.6	0.54615	0.855	
0.6	0.550051	0.861	0.548
0.3	0.670186	1.049	
0.3	0.663494	1.039	
0.3	0.677461	1.060	0.670
0.0	0.74917	1.173	
0.0	0.757027	1.185	
0.0	0.788355	1.234	0.765

Experiment 4: Toluene Sorption Study

Sept ,1994

TRIAL 1

filter mass = 3682 g
flow reading of 38; flow = 10.4 L/min

TIME (min)	INLET (ppm)	OUTLET (ppm)	C/Co (-)
0.917	93.5		
1.217		28.7	0.30
1.416		31	0.33
1.833		37	0.39
2		39	0.41
2.383	96		
2.833		58.7	0.60
3		60.6	0.62
3.167		62.8	0.64
3.75	99.6		
4.167		73.1	0.73
4.4167		74.4	0.75
4.583		75.4	0.76
4.917	100		
5.167	100		
5.583		78.9	0.79
5.75		80.2	0.80
6		81.6	0.81
6.167		82.6	0.82
6.75	101		
7.25		84.5	0.83
7.417		85	0.83
7.583		85.8	0.84
7.833		86.2	0.85
8		86.7	0.85
8.417	103		
8.667	102		
8.917	102		
9.25		88.7	0.86
9.583		89.1	0.87
10		90.2	0.88
10.417	104		
10.75	104		
11.25		91.5	0.88
12		92.5	0.89

12.667	105		
13.5		93.5	0.88
14.5		94.9	0.89
15.167	108		
16	107		
16.75		98	0.90
17.75		99	0.91
18.417	111		
19		101	0.84
20		103	0.85
21	130		
21.583		114	0.89
22.583		117	0.91
23.333	127		
23.916		117	0.92
24.5	127		
25.5		118	0.93
26	126		
26.5	125		
27	125		
27.667		118	0.95
28.667		118	0.95
29.333	124		
30		118	0.95

TRIAL 2

filter mass = 3767 g
Flow reading of 40: flow = 11.0 L/min

TIME (min)	INLET (ppm)	OUTLET (ppm)	C/Co (-)
0.5	124		
1.167		28	0.218
1.417		36.9	0.287
1.667		44.3	0.345
2	133		
2.333		62.8	0.465
2.583		68.5	0.507
2.833		73.9	0.547
3.25	137		
3.5	137		
3.833		88.2	0.644
4.0833		91.1	0.665
4.333		93.8	0.685

4.75	137		
5.167		104	0.754
5.417		106	0.768
5.667		107	0.775
6	139		
6.25	139		
6.667		108	0.774
7		110	0.789
7.416	140		
8		113	0.807
8.416	140		
9		113	0.807
9.416	140		
10		115	0.824
10.416	139		
11		119	0.853
11.416	140		
12		120	0.860
12.416	139		
13		120	0.857
13.416	139		
14		121	0.873
14.416	138		
15		121	0.877
15.416	138		
16		122	0.884
16.5	138		
17		122	0.884
17.5	138		
18		123	0.891

APPENDIX B

STATISTICAL ANALYSIS

OUTPUT FROM SAS PROGRAMS

Data Analysis, Experiment 3
2-WAY ANOVA Comparison of Filters With Different Flow Rates

Data from Sept. 6, 1994
Units of mg/h

Analysis of Variance Procedure
Class Level Information

Class	Levels	Values
FILTER	3	1 2 3
HT	4	0 0.3 0.6 0.9

Number of observations in data set = 36

Analysis of Variance Procedure

Dependent Variable: MLOAD

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	11	1715330.569	155939.143	1695.19	0.0001
Error	24	2207.745	91.989		
Corrected Total	35	1717538.314			

R-Square	C.V.	Root MSE	MLOAD Mean
0.998715	4.040677	9.591108	237.3639

Source	DF	Anova SS	Mean Square	F Value	Pr > F
FILTER	2	82467.580	41233.790	448.25	0.0001
HT	3	1569383.489	523127.830	5686.83	0.0001
FILTER*HT	6	63479.501	10579.917	115.01	0.0001

PAIR-WISE TESTING

T tests (LSD) for variable: MLOAD

NOTE: This test controls the type I comparisonwise error rate not the experimentwise error rate.

Alpha= 0.05, Confidence= 0.95, df= 24, MSE= 91.98936, Critical Value of T= 2.06390, Least Significant Difference= 8.0813

Comparisons significant at the 0.05 level are indicated by '***'.

FILTER Comparison		Lower Confidence Limit	Difference Between Means	Upper Confidence Limit	
1	- 3	14.135	22.217	30.298	***
1	- 2	102.718	110.799	118.880	***
3	- 1	-30.298	-22.217	-14.135	***
3	- 2	80.501	88.583	96.664	***
2	- 1	-118.880	-110.799	-102.718	***
2	- 3	-96.664	-88.583	-80.501	***

Tukey's Studentized Range (HSD) Test for variable: MLOAD

NOTE: This test controls the type I experimentwise error rate.

Alpha= 0.05 Confidence= 0.95 df= 24 MSE= 91.98936
Critical Value of Studentized Range= 3.532
Minimum Significant Difference= 9.7783

Comparisons significant at the 0.05 level are indicated by '***'.

FILTER Comparison		Simultaneous Lower Confidence Limit	Difference Between Means	Simultaneous Upper Confidence Limit	
1	- 3	12.438	22.217	31.995	***
1	- 2	101.021	110.799	120.577	***
3	- 1	-31.995	-22.217	-12.438	***
3	- 2	78.804	88.583	98.361	***
2	- 1	-120.577	-110.799	-101.021	***
2	- 3	-98.361	-88.583	-78.804	***

Scheffe's test for variable: MLOAD

NOTE: This test controls the type I experimentwise error rate but generally has a higher type II error rate than Tukey's for all pairwise comparisons.

Alpha= 0.05 Confidence= 0.95 df= 24 MSE= 91.98936
Critical Value of F= 3.40283

Minimum Significant Difference= 10.215

Comparisons significant at the 0.05 level are indicated by '***'.

FILTER Comparison	Simultaneous Lower Confidence Limit	Difference Between Means	Simultaneous Upper Confidence Limit	
1 - 3	12.002	22.217	32.431	***
1 - 2	100.584	110.799	121.014	***
3 - 1	-32.431	-22.217	-12.002	***
3 - 2	78.368	88.583	98.797	***
2 - 1	-121.014	-110.799	-100.584	***
2 - 3	-98.797	-88.583	-78.368	***

Exp 3: Data Sept. 8, 1994

Units g/h

Class Level Information

Class	Levels	Values
FILTER	3	1 2 3
HT	4	0 0.3 0.6 0.9

Number of observations in data set = 36

Dependent Variable: MLOAD

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	11	3.55699067	0.32336279	1060.30	0.0001
Error	24	0.00731933	0.00030497		
Corrected Total	35	3.56431000			

R-Square	C.V.	Root MSE	MLOAD Mean
0.997946	1.993545	0.017463	0.876000

Source	DF	Anova SS	Mean Square	F Value	Pr > F
FILTER	2	0.17153117	0.08576558	281.22	0.0001
HT	3	3.26127200	1.08709067	3564.56	0.0001

FILTER*HT	6	0.12418750	0.02069792	67.87	0.0001

PAIR-WISE TESTING

T tests (LSD) for variable: MLOAD

NOTE: This test controls the type I comparisonwise error rate not the experimentwise error rate.

Alpha= 0.05 Confidence= 0.95 df= 24 MSE= 0.000305
Critical Value of T= 2.06390
Least Significant Difference= 0.0147

Comparisons significant at the 0.05 level are indicated by '***'.

FILTER Comparison	Lower Confidence Limit	Difference Between Means	Upper Confidence Limit	
1 - 3	-0.010131	0.004583	0.019298	
1 - 2	0.133952	0.148667	0.163381	***
3 - 1	-0.019298	-0.004583	0.010131	
3 - 2	0.129369	0.144083	0.158798	***
2 - 1	-0.163381	-0.148667	-0.133952	***
2 - 3	-0.158798	-0.144083	-0.129369	***

Tukey's Studentized Range (HSD) Test for variable: MLOAD

NOTE: This test controls the type I experimentwise error rate.

Alpha= 0.05 Confidence= 0.95 df= 24 MSE= 0.000305
Critical Value of Studentized Range= 3.532
Minimum Significant Difference= 0.0178

Comparisons significant at the 0.05 level are indicated by '***'.

FILTER Comparison	Simultaneous Lower Confidence Limit	Difference Between Means	Simultaneous Upper Confidence Limit	
1 - 3	-0.013221	0.004583	0.022388	
1 - 2	0.130862	0.148667	0.166471	***

3	- 1	-0.022388	-0.004583	0.013221	
3	- 2	0.126279	0.144083	0.161888	***
2	- 1	-0.166471	-0.148667	-0.130862	***
2	- 3	-0.161888	-0.144083	-0.126279	***

Scheffe's test for variable: MLOAD

NOTE: This test controls the type I experimentwise error rate but generally has a higher type II error rate than Tukey's for all pairwise comparisons.

Alpha= 0.05 Confidence= 0.95 df= 24 MSE= 0.000305
Critical Value of F= 3.40283
Minimum Significant Difference= 0.0186

Comparisons significant at the 0.05 level are indicated by '***'.

FILTER Comparison		Simultaneous Lower Confidence Limit	Difference Between Means	Simultaneous Upper Confidence Limit	
1	- 3	-0.014016	0.004583	0.023182	
1	- 2	0.130068	0.148667	0.167266	***
3	- 1	-0.023182	-0.004583	0.014016	
3	- 2	0.125484	0.144083	0.162682	***
2	- 1	-0.167266	-0.148667	-0.130068	***
2	- 3	-0.162682	-0.144083	-0.125484	***

Experiment 2A
Comparison of Removal Effeciency of Benzene, Toluene, Xylene For Filter 3

Comparison on the basis of C/Co using average inlet Co.

2-WAY ANOVA unequal replication using PROC GLM

Data from May 12, 1994.

MLOAD refers to C/Co
General Linear Models Procedure

Class Level Information

Class	Levels	Values
FILTER	3	1 2 3
HT	4	0 0.3 0.6 0.9

Number of observations in data 18 23

Dependent Variable: MLOAD

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	11	3.72330489	0.33848226	427.78	0.0001
Error	6	0.00474750	0.00079125		
Corrected Total	17	3.72805239			

R-Square	C.V.	Root MSE	MLOAD Mean
0.998727	7.830574	0.028129	0.359222

Source	DF	Type I SS	Mean Square	F Value	Pr > F
FILTER	2	0.00484743	0.00242371	3.06	0.1211
HT	3	3.71044356	1.23681452	1563.11	0.0001
FILTER*HT	6	0.00801390	0.00133565	1.69	0.2703

Source	DF	Type III SS	Mean Square	F Value	Pr > F
FILTER	2	0.00604152	0.00302076	3.82	0.0852
HT	3	3.71044356	1.23681452	1563.11	0.0001
FILTER*HT	6	0.00801390	0.00133565	1.69	0.2703

Data From May 19, 1994

Class Level Information

Class	Levels	Values
FILTER	3	1 2 3
HT	4	0 0.3 0.6 0.9

Number of observations in data set = 21

Dependent Variable: MLOAD

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	11	3.33500121	0.30318193	581.95	0.0001

Error	9	0.00468875	0.00052097
Corrected Total	20	3.33968995	

R-Square	C.V.	Root MSE	MLOAD Mean
0.998596	4.201510	0.022825	0.543252

Source	DF	Type I SS	Mean Square	F Value	Pr > F
FILTER	2	0.06956605	0.03478302	66.77	0.0001
HT	3	3.23322304	1.07774101	2068.71	0.0001
FILTER*HT	6	0.03221212	0.00536869	10.31	0.0013

Source	DF	Type III SS	Mean Square	F Value	Pr > F
FILTER	2	0.07436453	0.03718227	71.37	0.0001
HT	3	3.23322304	1.07774101	2068.71	0.0001
FILTER*HT	6	0.03221212	0.00536869	10.31	0.0013

T tests (LSD) for variable: MLOAD

NOTE: This test controls the type I comparisonwise error rate not the experimentwise error rate.

Alpha= 0.05 Confidence= 0.95 df= 9 MSE= 0.000521
Critical Value of T= 2.26216
Least Significant Difference= 0.0276

Comparisons significant at the 0.05 level are indicated by '***'.

FILTER Comparison	Lower Confidence Limit	Difference Between Means	Upper Confidence Limit	
3 - 1	0.07269	0.10029	0.12788	***
3 - 2	0.10836	0.13596	0.16356	***
1 - 3	-0.12788	-0.10029	-0.07269	***
1 - 2	0.00807	0.03567	0.06327	***
2 - 3	-0.16356	-0.13596	-0.10836	***
2 - 1	-0.06327	-0.03567	-0.00807	***

Exp 3A: Data from May 12, 1994
Compare Mass Carbon Removal Effeciency Between Filters 1 and 3
2-Way ANOVA Unequal Replication

General Linear Models Procedure
Class Level Information

Class	Levels	Values
FILTER	2	1 2
HT	4	0 0.3 0.6 0.9

Number of observations in data set = 13

Dependent Variable: MLOAD, MLOAD = carbon removal effeciency

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	7	2.49275926	0.35610847	1052.38	0.0001
Error	5	0.00169192	0.00033838		
Corrected Total	12	2.49445119			

R-Square	C.V.	Root MSE	MLOAD Mean
0.999322	5.262151	0.018395	0.349576

Source	DF	Type I SS	Mean Square	F Value	Pr > F
FILTER	1	0.00127222	0.00127222	3.76	0.1102
HT	3	2.48682084	0.82894028	2449.70	0.0001
FILTER*HT	3	0.00466621	0.00155540	4.60	0.0669

Source	DF	Type III SS	Mean Square	F Value	Pr > F
FILTER	1	0.00066550	0.00066550	1.97	0.2197
HT	3	2.41687120	0.80562373	2380.79	0.0001
FILTER*HT	3	0.00466621	0.00155540	4.60	0.0669

Data From May 19, 1994

Class Level Information

Class	Levels	Values
FILTER	2	1 2
HT	4	0 0.3 0.6 0.9

Number of observations in data set = 15

Dependent Variable: MLOAD

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	7	2.40936399	0.34419486	247.04	0.0001
Error	7	0.00975278	0.00139325		
Corrected Total	14	2.41911677			

R-Square	C.V.	Root MSE	MLOAD Mean
0.995968	6.961235	0.037326	0.536203

Source	DF	Type I SS	Mean Square	F Value	Pr > F
FILTER	1	0.00062104	0.00062104	0.45	0.5258
HT	3	2.39495900	0.79831967	572.99	0.0001
FILTER*HT	3	0.01378395	0.00459465	3.30	0.0877

Source	DF	Type III SS	Mean Square	F Value	Pr > F
FILTER	1	0.00264560	0.00264560	1.90	0.2106
HT	3	2.38088018	0.79362673	569.62	0.0001
FILTER*HT	3	0.01378395	0.00459465	3.30	0.0877

MODEL FITTING
NON-LINEAR REGRESSION

Model Fitting: Experiemnt 1A

C/Co vs Height
Lumped Data

Non-Linear Least Squares Iterative Phase
Dependent Variable CCO Method: Marquardt

NOTE: Convergence criterion met.

Non-Linear Least Squares Summary Statistics Dependent Variable CCO

Source	DF	Sum of Squares	Mean Square
Regression	1	4.1280988966	4.1280988966
Residual	15	0.0208869775	0.0013924652
Uncorrected Total	16	4.1489858741	
(Corrected Total)	15	2.6543952704	

Parameter	Estimate	Asymptotic Std. Error	Asymptotic 95 % Confidence Interval Lower	Upper
K	5.755454442	0.32809601909	5.0561369898	6.4547718941

Experiemnt 3

C/Co vs Height

NOTE: Convergence criterion met.

Non-Linear Least Squares Summary Statistics Dependent Variable CCO

Source	DF	Sum of Squares	Mean Square
Regression	1	2.2707434002	2.2707434002
Residual	7	0.0289555998	0.0041365143
Uncorrected Total	8	2.2996990000	
(Corrected Total)	7	1.3161958750	

Parameter	Estimate	Asymptotic Std. Error	Asymptotic 95 % Confidence Interval Lower	Upper
K	3.797770725	0.38623231695	2.8844690901	4.7110723607

APPENDIX C

QA/QC RESULTS

TOLUENE CALIBRATION PROCEDURE

Repeatability Test

- 500 uL pure toluene + 10 ml methanol repeated 3 times
- 10 uL injected each bag
- 4 samples withdrawn from each bag

- bag concentration - 0.206 g/m^3

CV = coefficient of variation
sd = standard deviation

RESULTS

DATE	TIME	RUN	AREA	RT	Worst Case Relative Error
Standard Vial 1					
09/22/94	21:46:45	Run 5	37180396	2:54	
09/22/94	21:51:07	Run 6	37271000	2:54	2.36 %
09/22/94	21:55:29	Run 7	36776800	2:54	
09/22/94	21:59:51	Run 8	36815292	2:54	
		ave	37010872		
		sd	251294		
		CV	0.68	%	
Standard vial 2					
09/22/94	22:04:13	Run 9	36077752	2:54	
09/22/94	22:08:35	Run 10	35993936	2:54	
09/22/94	22:12:57	Run 11	36059608	2:54	
09/22/94	22:17:19	Run 12	36187404	2:54	
		ave	36079675		
		sd	80339		
		CV	0.22	%	
Standard Vial 3					
09/22/94	22:21:41	Run 13	36464744	2:54	
09/22/94	22:26:03	Run 14	35922624	2:54	
09/22/94	22:30:25	Run 15	35801040	2:54	-1.68 %
09/22/94	22:34:48	Run 16	36396668	2:54	
		ave	36146269		
		sd	333330		
		CV	0.92	%	
		overall mean	36412272		
		overall sd	495520		
		overall CV	1.36	%	

CO_2 CALIBRATION PROCEDURE

Sample Repeatability
Performed Aug 10, 1994

1) Four tedlar bags were prepared using dilutions of a CO_2 gas standard (82700 ppm, Matheson). 2) Five 10 mL samples were withdrawn from each bag and injected into the GC.
3) A sample of a known CO_2 standard was injected into the GC and compared against predictions from the calibration curve.

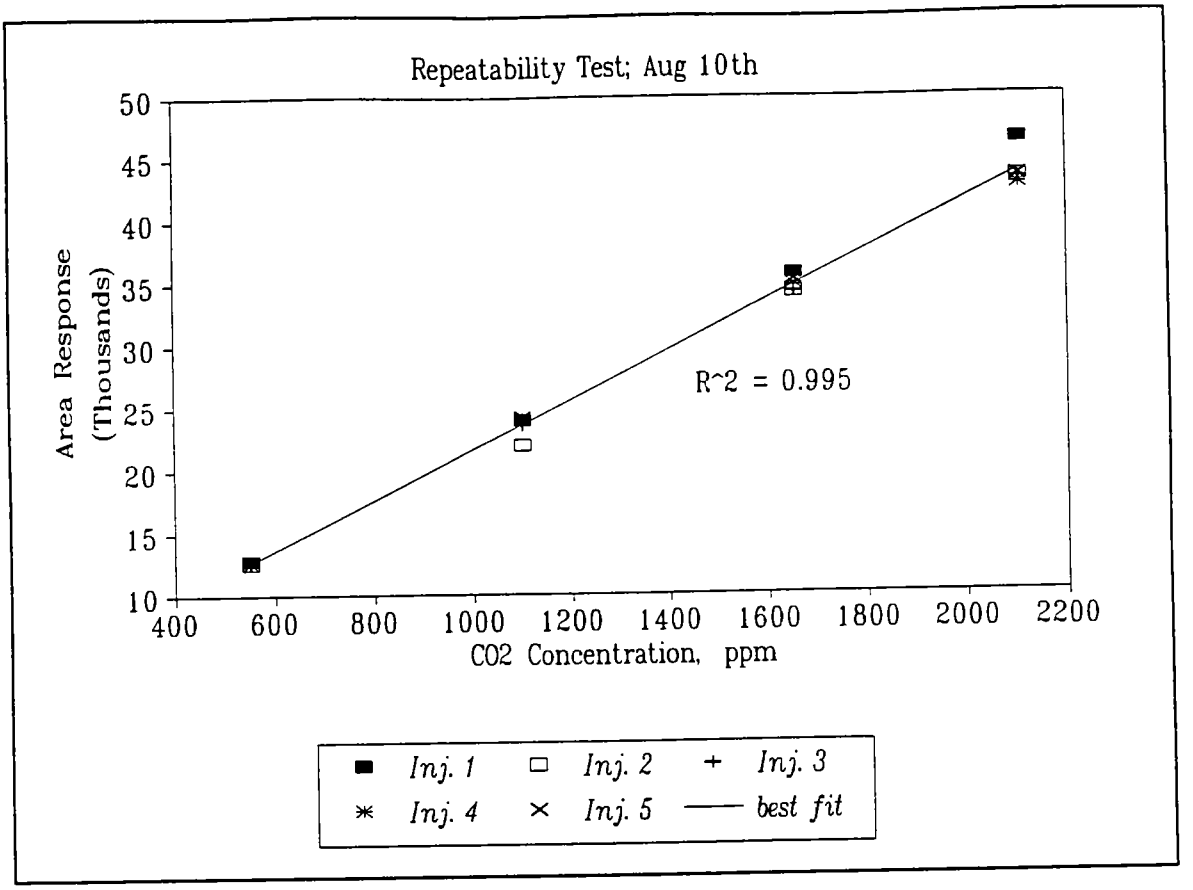
RESULTS

				Area Response						
Bag #	Vol CO_2	Vol N_2	CO_2 Conc.	Inj. 1	Inj. 2	Inj. 3	Inj. 4	Inj. 5	ave.	sd
1	10	1500	551	12813	12532	12564	12574	12817	12660	127
2	20	1500	1103	24028	21923	23571	24279	24154	23591	868
3	30	1500	1654	35750	34204	34168	34791	35209	34824	604
4	40	1570	2107	46342	43293	43115	42719	43414	43777	1304

The following figure illustrates the calibration curve for the above values.

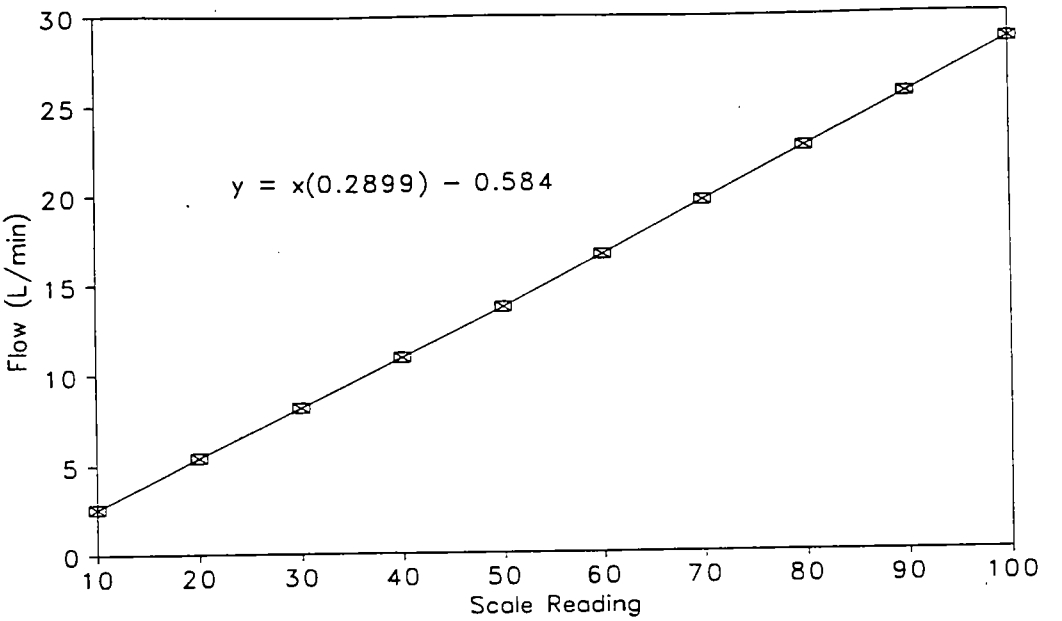
Calibration Curve Check:

predicted from curve:	823	856 ppm
actual value:	821	821 ppm
relative error:	+0.2%	+4.4%

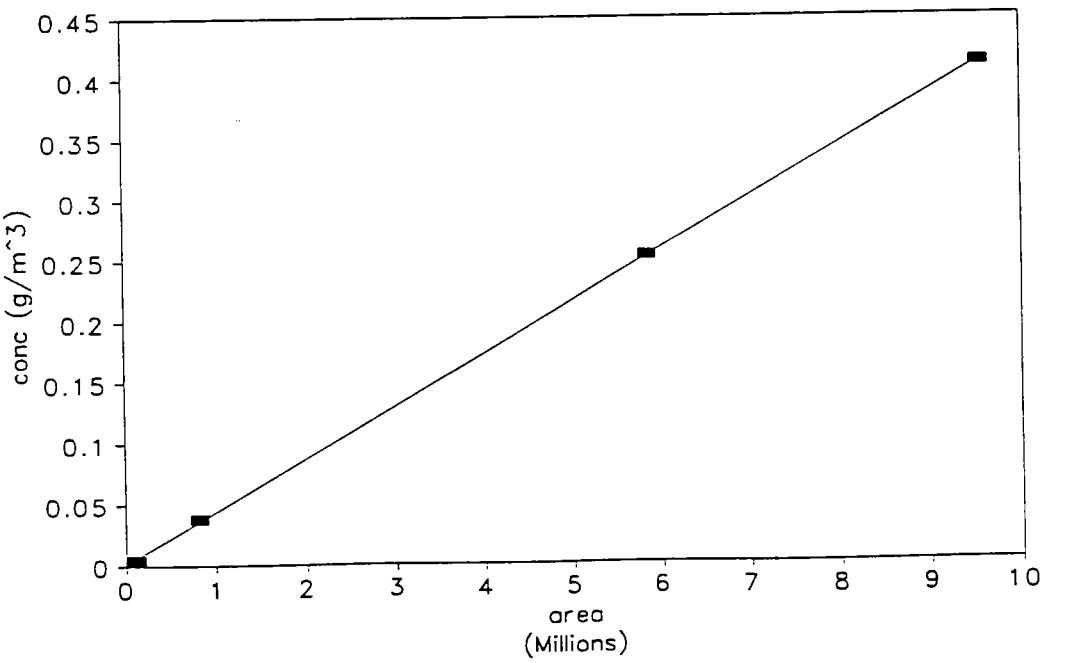

Repeatability Test; Aug 10th
Area Response (Thousands)
50
45
40
35
30
25
20
15
10
400
600
800
1000
1200
1400
1600
1800
2000
2200
CO2 Concentration, ppm
R^2 = 0.995
Inj. 1
Inj. 2
Inj. 3
Inj. 4
Inj. 5
best fit

APPENDIX D

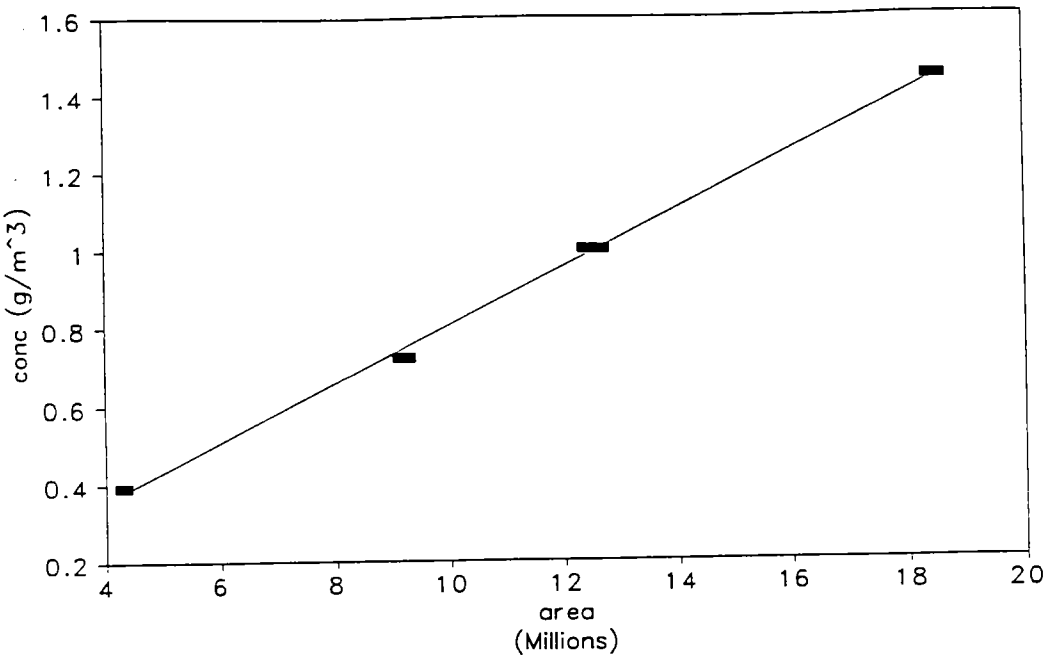
SAMPLE CALIBRATION CURVES



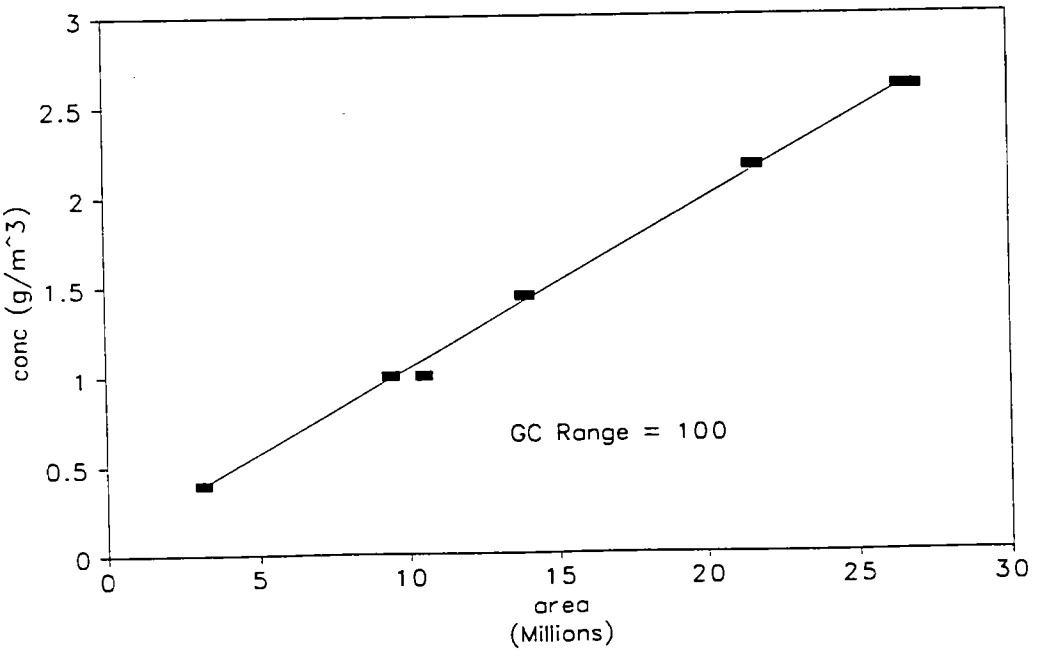
Rotameter Calibration Curve:



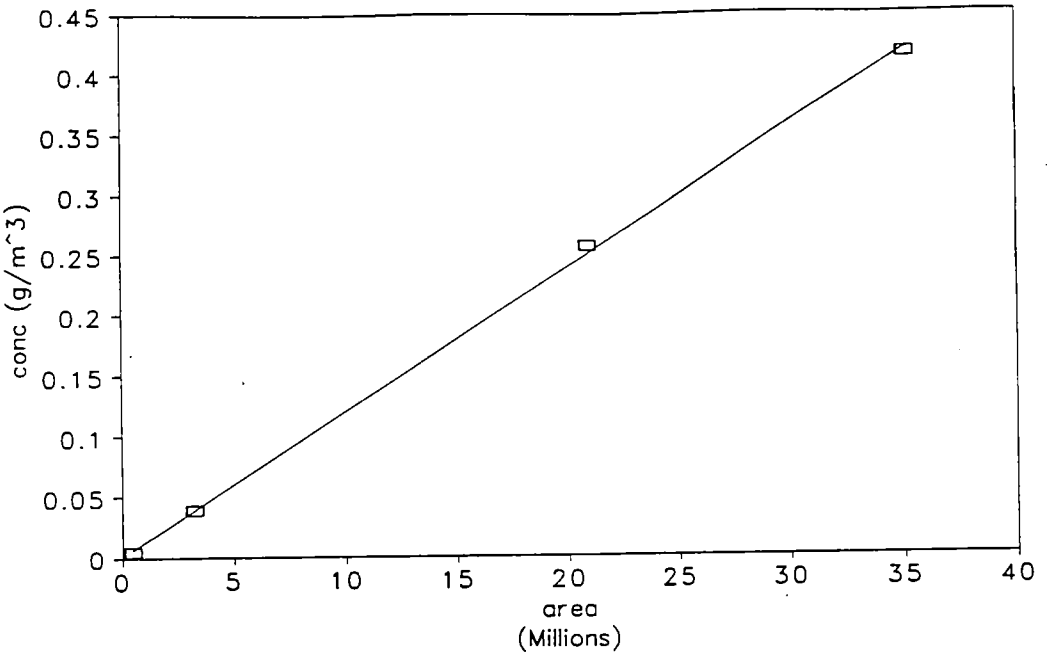
Toluene Calibration Curve: May 12, 1994



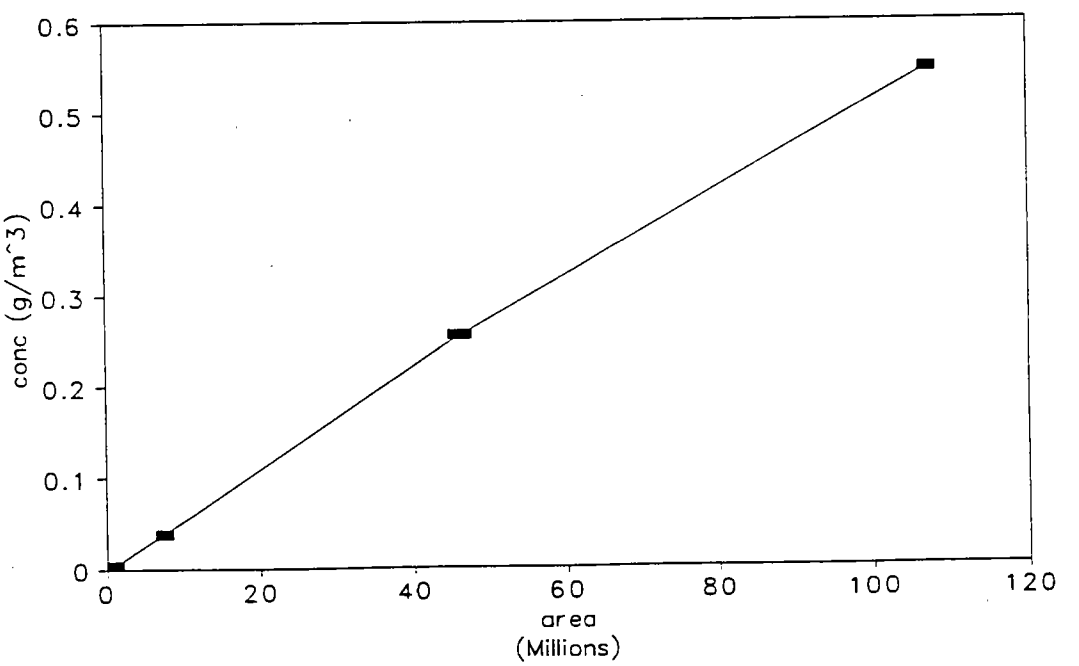
Toluene Calibration Curve: Sept. 7, 1994 (GC Range = 100)



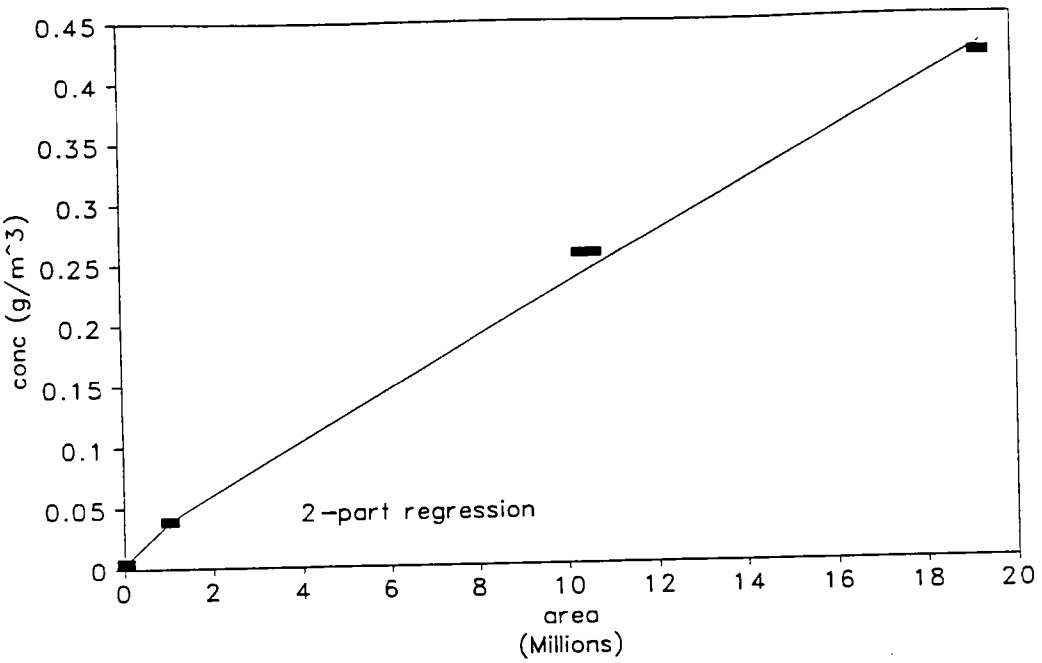
Toluene Calibration Curve: Linearity Check Oct., 1994 (GC Range = 100)



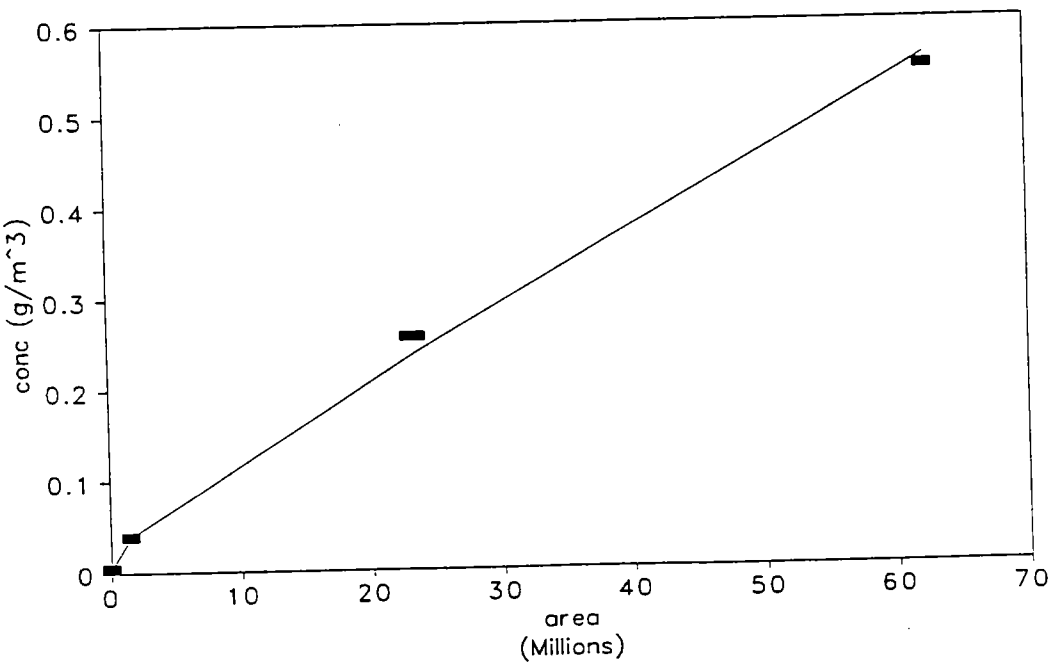
Benzene Calibration Curve: May 4, 1994



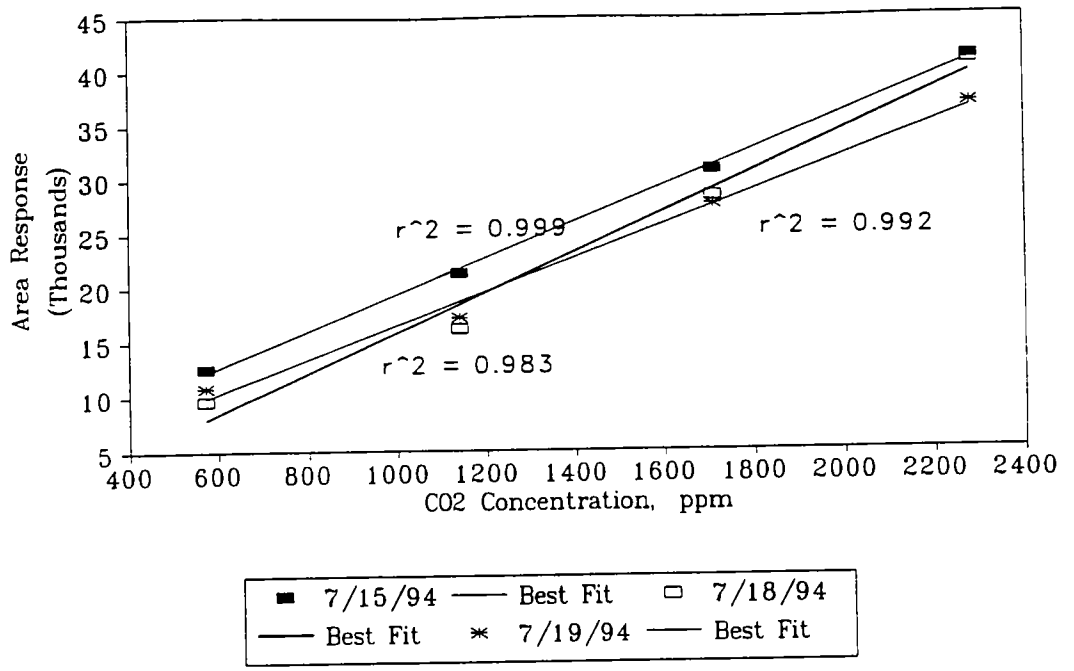
Benzene Calibration Curve: May 19, 1994



o-Xylene Calibration Curve: May 4, 1994



o-Xylene Calibration Curve: May 19, 1994



CO_2 Calibration Curves