Granular Activated Carbon Sorption as a Load Equalization Mechanism in Operation of Air Pollution Control Devices

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GRANULAR ACTIVATED CARBON SORPTION
AS A LOAD EQUALIZATION MECHANISM
IN OPERATION OF AIR POLLUTION CONTROL DEVICES

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Civil and Environmental Engineering

by

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ABSTRACT

Transient periods of unsteady loading pose a challenge in design and operation of bioreactors for air pollution control. As a potential means of overcoming some of these challenges, a systematic study of granular activated carbon (GAC) sorption was conducted to further evaluate its potential as a load equalization mechanism for unsteady loading of volatile organic carbons (VOCs). GAC columns were experimentally tested under dynamic loading conditions involving variations in contaminant concentrations, gas flow rates, and relative humidity. Toluene was used as model VOC, and BPL 4×6 mesh GAC was used as a model adsorbent.

The research was divided into four tasks. These involved evaluation of GAC load equalization for transient loading conditions involving: (1) intermittent toluene loading with contaminant non-loading intervals occurring for relatively long periods of time (e.g., two to seven days); (2) intermittent toluene loading with high relative humidity gas streams; (3) loading condition characterized by a single concentration spike and a series of concentration spikes of various intensity and duration; and (4) intermittent loading with turndown of air flow rates during pollutant non-loading periods.

Collectively, experimental testing and results from simulations performed using a pore and surface diffusion model (PSDM) demonstrated that GAC columns have the potential to serve as an effective strategy in management of a wide variety of transient loading conditions. GAC columns can provide a more even and attenuated loading concentration when dynamically varying concentration spikes in influent occur and provide supplemental feed during intervals when no contaminants would otherwise be supplied to the biofilter. Such performance proved to be viable even in conditions of high gas humidity and intermittently reduced flow rates. Overall,
GAC sorption may prove practical application in alleviating adverse impacts of starvation conditions in bioreactors, dampening spikes in contaminant concentrations to prevent reduction in treatment efficiency, and in reducing costs due to reduced size requirement for the downstream air pollution control device.
CHAPTER 1
INTRODUCTION

1.1 Rationale

In recent years, biological systems have been applied to treat gas-phase contaminants produced from a wide variety of sources. Advantages of these systems generally include relatively low cost, environmental safe operation, and high pollutant removal efficiency. Biological treatment options are particularly attractive in comparison to physical/chemical treatment technologies (e.g., incineration, adsorption) when treating volatile organic compounds (VOCs) present at low concentrations in high-volumetric flows. High volumetric flows containing low concentrations of the contaminant are generally more expensive to treat by conventional physico-chemical methods. In particular, biofilters are among the most widely used biological systems for air pollution control. A biofilter is a packed-bed, attached-growth biological reactor in which microorganisms grow attached to a support medium. Contaminants in the gas stream passing through the bed serve as carbon and energy source for the microbial population. Despite numerous successful installations, however, biofilter systems may experience diminished performance when subjected to transient feed conditions and process shutdowns as they frequently occur in field applications (Webster et al., 1999).

In many real-world application, contaminated gas stream properties are highly variable with respect to time. Dynamic variation in contaminant composition, concentration, and gas flow rate pose a challenge in applying biofiltration as an air pollution control technology. For instance, elevated contaminant concentration levels can exceed treatment capacity, resulting in appreciable contaminant breakthrough and failure to achieve target treatment efficiency. On the other hand, very low pollutant concentrations may cause starvation conditions that can result in
reduced biomass and treatment efficiency. Ultimately, dynamically-varying characteristics of a waste gas can make it difficult to provide a rational basis for biofilter design.

Previous studies have demonstrated that columns packed with granular activated carbon (GAC) can serve as passively-controlled load equalization devices as a pre-treatment step prior to treating contaminated gases via biofiltration in some cases. The rationale for such system is that GAC columns can temporarily accumulate contaminants during intervals of high influent pollutant concentration and then desorb contaminants during intervals of lower loading. This can result in equalized contaminant concentration levels. Use of such systems has the potential to mitigate many of the adverse impacts of unsteady loading on biofilter performance. Several facets of GAC load equalization systems, however, remain unexplored.

1.2 Objectives

The overall objective of research described in this dissertation was to evaluate the potential benefits of GAC columns as load equalization devices for air pollution control systems (e.g., biofilters) treating VOCs in gas streams under various dynamic loading conditions. Four specific objectives were to:

(1) Evaluate the potential for passively-operated GAC pre-treatment systems to mitigating the adverse effects of long-term periods of no contaminant loading (i.e., process shutdowns);

(2) Determine the effect of relative humidity on load equalization by GAC columns subjected to intermittent loading;

(3) Evaluate the potential of passively-operated GAC pre-treatment systems to mitigate adverse effects of transient spikes of contaminant concentrations; and
(4) Evaluate the effects of decreasing gas flow rates during contaminant non-loading intervals on GAC load equalization performance.

1.3 Scope and Organization of Dissertation

This dissertation is organized as follows. Chapter 2 provides a literature review pertinent to the studies conducted. An overview of biofiltration, projected as the main application of GAC load attenuation, is provided, along with review of the unsteady loading condition which can pose design challenge for biofilters. Various strategies previously investigated to manage unsteady loading are presented, with particular attention to GAC column adsorption. Pertinent to GAC column load equalization, a brief review of the process and modeling of adsorption is also presented.

Chapter 3 summarizes results from a modeling activity conducted to assess how columns packed with granular activated carbon (GAC) can be utilized to provide supplemental feed of volatile organic compounds (VOCs) to biofilters during long-term (>2 days) periods of low or no loading. A pore and surface diffusion model (PSDM), previously calibrated from experimental data, was used to simulate the dynamics of VOC adsorption and desorption in GAC columns subjected to weekend (i.e., two day) and extended shutdown (i.e., one week) periods.

Chapter 4 describes results from experiments and model simulations conducted to evaluate load equalization processes during unsteady contaminant loading in high humidity gas streams. A series of experiments was conducted with columns packed with GAC subjected to intermittent toluene loading in air streams containing up to 90% relative humidity. Model simulations were conducted in an effort to understand and explain the mechanisms of adsorption pertinent to GAC load attenuation under high water vapor concentrations.
Chapter 5 addresses GAC column performance under highly dynamic condition of loading. Results from experiments and numerical modeling conducted to assess the potential for using granular activated carbon (GAC) columns to attenuate peak loading of highly variable toluene concentrations are presented. The experimental regime included testing of GAC columns subjected to isolated spikes in toluene concentration as well as complex loading patterns involving multiple spikes in series, intended to simulate the highly dynamic, complex loading conditions commonly encountered in industrial applications. A MATLAB code was used to implement a pore and surface diffusion model to allow simulation of transient loadings of varying intensity and duration.

Chapter 6 summarizes results from experiments conducted to assess GAC column performance when gas flow rate during the non-loading period is reduced. A simple mass-balance model, validated by experimental data gathered for various loading concentrations and flow rates is presented.

Overall conclusions and recommendations for further research are outlined in Chapter 7. All reference materials cited are listed in the “References” section. Supplementary materials referenced in some chapters of this dissertation appear in appendices.
CHAPTER 2
LITERATURE REVIEW

This chapter presents an overview of biofiltration in Section 2.1. Section 2.2 contains a summary of challenges posed by transient loading in the design and operation of biofiltration systems. Section 2.3 describes various operating strategies and design modifications that have been introduced in previously reported attempts to improve performance of biofilters subjected to unsteady loading conditions. Adsorption, an essential component of the research described in this dissertation, is reviewed in Section 2.4. The pore and surface diffusion model (PSDM) which was employed to describe adsorption dynamics in fixed beds, is discussed in Section 2.5. A brief overview of the ideal adsorbed solution theory (IAST), used to describe multi-component adsorption, is presented in Section 2.6.

2.1 Overview of Biofiltration

A biofilter is a packed-bed, fixed-film bioreactor used to treat gas-phase contaminants. Biofilters have found increasing popularity in three general markets: (1) treatment of odors; (2) treatment of VOCs and hazardous air pollutants (HAPs); and (3) treatment of petroleum hydrocarbons (Devliny et al., 1999). Biofilters are an attractive treatment technology due to their comparatively low cost, operational simplicity, and lack of secondary pollutant generation.

In a biofilter, microorganisms growing attached to the solid support medium in a biofilm layer transform contaminant in the gas stream as it passes through the medium. The different steps in the overall process of contaminant transformation within a biofilter are largely sequential (Devliny, et al., 1999). Figure 2.1 depicts the basic elements of contaminant transport and degradation in a biofilter. The process begins with contaminant transport from the bulk gas stream, by advection and diffusion processes, to a water and biofilm layer attached to a solid
support medium. The contaminants may dissolve in water, be taken up by living microbial cells, adsorb to the packing medium or biofilm organic matter, absorb within organic matter in the biofilm or packing medium, or collect at the surface of the water. Contaminants entering the biofilm can be metabolized by microorganisms which produce CO₂, water, biomass, and other metabolic by-products. Consumption of contaminants within the biofilm results in concentration gradients that serve as a driving force for contaminant transport from air to the water/biofilm layer. Untransformed contaminants may exit the system with the gaseous products in the effluent.
It is generally assumed that contaminated gas streams pass through biofilters in an essentially plug-flow manner. As contaminants are consumed by microorganisms along the length of the biofilter, progressively lower contaminant concentrations are found near the effluent end of the biofilter. Because more contaminant mass is available near the inlet, more microorganisms can be maintained and grow near that point. There is, therefore, a longitudinal stratification of biomass in biofilters (Devinny et al., 1999).

2.2 Unsteady Loading Condition: A Design and Process Challenge for Biofilters

The unsteady nature of many industrial processes results in variable concentrations of contaminants in waste gas streams (Mohseni and Allen, 1997; Dirk-Faitakis and Allen, 2003). Fluctuations in contaminant concentrations may be due to seasonal changes in operation, daily variations in operating conditions, and even at a higher frequency (e.g., hourly variations), due to changing process conditions and operations (Wani et al., 2000). Downtimes in industrial processes, when operations are interrupted, may occur on weekends, on week-long periods due to process shutdowns, or even longer. Volumetric flow rate of gas to a biofilter may be reduced to save on power costs during intervals of no contaminant loading. Generally, the unsteady nature of loadings that may be imposed on biofilters can be grouped into the following:

- Transient periods of low or no contaminant loading.
- Transient periods of elevated contaminant loading.
- Transient periods of low or no gas flow.
- Transient periods of high gas flow.

Impacts of these various unsteady-state loading scenarios on biofilter performance are described in the following sub-section.
2.2.1. Effects of Unsteady Loading to Biofilters

The effects of unsteady loading to biofilters reported in literature range from impacts on biofilter performance in terms of removal efficiency and elimination capacity, changes in the duration of biofilter re-startup and re-acclimation after periods of system upsets (change in loading conditions), and consequences on the microbial population in the biofilter.

Overall performance and removal efficiency have generally been observed to decrease when biofilters were subjected to intermittent loading (Moe and Qi, 2004; Qi and Moe, 2006) and shock loading conditions (Song and Kinney, 2005; Wani et al., 2000, Mohseni et al., 1998). With increased airflow, diminished performance was also observed (Wani et al., 2000; Gibson and Otten, 1997). At higher gas flowrate, decreased performance efficiency has been attributed to decreased residence time of contaminants in the bioreactor. This leads to a reduced contact time for sufficient biotransformation of the contaminants in the gas stream.

Re-acclimation after variations in loading conditions is a commonly studied effect of unsteady loading conditions in biofilters. Re-acclimation is important in biofilter design and operation because of the potential for low removal efficiencies that may last for several hours to more than a day (Martin and Loehr, 1996). A biofilter’s ability to resume high pollutant transformation (i.e., re-acclimate) after a period of shutdown or disturbance in loading conditions of the system have been reported (Martin and Loehr, 1996; Wani et al., 2000; Moe and Qi, 2004; Qi and Moe, 2006). Various responses were obtained owing to the fact that different types of packing medium, types of contaminants, and operating conditions have been tested. Generally, studies suggest that short-term variations (e.g., hourly variations, or variations within a day) in contaminant concentration generally do not affect the long-term performance of a biofilter. Furthermore, re-acclimation of a biofilter after short-term loading variations may occur within a
few hours. On the other hand, at longer periods of loading variations (e.g., shutdowns over weekend intervals, or week long periods) re-acclimation may take longer to occur. Generally, the longer that a disturbance due to unsteady loading has occurred, the longer it takes for the biofilter system to resume prior performance.

Other studies on the effects of unsteady loading have been conducted to evaluate consequences on the microbial consortium itself. For instance, differences in the physiological state of microbial populations present in continuously-operated and periodically-operated biofilter were reported (Moe and Irvine, 2001). Significant loss of biomass has also been observed during periods of starvation, which may be the cause for the slow re-acclimation rate after starvation (Cox and Deshusses, 2002). Various microbial responses during starvation conditions, when extracellular electron donors are not readily available, may include degradation of intracellular storage products, change in enzyme concentrations, change in metabolic pathways expressed, formation of spores and other resistant structures, and cell decay (Moe and Qi, 2004). The relative abundance of species in consortia may also be altered after sufficiently long starvation periods because microbial species differ in their rate of decay (Characklis et al., 1990).

2.3 Managing Transient Loadings to Biofilters

In an effort to mitigate the adverse effects of unsteady loading and maintain stable bioreactor performance during periods of unsteady loading conditions, several design and operation modifications have been proposed in recent years. Among these are 1) flow reversal, 2) slip-feed system, 3) sequencing batch biofilter operation, 4) liquid scrubber systems for load dampening, and 5) combined adsorption-biofiltration processes. Each of these is discussed in the following subsections.
2.3.1 Flow Reversal

Flow reversal, also referred to as flow directional switching (FDS), involves periodically switching the direction of airflow through a biofilter column (see Figure 2.2). Such operation has been observed to result in more uniform distribution of microbial population density and activity along the heights of biofilters in comparison to conventional unidirectionally operated systems (Song and Kinney, 2000). This strategy was also shown to increase reaction capacity in biofilter response to transient loadings. Loading conditions, which resulted in breakthrough of untreated contaminant was eliminated or reduced (Kinney, 1996; Song and Kinney, 2000; Wright, 2005; Wright, 2005a; Wright et al., 2005b). A significant unknown in application of flow reversal to
control transient loadings is the operational time that should be used between flow reversal events (Wright et al., 2005b).

2.3.2. Slip-Feed System

A “slip-feed” system (Figure 2.3) refers to a process in which a fraction of the inlet feed is redirected to otherwise carbon-deprived sections of a biofilter. For the case of continuous operation, such operation may better maintain biomass activity throughout the height of a biofilter. This has the potential to improve performance, especially during dynamic loading conditions (Kinney et al., 1999). During extended periods of low or no inlet contaminant loading, a surrogate compound may also be introduced to provide supplemental feed to a biofilter (Wright

![Figure 2.3. Schematic diagram of a biofilter operating on a slip-feed system (Park and Kinney, 2001).](image-url)
et al., 2005a). Using various slip feed fractions, Park and Kinney (2001) reported that as long as the biomass received at least trace contaminant concentrations, degradation capacity can be maintained to respond quickly to contaminant loading upon restart. They reported that slip-feed mass fractions ranging from 1-10% (of baseline inlet contaminant loading 45 g/m$^3$-h toluene) provided the same extent of improvement in biomass activity, while reducing the time required to achieve 90% removal efficiency by 65% and 70% after 3-day and 7-day shutdown periods, respectively, in comparison to a system without slip feed. There are certain disadvantages to this process, however, specifically when a supplemental contaminant is fed to biofilters. These disadvantages are that: (A) In many cases, contaminants are expensive and their use as a supplemental feed would result in an increased operational cost; and (B) If the supplemental contaminants are not completely degraded in the biofilter, then such a practice will directly increase overall contaminant mass emitted by the facility.

2.3.3. Sequencing Batch Biofilter (SBB)

The term “Sequencing Batch Biofilter” operation was first proposed by Li and Moe (2003) to describe biofilters employing the principles of sequencing batch reactors (SBRs) used in wastewater treatment (Irvine et al., 1997; Wilderer et al., 2001; Chiesa et al., 1985) to biofilters treating gas-phase contaminants. The SBB consists of one or more biofilters packed with media comprised of sorptive material, such as powdered activated carbon (PAC), and operates with three distinct periods in one cycle (Li and Moe, 2003): FEED, REACT, and IDLE (see Figure 2.4). This strategy was reported to effect superior performance under shock loading conditions based on overall mass of contaminants removed and minimum instantaneous removal efficiency (Atoche and Moe, 2004). In another study, Li and Moe (2004) assessed the microbial populations in SBB and a conventional continuous-flow biofilter using the molecular techniques.
of denaturing gradient gel electrophoresis (DGGE). The difference in the DGGE patterns observed in their systems suggests that the SBB operating strategy may lead to microbial selection that favors superior performance in comparison to conventional continuous-flow biofilters.

2.3.4. Liquid Scrubbers in Series Prior to Biofilters

In an effort to dampen transient loadings to a vapor-phase bioreactor, Al-Rayes et al. (2001) proposed use of an absorber upstream of the process to treat VOC-laden gases. This system is expected to temporarily absorb contaminants and later desorb contaminants, thereby

Figure 2.4. Schematic diagram of a sequencing batch biofilter (Li and Moe, 2003).
providing VOCs to a bioreactor during shutdown periods. Using water as scrubbing liquid, Al-Rayes et al. (2001) reported that the load dampening system works effectively for hydrophilic, but not hydrophobic VOCs. A similar system using oil as the absorbent was also investigated for its potential to act as buffer for shock loadings of pollutants in waste gas streams for biological treatment (Koutinas et al., 2006). When performance of an oil-absorber – bioscrubber (OAB) system was compared to that of a bioscrubber only (BO), they found that the former had more stable performance during shock loading of dichloroethane. Stable performance, characterized by stable CO₂ production and low levels of effluent dichloroethane and total organic carbon, was observed with OAB.

2.3.5. Addition of Activated-Carbon to the Biofilter Packing Medium

Addition of activated carbon to biofilter packing media to improve performance during transient loading was first suggested by Ottengraf (1983, 1986). In a patent, Ottengraf (1983), claimed that prevention of the “aging” phenomena and reduction of flow resistance in biofilters may be realized by thoroughly mixing suitable inert materials (particle diameter = 3 to 10 mm) with the natural packing material. The inert materials may be an adsorbing material (e.g., activated carbon particles) that may be favorable when the biofilter is subjected to variable loads. With good adsorbing and desorbing properties, the adsorbent may adsorb at periods of peak loading and desorb at periods of reduced loading to sustain microbial growth. Although the potential of this strategy had been endorsed by other researchers (Weber and Hartmans, 1995; Swanson and Loehr, 1997; Devinny et al., 1999), the benefits of incorporating activated carbon into packing material was challenged in the work of Mohseni and Allen (1997). In studying biofiltration of α-pinene in wood-chip/activated carbon biofilters, they found that unlike the initial start-up period, after long-term operation, the GAC-containing biofilter did not show any
increase in instantaneous pinene removal in comparison to a control biofilter constructed without GAC. Presence of activated carbon within the packing media did not improve the transient response of the biofilter and did not provide a buffering capacity to the biofilter during restart following shutdown (Mohseni and Allen, 1997).

2.3.6. Use of GAC Adsorption Columns in Series Prior to Biofilters (i.e., Coupled Systems)

Ottengraf’s (1986) idea of using activated carbon to alleviate effects of unsteady loading in biofilters, evolved to its use as an in-series pre-treatment process utilized prior to biofiltration of waste gases. This was first experimentally demonstrated by Weber and Hartmans (1995) who tested three biofilter configurations for treatment of toluene-containing waste gases: a biofilter without activated carbon, activated carbon mixed with compost within a biofilter, and a system consisting of an activated carbon column in series before a biofilter. Their results indicated removal efficiencies similar to 50%, for the first and second configurations. For the third system, an activated carbon column in series before the biofilter, fluctuating concentrations (between 0 – 1000 mg/m$^3$) were buffered to about 300 mg/m$^3$ by the GAC column. The resulting attenuated toluene concentrations were subsequently completely degraded in a downstream biofilter.

In later work reported by Li and Moe (2005), a coupled system was applied to a model gas stream containing a two-component mixture of acetone and toluene under intermittent loading conditions (8 hours per day). Their results indicate more complete contaminant removal and improved biofilter performance. These were attributed to a decreased magnitude of peak loading and more uniform contaminant loading as a function of time. Results also demonstrate that the degree of load equalization achieved for different constituents in multi-contaminant gas streams can vary markedly because of competitive sorption. Moe and Li (2005) proposed a design methodology for activated carbon load equalization systems applied to biofilters treating
intermittent loading (8 hrs per day). Using both experimental and model data for toluene adsorption on activated carbon (Calgon BPL 4x6 mesh) a design method that provides guidance in reactor sizing and operating parameter estimation was developed.

In so far as these studies are concerned, attention was laid on performance of the coupled system when subjected to intermittent loading and variation in feed concentration on a daily basis or shorter period of time. Performance of the coupled system during longer periods of low or no-contaminant loading, as well as low gas flows, scenarios that may be commonly expected in real-world operation, have not yet been systematically investigated until now. In addition, performance of coupled systems under humid air flow conditions has not been studied previously.

2.4 Overview of the Adsorption Process

Adsorption refers to a process of preferential partitioning of ions or molecules (the adsorbate) of one phase (usually liquid or gas) on to a solid surface (the adsorbent). This arises as a result of unsaturated and unbalanced molecular forces that the solid surface tends to satisfy by attracting and retaining on its surface the molecules, atoms, or ions of the gas or liquid (Bansal and Goyal, 2005). Depending on the nature of forces that bind the adsorbate on the solid surface, adsorption may be of two types: physical adsorption (physisorption) or chemical adsorption (chemisorption) (Yang, 1987; Bansal and Goyal, 2005). In physical adsorption, the adsorbate is bound to the solid surface by relatively weak van der Waals forces. Chemical adsorption, on the other hand, involves exchange or sharing of electrons between adsorbate molecules and the adsorbent surface that may result in a chemical reaction. While physisorption is generally reversible, chemisorption is seldom reversible (Sawyer et al., 1994).
2.4.1. Adsorption Transport and Kinetics

The overall adsorption process begins with adsorbate transport to a surface adsorption site through various transport processes: bulk fluid transport, film transport, and intraparticle transport. Of these, film and intraparticle transport are normally the slowest and therefore rate-limiting steps controlling design of adsorption systems (LaGrega et al., 1994).

*Bulk fluid transport.* By bulk fluid transport, diffusion or mixing of the adsorbates in fluid occur as a result of adsorbate concentration gradients and non-uniformity of flow (Tien, 1994). Dispersion may occur along the main flow direction (axial dispersion) or transverse to the main flow direction (radial direction). For the simple case of a single-solute, single-phase plug flow through a cylindrical packed bed, dispersion is expressed as (Tien, 1994):

\[
\frac{\partial C}{\partial t} = \frac{E_r}{r} \frac{\partial}{\partial r} \left[ r \frac{\partial C}{\partial r} \right] + E_z \frac{\partial^2 C}{\partial z^2} - \left( \frac{\mu_s}{\varepsilon} \right) \frac{\partial C}{\partial z}
\]

Where \( C \) = solute concentration
\( t, r, z \) = variables for time, radial distance, and axial distance, respectively
\( \mu_s \) = superficial velocity
\( \varepsilon \) = fixed bed porosity
\( E_r, E_z \) = radial and axial dispersion coefficients, respectively.

*Film mass transport.* Film mass transport, or interphase transport, refers to adsorbate transport from the bulk fluid phase to the external surface of an adsorbent material. This, as earlier mentioned, may be a rate-limiting factor in the overall process because it usually proceeds more slowly than bulk transport. For an arbitrary spherical adsorbent pellet, interphase mass transfer of a single species may be expressed as (Tien, 1994):

\[
\overline{\frac{\partial q}{\partial t}} = k_f a (C_b - C_r)
\]
Where \( \bar{q} \) = average adsorbed phase concentration (on a mass basis)

\( k_f \) = interphase (or external) mass transfer coefficient

\( a \) = specific surface area (area/mass adsorbent)

\( C_b, C_s \) = adsorbate concentration in the bulk of fluid and at the fluid-pellet interface, respectively.

**Intraparticle mass transport.** Intraparticle mass transport involves diffusion of adsorbate molecules into the interior of adsorbent pellets. Adsorbents are generally microporous materials with high specific surface area and void spaces (pores) that may be occupied by the fluid. Intraparticle transport, therefore, may be by both pore and surface diffusion. In pore diffusion, transport of molecules into a pore volume may occur by bulk diffusion in macropores (>150Å), or by Knudsen diffusion in micropores (Crittenden and Weber, 1978). On the other hand, molecules may diffuse along the surfaces of pore walls. Both types of intraparticle diffusion may be operative simultaneously or individually (Tien, 1994; Crittenden and Weber, 1978).

### 2.4.2. Equilibrium Adsorption of Gases

After sufficient time for adsorption has taken place, a point of saturation is reached such that the rate of adsorption becomes equal to the rate of desorption. At this point, there is a state of equilibrium. For a given gas-solid system, the amount adsorbed at equilibrium may be described as a function of both temperature \((T)\) and pressure \((P)\) or concentration \((C)\).

\[
q = f(P,T) \quad \text{or} \quad q = f(C,T)
\]

where \( q \) refers to the amount adsorbed per unit mass of adsorbent. At a constant temperature, when \( q \) is only a function of pressure or concentration, adsorption equilibrium data are referred to as adsorption isotherm.
Numerous isotherm models based on three general approaches are available to predict gas phase adsorption (Yang, 1987). These approaches are: Gibbs approach, Langmuir approach, and the potential theory approach. Gibbs equation is derived based on thermodynamic relationships and approaches. The Langmuir isotherm equation was developed based on several assumptions, among which, is the unimolecular layer of adsorbates covering the adsorbent surface (Werner and Winters, 1986; Tien, 1994). A popular modification of the Langmuir isotherm is the Braunauer-Emmett-Teller (BET) equation, which assumes multi-molecular adsorption on the adsorbent surface and is generally more applicable than the Langmuir isotherm (Sawyer, 1994). Potential theory, on the other hand, postulates an adsorption space in the vicinity of the adsorbent surface, and an adsorption potential, which is equal to the decrease in the potential energy of an adsorbate molecule relative to that in the bulk phase (Tien, 1994). Several relationships have evolved from this potential theory and are presented elsewhere (Tien, 1994). All isotherms should reduce to the Henry’s law form at extreme dilution (Yang, 2003); where an exponentially decaying function of site density with respect to the heat of adsorption is assumed, the classical empirical Freundlich isotherm is obtained.

### 2.5 Pore and Surface Diffusion Model

The pore and surface diffusion model (PSDM) described by Crittenden et al. (1988) and Hand et al. (1997) was used to simulate the dynamic toluene adsorption and desorption on granular activated carbon (GAC) under various transient loading conditions. The PSDM is a dynamic fixed-bed model that incorporates several assumptions (Mertz et al., 1999): (1) constant flow rate; (2) plug-flow conditions exist in the bed; (3) linear driving force describes the local bulk phase mass flux at the exterior surface of the adsorbent particle; (4) local adsorption equilibrium exists between the solute adsorbed onto the GAC particle and the solute in the intra-
aggregate stagnant fluid; (5) intraparticle mass flux is described by surface and pore diffusion; (6) adsorption equilibrium of individual compounds can be represented by the Freundlich isotherm equation, while competition between compounds is described by the Ideal Adsorbed Solution Theory (IAST); and (7) there are no interactions between the adsorbing compounds during the diffusion process. The mechanisms and assumptions incorporated in the model are shown schematically in Figure 2.5. Mass flux in the fluid phase is described by a linear driving force defined by adsorbate concentration, $C_b$ (mol/m$^3$), in the bulk gas phase, and adsorbate
concentration, $C_s$ (mol/m$^3$), on the external surface of the adsorbent. $K_f$ (m/s) refers to the film diffusion coefficient. Intraparticle transport is governed by pore and surface diffusion and described by the parameters: pore diffusion coefficient, $D_p$ (m$^2$/s); surface diffusion coefficient, $D_s$ (m$^2$/s); solid-phase concentration, $q$ (mol/kg); apparent adsorbent density, $\rho_a$ (kg/m$^3$); particle porosity or void fraction, $\varepsilon$ (dimensionless); adsorbate concentration in the pores, $C_p$ (mol/m$^3$); and adsorbent particle radius, $R$ ($0 \leq r \leq R$).

Two partial differential equations (PDEs), obtained for each adsorbing component from mass balances on the bulk gas phase and the adsorbed phase, are coupled together from an assumption of local equilibrium at the exterior of the adsorbent particle. Derivation of these equations has been presented previously (Friedman, 1984; Mertz et al., 1999). The bulk gas phase mass balance for component $i$ is given by (see Nomenclature section at the end of chapter for definition of variables):

$$\frac{\partial C_i}{\partial t} + V \frac{\partial C_i}{\partial z} + \frac{3 k_f (1 - \varepsilon)}{\varepsilon R} \left[ C_i(z,t) - C_{pi}(r = R, z, t) \right] = 0 \quad (2.1)$$

The initial and boundary conditions are respectively:

$$C_i(z,t) = 0 \quad \text{at} \quad 0 \leq z \leq L, t = 0 \quad (2.2)$$

$$C_i(z,t) = C_{oi}(t) \quad \text{at} \quad z = 0, t > 0 \quad (2.3)$$

In the adsorbent, the intraparticle phase mass balance for component $i$ in an assumed spherical particle is given by:
\[
\frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 D_{s,i} \frac{\partial q_i(r,z,t)}{\partial r} + \frac{r^2 D_{p,i}}{\rho_a} \frac{\partial}{\partial r} C_{p,i}(r,z,t) \right] = \frac{\partial}{\partial t} \left[ q_i(r,z,t) + \frac{\varepsilon_p}{\rho_a} C_{p,i}(r,z,t) \right]
\] (2.4)

The initial condition and boundary conditions are, respectively:

\[
q_i(r,z,t) + \frac{\varepsilon_p}{\rho_a} C_{p,i}(r,z,t) = 0 \quad \text{at} \quad 0 \leq r \leq R, \quad t = 0 \quad (2.5)
\]

\[
\frac{\partial}{\partial r} \left[ q_i(r,z,t) + \frac{\varepsilon_p}{\rho_a} C_{p,i}(r,z,t) \right] = 0 \quad \text{at} \quad r = 0, \quad t \geq 0 \quad (2.6)
\]

\[
D_{s,i} \rho_a \frac{\partial q_i(r = R,z,t)}{\partial r} + D_{p,i} \varepsilon_p \frac{\partial C_{p,i}(r = R,z,t)}{\partial r} = k_{ji} \left[ C_i(t) - C_{p,i}(r = R,z,t) \right] \quad (2.7)
\]

Concentration of component \( i \) in the bulk gas phase and in the adsorbent particles are coupled in equation 2.8 with the assumption that the adsorption reaction rate is much faster than the mass transfer rate (assumption of local equilibrium).

\[
C_{p,i}(r,z,t) = \frac{q_i(r,z,t)}{\sum_{k=l}^{m} q_k(r,z,t)} \left[ \frac{\sum_{k=i}^{m} n_k q_k(r,z,t)}{n_i K_i} \right]^{n_i} \quad (2.8)
\]

In the AdDesignSTM software package (Michigan Technological University), differential equations describing the dynamics in a fixed-bed adsorber were solved numerically using the method of orthogonal collocation to convert the partial differential equations into a set of
ordinary differential equations. The resulting set of ordinary differential equations, in turn, is solved using the backward differentiation method formula or the Gear's stiff method. Calculations using the PSDM require equilibrium parameters, kinetic parameters, physico-chemical properties of adsorbing compound(s) and adsorbent, gas properties, concentration data, and column dimensions.

<table>
<thead>
<tr>
<th>Nomenclature:</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{0,i} )</td>
</tr>
<tr>
<td>( C_i(z,t) )</td>
</tr>
<tr>
<td>( C_{p,i}(r,z,t) )</td>
</tr>
<tr>
<td>( D_{p,i} )</td>
</tr>
<tr>
<td>( D_{s,i} )</td>
</tr>
<tr>
<td>( k_{f,i} )</td>
</tr>
<tr>
<td>( L )</td>
</tr>
<tr>
<td>( m )</td>
</tr>
<tr>
<td>( q_i(r,z,t) )</td>
</tr>
<tr>
<td>( R )</td>
</tr>
<tr>
<td>( V )</td>
</tr>
</tbody>
</table>

**Greek letters**

\( \varepsilon_p \) | particle void fraction (porosity) |
\( \rho_{a} \) | apparent adsorbent density (M/L³) |
\( \varepsilon \) | bed void fraction |

**subscripts**

\( i \) | component number \( i \) |

### 2.6 The Ideal Adsorbed Solution Theory (IAST)

Various equations have been proposed for calculating equilibrium adsorption capacities of mixtures of vapors on activated carbon. In the AdDesigns simulation of the pore and surface diffusion model (PSDM), competitive interactions between multi-component gas mixtures were
estimated using the ideal adsorbed solution theory. IAST was the first major theory predicting mixed gas adsorption from pure component isotherms and remain the most widely accepted (Yang, 2003). First proposed by Myers and Prausnitz (1965), it is sometimes called the Myers-Prausnitz theory.

The IAST is a thermodynamic adsorption model which uses the concept of the activity coefficient for the components in adsorbed phase. The adsorbed phase is assumed an ideal solution in equilibrium with the bulk gas phase. The essential idea of the calculation lies on the recognition that in ideal solution, the partial pressure of an adsorbed component is given by the product of its mole fraction in the adsorbed phase and the pressure which it would exert at the same temperature and spread pressure as those of the mixture (Myers and Prausnitz, 1965). IAST is based on the concept of spreading pressure which is assumed constant for all the components at equilibrium (Yang, 2003). The spreading pressure for a given component is given by:

$$\pi = \frac{RT}{A} \int_0^{P_o} \frac{q}{P} dP$$

(2.9)

where $q$ is the amount of any pure component that is in the adsorbed phase and is related to $P$ by any pure component isotherm. $A$ is the surface area occupied by the adsorbate. Assuming the activity coefficients are unity for all components in the adsorbed mixture, the IAS model results to the following equations for a two-component system (Yang, 2003):

$$\int_0^{P_o} \frac{q_1}{P} dP = \int_0^{P_o} \frac{q_2}{P} dP$$

(2.10)
Raoult’s law can be written for the two species:

\begin{align}
PY_1 &= P_1^o X_1 \\ 
PY_2 &= P_2^o X_2 = P_2^o (1 - X_1)
\end{align}

where \( P_i^o \) is the equilibrium vapor pressure for adsorption of pure \( i \) at the same spreading pressure and temperature as the adsorbed mixture. The above equations are solved to yield algebraic equations if the isotherms have certain forms like Langmuir and Freundlich equations. Otherwise, Equation 2.10 must be solved numerically. Details of calculations of the IAST for systems following the Freundlich isotherm are presented elsewhere (Crittenden et al., 1985).
CHAPTER 3
USE OF GAC ADSORPTION COLUMNS TO MITIGATE THE ADVERSE EFFECTS OF VARIOUS SHUTDOWN CONDITIONS ON BIOFILTER PERFORMANCE

3.1 Introduction

Many biofilters are subjected to temporary loading conditions in which the influent VOC content is very low or completely absent. Such periods of low loading or no loading can impose starvation conditions on the microbial populations in biofilters. In cases where duration of the starvation period is relatively short (e.g., a few hours), contaminant removal in biofilters generally returns to the level observed before the starvation condition shortly after resumption of contaminant loading. In cases where the influent contaminant loading is suspended for a longer period (e.g., days or weeks), diminished contaminant removal for a period lasting several hours or even days following resumption of contaminant loading has been reported. In general, the length of time required to resume high contaminant removal efficiency depends on the duration of the shutdown period, with longer duration shutdown periods generally requiring longer time for biofilter recovery (Park and Kinney, 2001; Cox and Deshusses, 2002; Dirk-Faitakis and Allen, 2003; Moe and Qi, 2004).

One approach for minimizing the adverse effects of low or no loading in biofilters is to provide supplemental feed of contaminants or surrogate compounds during extended “off periods” (periods of low influent concentrations) to maintain induction of degradative enzymes and minimize starvation. Park and Kinney (2001) demonstrated that supplemental feed at a contaminant mass loading rate equal to a relatively small fraction of that during “normal loading” (e.g., 12%) could markedly decrease the length of time required for a biofilter to regain high removal efficiency following shut-down periods as long as 7 days. Two disadvantages of supplementing contaminant feed to biofilters, however, are that (a) in many cases contaminants
are expensive and their use as a supplemental feed would result in an increased operational cost, and (b) if the supplemental contaminants are not completely degraded in the biofilter, then such a practice will directly increase overall contaminant mass emitted by the facility.

An alternate strategy for providing supplemental feed to biofilters during periods of low or no loading is to use a coupled system comprised of a granular activated carbon (GAC) adsorption column followed by a biofilter. Ottengraf (1986) proposed that using GAC in this manner could allow contaminant adsorption during periods of peak loading and desorption during periods of reduced loading to sustain microbial growth. If successful, such an approach would eliminate both disadvantages noted above because (a) there is no need to purchase chemicals to be added -- the waste stream being treated is the source of contaminant mass fed to the biofilter during intervals when starvation would otherwise occur; and (b) because no additional chemical mass is intentionally added to the air stream, there is no potential for increased air emissions. Weber and Hartmans (1995) experimentally demonstrated that operation of coupled systems was indeed feasible. Later testing confirmed that more complete contaminant removal could be attained and diminished performance due to starvation could be minimized in coupled systems (Li and Moe, 2005). While these previous studies demonstrated some of the potential advantages of using GAC columns in series before biofilters, design methodologies presented to date have focused on use of GAC to control maximum contaminant concentration exiting from the GAC column and entering the biofilter (Moe and Li, 2005). Systematic investigation of the ability of GAC columns to provide supplemental feed to biofilters during periods of low or no loading is currently lacking.

This chapter reports results from a modeling effort conducted to assess how columns packed with granular activated carbon (GAC) can be utilized to provide supplemental feed of
volatile organic compounds (VOCs) to biofilters during long-term (>2 days) periods of low or no loading. The minimum loading conditions that would be imposed on a biofilter by GAC columns during periods of low or no loading was systematically assessed. A pore and surface diffusion model (PSDM), previously calibrated using experimental data, was used to predict the dynamics of toluene adsorption and desorption in GAC columns subjected to weekend (i.e., two day) and extended (i.e., one week) shutdown periods. Simulations were conducted for a variety of influent contaminant concentrations and empty bed contact times.

3.2 Model Simulations

Simulations of fixed-bed adsorption-desorption processes under various loading conditions (i.e., various EBCTs, influent concentrations, and shutdown conditions) were conducted using the PSDM previously reported to qualitatively and quantitatively predict the pattern of VOC exiting GAC columns during intermittent loading conditions (Li and Moe, 2005; Moe and Li, 2005). This model was previously validated using adsorption data for Calgon BPL 4×6 mesh GAC at a superficial air velocity of 300 m/hr (Moe and Li, 2005). Simulations reported herein were performed for the same GAC type and superficial air velocity. Simulations were performed using the AdDesignSTM software package (Michigan Technological University), which utilizes an orthogonal collocation method used to convert partial differential equations of the PSDM into a set of ordinary differential equations that are solved using a backward differential method. The PSDM is a dynamic fixed-bed model developed based on assumptions and governing equations described by Crittenden et al. (1988). Calculations using this model require equilibrium and kinetic parameters, physical properties of adsorbing compound and adsorbent, fluid properties, influent concentrations, flow characteristics, and column dimensions. A summary of parameter values and data input to the model is shown in Table 3.1.
Table 3.1. Summary of parameter values and data input to AdDesignSTM for PSDM simulations of GAC column performance under conditions of weekend and extended weekend shutdowns.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fixed bed properties</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bed length</td>
<td>12.5 – 83.3 (a)</td>
<td>cm</td>
</tr>
<tr>
<td>Bed diameter</td>
<td>7.62 (a)</td>
<td>cm</td>
</tr>
<tr>
<td>Bed porosity</td>
<td>0.483 (a)</td>
<td>dimensionless</td>
</tr>
<tr>
<td><strong>Adsorbent properties (Calgon BPL 4×6 mesh)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particle apparent density</td>
<td>0.85 (b)</td>
<td>g/cm(^3)</td>
</tr>
<tr>
<td>Average particle diameter</td>
<td>0.372 (b)</td>
<td>cm</td>
</tr>
<tr>
<td>Particle void fraction</td>
<td>0.595 (b)</td>
<td>dimensionless</td>
</tr>
<tr>
<td>Particle shape factor</td>
<td>0.72 (b)</td>
<td>dimensionless</td>
</tr>
<tr>
<td><strong>Freundlich isotherm parameters</strong></td>
<td>152 (c)</td>
<td>(mg/g)(L/mg)(^{1/n})</td>
</tr>
<tr>
<td>(1/n)</td>
<td>0.249 (c)</td>
<td>dimensionless</td>
</tr>
<tr>
<td><strong>Air properties</strong></td>
<td>23 (a)</td>
<td>°C</td>
</tr>
<tr>
<td>Density</td>
<td>(1.19 \times 10^{-3}) (d)</td>
<td>g/cm(^3)</td>
</tr>
<tr>
<td>Viscosity</td>
<td>1.79 \times 10^{-4} (d)</td>
<td>g/cm-s</td>
</tr>
<tr>
<td><strong>Kinetic Parameters</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(k_f) (film mass-transfer coefficient)</td>
<td>1.01 (e)</td>
<td>cm/s</td>
</tr>
<tr>
<td>(D_p) (pore diffusion coefficient)</td>
<td>(8.24 \times 10^{-2}) (f)</td>
<td>cm(^2)/s</td>
</tr>
<tr>
<td>(D_s) (surface diffusion coefficient)</td>
<td>(5.12 \times 10^{-6}) to (1.65 \times 10^{-5}) (g)</td>
<td>cm(^2)/s</td>
</tr>
<tr>
<td>Surface to pore diffusion flux ratio</td>
<td>16 (h)</td>
<td>dimensionless</td>
</tr>
</tbody>
</table>

\(a\) Assumed parameter consistent with experiments conducted by Moe and Li (2005).
\(b\) Data provided by Calgon Corp. (Pittsburgh, PA).
\(c\) Assumed parameter based on experimental measurements by Moe and Li (2005).
\(d\) Calculated by correlation using the StEPPTM database (Mertz, et al., 1999).
\(e\) Assumed parameter based on experimental fit determined by Moe and Li, 2005.
\(f\) Calculated using the Wilke-Lee modifications of the Hirschfelder-Bird-Spotz method (Mertz et al., 1999).
\(g\) Calculated by using Sontheimer correlation (Mertz, et al., 1999).
\(h\) Assumed parameter based on experimental fit by Crittenden et al. (1988) for gas-phase applications.
Simulations at various influent toluene concentrations (100 to 1000 ppm.) and empty bed contact times (1.5 seconds to 10 seconds) were conducted to determine the impact of different shutdown conditions. For each influent toluene concentration and empty bed contact time (EBCT) tested, a total of four intermittent loading scenarios were tested (see Table 3.2). For loading conditions A and C, the duration of no contaminant loading during weekend shutdown was assumed to last 64 hours (i.e., no loading from 5:00 p.m. Friday evening until start of operation at 9:00 a.m. Monday morning). For loading conditions B and D, the duration of no contaminant loading during “extended shutdown” was assumed to last 232 hours (i.e., no loading from 5:00 p.m. Friday evening until start of operation at 9:00 a.m. Monday a week later). During all shutdown periods, it was assumed that uncontaminated air continued to flow through the GAC at the same rate as toluene-contaminated air did during the loading interval.

Table 3.2. Summary of shutdown conditions tested.

<table>
<thead>
<tr>
<th>Loading Condition</th>
<th>Toluene loading interval</th>
<th>Intended to Simulate</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>24 hr/day, 5 days/week</td>
<td>Weekend shutdown in an otherwise continuous process</td>
</tr>
<tr>
<td>B</td>
<td>Same as loading condition “A” followed by 1-week shutdown</td>
<td>“Extended shutdown” in a process otherwise operating continuously during 5-day work weeks</td>
</tr>
<tr>
<td>C</td>
<td>8 hr/day, 5 days/week</td>
<td>Weekend shutdown in a process operating 8 hr/day</td>
</tr>
<tr>
<td>D</td>
<td>Same as loading condition “C” followed by 1-week shutdown</td>
<td>“Extended shutdown” in a process otherwise operating 8 hr/day during 5-day work weeks</td>
</tr>
</tbody>
</table>
3.3 Results and Discussions

When contaminated air is first loaded to a new GAC column, adsorption initially occurs at sites within the carbon bed at spatial locations closest to the inlet. Consequently, no adsorbate is initially detected in the effluent at the other end of the column. As further contaminant mass enters the column and activated carbon near the inlet becomes saturated, the mass transfer zone moves further into the column. In the case of continuous contaminant loading (i.e., constant concentration entering the GAC column as a function of time), all adsorption sites along the length of the GAC bed eventually become saturated and after some period, the effluent concentration \( C \) becomes equal to the inlet concentration \( C_o \), resulting in a dimensionless effluent concentration \( C/C_o \) equal to a value of 1.0 at steady-state. An example of model prediction of this phenomenon is shown in Figure 3.1 (see line “a”).

In somewhat of a contrast, however, model simulations indicate that a different pattern will occur when the influent contaminant loading is intermittent as a function of time with a fixed periodicity. After an initial period of contaminant accumulation within the GAC column following the start of contaminant loading, model simulations suggest that a cyclic succession of maximum and minimum concentrations will occur. When the observed pattern of effluent concentrations changes in a fixed, reproducible manner, the system is said to be at quasi-steady-state. An example of model predictions of this phenomenon is shown in Figure 3.1 (see line “b”). Results shown here are for model data only; however, patterns of consistently repeatable maximum dimensionless effluent concentration \( C_{max}/C_o \) and minimum dimensionless effluent concentration \( C_{min}/C_o \) have been experimentally determined to closely follow model predictions (Moe and Li, 2005; Li and Moe, 2005).
The minimum concentration exiting the GAC column, expressed as \( \frac{C_{\text{min}}}{C_{\text{o}}} \), is an important parameter because it represents the minimum concentration that would enter a biofilter located in series downstream. For data depicted for intermittent loading in Figure 3.1, corresponding to one of the Loading Condition A simulations (see Table 3.2), the minimum dimensionless effluent concentration was 0.23, which corresponds to 23 ppm\(_{v}\) toluene since the influent concentration during the loading interval was 100 ppm\(_{v}\) in this case. Thus, a biofilter located in series downstream would receive a toluene concentration \( \geq 23 \) ppm\(_{v}\) at all times after

Figure 3.1. Predicted toluene concentration exiting from a GAC adsorption column during (a) continuous loading and (b) intermittent loading with toluene entering the column 24-hr/day for 5 days per week followed by weekends of no loading. Profiles shown are for influent concentration of 100 ppm\(_{v}\) at EBCT = 4.0 seconds.
quasi-steady-state is reached in the GAC column. This would provide the key advantage of preventing “starvation” conditions in the biofilter. In the absence of a GAC column, the biofilter would receive no contaminant loading for a period of 64 hours and would likely experience a lag period of low contaminant removal following resumption of contaminant loading at the start of a new work-week (Park and Kinney, 2001; Cox and Deshusses, 2002; Moe and Qi, 2004).

Figures 3.2 and 3.3 depict more comprehensive results from modeling of loading conditions A and B (see Table 3.2). For illustrative purposes, Figure 3.2 depicts model predictions of the dimensionless toluene concentration exiting the GAC columns (C/Co) during a two week period after quasi-steady state was reached. Each graph in the figures shows data for GAC columns with a different EBCT. In Figure 3.3, for clarity of presentation, time zero depicted in the graphs is the time when effluent toluene concentration starts to decrease as a result of the extended shutdown imposed.

As clearly shown in Figure 3.2, the minimum dimensionless toluene concentration (C_{min}/C_o) exiting the GAC columns is greater for lower toluene concentrations than for higher toluene concentrations. For example, at an EBCT of 7.0 seconds, C_{min}/C_o was 0.32 for an influent toluene concentration of 100 ppmv, while it was 0.07 for an influent toluene concentration of 1000 ppmv. Also evident from Figure 3.2 is that the value of C_{min}/C_o increases as the EBCT increases. The same trends are also observed in the case of week-long extended shutdown periods (Figure 3.3).

Comparison of Figures 3.2 and 3.3 reveals that C_{min}/C_o decreases as the duration of the shutdown period increases. For example, at an EBCT of 4.0 seconds and influent toluene concentration of 100 ppmv, weekend shutdowns (loading condition A) resulted in C_{min}/C_o of 0.23 while the extended week-long shutdown (loading condition B) resulted in C_{min}/C_o of 0.07.
Figure 3.2. Model simulation results for loading condition A – continuous loading with weekend shutdown. Shown are results during 14 days of quasi-steady state for various EBCT and influent toluene concentration, $C_o$. 
Figure 3.3. Model simulation results for loading condition B – continuous loading with extended weekend shutdown. Shown are results during 14 days of quasi-steady state for various EBCT and influent toluene concentration, $C_0$. 
While $C_{\text{min}}/C_o$ provides a useful measure of the intensity of famine or starvation conditions which may be experienced by a biofilter and can likely be used as a key parameter in evaluating the ability of GAC columns to provide supplemental feed to biofilters during intervals of low or no loading, it does not capture all of the relevant loading properties of interest in biofilter design and operation. The duration that a minimal or zero loading is sustained to a biofilter is also important. For example, Dirk-Faitakis and Allen (2003) observed that short periods (e.g., minutes or hours) of no loading did not have any obvious adverse effects on biofilter performance while longer periods (e.g., days) did have an adverse effect. To capture a measure of this effect, the duration of time in which the dimensionless effluent concentration ($C/C_o$) was less than 0.05 (with 5% of the influent concentration arbitrarily selected as a level of famine intensity of potential interest) is shown in Figure 3.4.

As shown in the Figure 3.4A, many of the EBCTs and toluene concentrations did not result in any duration of famine conditions more intense than the threshold selected for this

![Figure 3.4](image-url)

Figure 3.4. Duration of time in which $C/C_o < 0.05$ for loading conditions A and B.
analysis ($C/C_o \leq 0.05$). For example, EBCTs of 7 and 10 seconds were sufficient to maintain the effluent from the GAC column (influent to a downstream biofilter) at a $C/C_o$ level $\geq 0.05$ at all toluene conditions tested during weekend shutdown (see Figure 3.4A). In other cases, corresponding to loading at higher toluene concentrations and/or lower EBCTs, the threshold was crossed for some period of time. For example, at an influent toluene concentration of 400 ppmv and an EBCT of 1.5 seconds, the threshold was crossed for a duration of 0.78 days. In the case of the extended shutdown (Figure 3.4B), there were many more instances when $C/C_o$ was $\leq 0.05$, and the durations of the famine were generally much longer. As shown, however, the duration of the famine period decreased as the EBCT increased and influent toluene concentration decreased. At an influent toluene concentration of 100 ppmv, an EBCT of 4 seconds or longer would result in no duration of $C/C_o \leq 0.05$.

Graphs such as those presented in Figure 3.4 may be useful from a design or analysis perspective because they allow selection of conditions that do not exceed user-selected thresholds. For example, if a designer was faced with a toluene-contaminated waste gas with an influent concentration of 400 ppmv under conditions corresponding to loading condition A and they wanted to ensure that $C/C_o$ was $\leq 0.05$ for no more than 0.5 days, then it can been seen from Figure 3.4A that the minimum required GAC column EBCT should be between 1.5 and 4 seconds. Additional simulations could be performed to further delineate the EBCT between these two values that would be necessary to meet the design objective.

Figures 3.5 and 3.6 depict modeling results from loading conditions C and D (see Table 3.2). In Figure 3.6, for clarity of presentation, time zero depicted in the graphs is the time when effluent toluene concentration started to decrease as a result of the extended shutdown, and data is shown only for the interval before the effluent concentration began to increase following
Figure 3.5. Model simulation results for loading condition C – intermittent loading (8 hr/day) with weekend shutdown. Shown are results during 14 days of quasi-steady state for various EBCT and influent toluene concentration, $C_0$. 

$\text{EBCT} = 1.5 \text{ sec}$

$\text{EBCT} = 4.0 \text{ sec}$

$\text{EBCT} = 7.0 \text{ sec}$

$\text{EBCT} = 10.0 \text{ sec}$
Figure 3.6. Model simulation results for loading condition D – intermittent loading (8 hr/day) with extended weekend shutdown. Shown are results during 14 days of quasi-steady state for various EBCT and influent toluene concentration, $C_o$. 
resumption of contaminant loading. As was observed for loading conditions A and B, the value of \( C_{\text{min}}/C_o \) increased as the EBCT increased, and higher \( C_{\text{min}}/C_o \) values were observed for lower influent toluene concentrations than higher ones.

It should also be noted from Figure 3.5 that in the case when contaminants are loaded during only a fraction of the day (in this case, 8 hr per 24 hour period), simulations indicate that in addition to making \( C_{\text{min}}/C_o > 0 \) (and thereby decreasing or eliminating starvation conditions), GAC columns can also result in \( C_{\text{max}}/C_o \) levels appreciably less than 1.0. This phenomenon was previously shown through modeling simulations and experimental observations for the case where contaminants are present 8 hr/day 7 days a week (Moe and Li, 2005; Li and Moe, 2005). Results reported herein extend the previous work for the case of shorter (i.e., 5-day) work weeks.

Figure 3.7 depicts the duration of time during which \( C/C_o \) was less than 0.05 for loading conditions C and D. As shown in the figure, trends are the same for loading condition C as was

![Figure 3.7](image-url)

**Figure 3.7.** Duration of time in which \( C/C_o < 0.05 \) for loading conditions C and D.
observed for loading condition A and B. Shorter duration of famine conditions were encountered for lower influent toluene concentration and higher EBCTs.

3.4 Conclusions

Results from model simulations indicate that GAC adsorption columns can accumulate toluene during periods of high loading and subsequently desorb contaminants to the gas flow when the influent concentration is low or zero. Consequently, installation of GAC adsorption columns in series prior to biofilters may prove useful in alleviating the adverse impacts of starvation during periods of operational shutdown when no contaminants would otherwise be supplied to the biofilter. From the work of Park and Kinney (2001), it may be expected that the performance and reacclimation after shutdown of a biofilter in a coupled system will be better than what may be observed with a stand-alone biofilter subjected to shutdown conditions. While it is important to note that experimental verification of the modeling results should be carried out prior to full-scale implementation, the results reported herein are a first step in better understanding the range of potential benefits of using coupled systems to minimize starvation conditions in biofilters.
CHAPTER 4
EFFECT OF WATER VAPOR ON ACTIVATED CARBON LOAD EQUALIZATION OF
GAS PHASE TOLUENE

4.1 Introduction

Aeration basins and other processes commonly employed in industrial wastewater treatment facilities often result in emission of gases that contain appreciable quantities of volatile organic compounds (VOCs). In response to regulatory pressure, controlling gaseous VOC emissions has become a substantial concern for many industries and municipalities. The low VOC concentrations and high relative humidity in air streams typically emitted by wastewater treatment processes make conventional physical-chemical air pollution control options (e.g., incineration or carbon adsorption) difficult and expensive. Biofilters are an attractive technology for treatment of gas-phase pollutants in many of these applications due to their comparatively low cost, operational simplicity, and lack of secondary pollutant generation (Devinny et al., 1999).

While biofilters have been successfully applied for odor abatement and VOC removal at many wastewater treatment facilities (where gases may be collected for treatment at the headworks of a plant, from covered activated sludge aeration basins, or other processes), several challenges in design and operation remain. Among these challenges is the fact that intermittent industrial discharges, fluctuations in wastewater pollutant concentrations, and variation in wastewater flow rates result in fluctuating VOC concentrations in the associated off-gases (Melcer et al., 1994; Zhu et al., 1999; Escalas et al., 2003). Transient periods of high and low influent pollutant loading can adversely affect biofilter performance (Cox and Deshusses, 2002; Atoche and Moe, 2004; Li and Moe, 2005; Qi and Moe, 2006).
Recent research has demonstrated that columns packed with granular activated carbon (GAC) can serve as passively-controlled load equalization devices as a pre-treatment step prior to biofiltration of gas-phase VOCs (Li and Moe, 2005; Moe and Li, 2005; Moe et al., 2007). The rationale for such systems is that during periods of high contaminant loading, GAC adsorbent can temporarily accumulate contaminants and then subsequently desorb them during intervals when concentration in the waste gas is low. This can serve several purposes including dampening fluctuations in organic loading to provide steady loading to biofilters, and providing continuous feed to systems over periods when wastes are not being generated (Li and Moe, 2005). While use of GAC load equalization in conjunction with biofiltration has the potential to increase reliability and decrease costs, previous studies on such integrated systems have focused on treatment of dry gases containing low or no relative humidity. Water vapor, however, is known to influence both GAC adsorption capacity and kinetics (Werner et al., 1985; Kawar et al., 1990; Keener et al., 1990; Cal et al., 1996; Russell and LeVan, 1997; Kim et al. 2004; Ramakrishnan et al., 2004).

The overall objective of this study was to determine effects of elevated relative humidity on load equalization by GAC columns subjected to dynamically varying loading of VOCs. Toluene served as a model VOC contaminant. Two sets of experiments conducted under intermittent loading condition are reported in this chapter. In the first set of intermittent loading experiments, fixed-bed GAC columns receiving intermittent toluene loading (toluene present in the gas stream 8 hr/day) were subjected to step increases in relative humidity to assess impacts of water vapor over a wide range of concentrations. In the second set of experiments, GAC columns of various packed bed depths were subjected to intermittent toluene loading in air containing 80% relative humidity to determine effects of high water vapor concentration on load
equalization as a function of empty bed contact time (EBCT). In addition to experimental testing, model simulations were conducted using a pore and surface diffusion model in an attempt to provide a mechanistic explanation for experimental observations. (Note: Initial experiments involving continuous loading studies were conducted to provide some baseline understanding of water vapor effects on toluene adsorption onto GAC within the context of specific system subsequently studied under intermittent loading condition. Results of these experiments are described in Appendix A).

4.2 Background

Moisture is ubiquitous in the environment. It is common in gas streams originating from many industrial sources. In gas adsorption processes, water may be considered as another adsorbate that has the potential to impact VOC adsorption. Competitive adsorption between water and organics can be considered a special case of multicomponent adsorption (Cal et al., 1997). Numerous studies have been conducted in an effort to understand and model effects of relative humidity on activated carbon adsorption. As further discussed in the following subsections, these studies have included a variety of adsorbates (usually grouped as either water-soluble/miscible or water-insoluble/immiscible), adsorbate partial pressures and concentrations, types of adsorbents (i.e., granular and powdered activated carbon, activated carbon-based monoliths, and activated carbon cloth), relative humidity levels, and temperatures. Effects of humidity on gas adsorption are reported based on 1) effects on the adsorption capacity of adsorbent; and 2) effects on the behavior of the breakthrough curve, including the time for breakthrough. These are further discussed in the following sections.
4.2.1 Reduced Adsorption Capacity

There are three possibilities with respect to the effect of relative humidity on adsorption capacity – reduced capacity, increased capacity, and no effect on adsorption capacity. Generally, reduced adsorption capacity with increased relative humidity of the gas stream has been reported (Cal et al., 1996; Gong and Keener, 1993; Jonas, 1985; Kawar and Underhill, 1990; Keener and Zhou, 1990; Kim et al., 2004a; Marbán and Fuertes, 2004; Middlebrooks, M. 2001; Ramakrishnan et al., 2004; Russell and LeVan, 1997; Werner, M. 1985). In all of these reports, there appears to be a relative humidity threshold at which reduced adsorption capacity starts to be observed. This threshold value may vary with the adsorbate-adsorbent system used, or with the adsorbate concentration. Some results have indicated that water vapor in the gas stream has a more profound effect on the adsorption capacity at lower adsorbate concentrations (Cal et al., 1997; Delage et al., 1999; Gong and Keener, 1993; Werner, 1985). On the other hand, magnitude of the effect of water vapor was observed to be greater at higher concentrations of methylene chloride than at lower concentrations (Gong and Keener, 1993). Non-dependence of gas adsorption on relative humidity was also reported for certain relatively water-soluble adsorbates. For instance, Cal et al. (1996) reported that presence of water vapor in the gas stream, along with acetone (350 and 500 ppmv) had little effect on acetone adsorption even at 90% relative humidity.

Reduced adsorption capacity of the adsorbent for humid gas streams has been attributed by some authors (e.g., Müller and Hung, 2000) to blockage of adsorption sites that would have otherwise been available for other adsorbates. These sites are H-bonding sites that may be present in the carbon surface to which water molecules may interact. Activated carbon, when it comes into contact with air, forms surface oxides which are essentially oxygen-containing radicals attached to the carbon atoms (Keener and Zhou, 1990). These are described as primary
adsorption site for water on carbon. In a generally accepted model for water adsorption, initial adsorption of water occurs on these surface oxides (primary centers), followed by clustering of water molecules and filling of the porous structure (Russell and LeVan, 1997). Molecular attraction may occur between water molecules themselves (secondary sites for water adsorption), thereby promoting growth of water clusters that can also block pores in activated carbon. As the density of these active sites is increased, continuous filling of pores with water results (Müller and Hung, 2000).

### 4.2.2 Effect on Breakthrough Curves

During continuous loading conditions, earlier adsorbate breakthrough usually results when high concentrations of water vapor are present in the gas stream (Jonas et al., 1985; Gong and Keener, 1993; Kim et al, 2004a). Similar to the earlier explanation for reduced adsorption capacity, earlier breakthrough due to presence of water in the gas stream could result from partial blockage of adsorption sites on the adsorbent surface. As there are fewer sites for adsorption, adsorbates come off with effluent, and hence, an earlier breakthrough from the adsorption bed is observed.

Alteration of the shape of the breakthrough curve could also be a manifestation of the effect of humidity on adsorption kinetics (Werner, 1986). For instance, Gong and Keener (1993), having observed widening and broadening of the breakthrough curve for toluene under high relative humidity conditions, described this using the concept of the adsorption mass transfer zone. According to the authors, the breakthrough curve observed from a dynamic adsorption process are a reflection of the moving mass transfer zone (MTZ) in the fixed bed, with thickness that is proportional to the width of the breakthrough curve itself. For a given adsorber and gas flowrate, factors that may affect the MTZ depth are changes in adsorption capacity for the
adsorbate and differences in the resistance and driving forces for mass transfer (Gong and Keener, 1993). With a decrease in mass transfer resistance and increase in driving force and adsorption capacity, the thickness of the MTZ is decreased. It is expected that the presence of high humidity in the gas stream increases resistance to mass transfer, with reduction in adsorption capacity. These then result in a longer MTZ, and hence, a broader breakthrough curve.

In view of the foregoing, the effect of humidity on the gas adsorption process can be described as dependent on the type of adsorbate-adsorbent system, adsorbate concentration, and the level of relative humidity. Such effects on the performance of GAC columns subjected to intermittent loading, however, have not been studied to date.

4.3 Materials and Methods

4.3.1 Granular Activated Carbon (GAC) Column and Experimental Apparatus

The adsorbent employed in this research was BPL 4×6 mesh GAC (Calgon Carbon Corp., Pittsburgh, PA), a bituminous coal-based activated carbon designed for use in vapor phase applications. GAC was rinsed with distilled water to remove fines, dried at 105°C, and stored in dessicators prior to use. Configuration of the experimental apparatus used in fixed-bed adsorption/desorption experiments is shown in Figure 4.1. Packed columns were constructed of PVC (ID 7.62 cm) pipe. Each column consisted of a stainless steel support mesh at the bottom, 6-cm depth glass beads to distribute air flow, a thin layer of glass wool, a layer of GAC, another thin layer of glass wool, and another 6-cm glass beads. As further described below, depth of the GAC layer varied between experiments. Some experiments employed columns comprised of a
single section while others used columns constructed with multiple sections in series to facilitate sampling at multiple bed depths.

Contaminant-free compressed air flowed through an electronic mass flow controller (Aalborg Instruments, Orangeburg, NY) to regulate air flow through the system. For all experiments, the air flow rate was 22.8 L/min, corresponding to superficial gas velocity of 300 m/hr in the packed columns. A portion of air flow passed through an aeration stone submerged in a 20 L glass carboy filled with deionized water to provide the desired level of humidification. For dry air experiments, the carboy was bypassed and all airflow was directed to the packed column. Liquid toluene (ACS reagent grade, Sigma, St. Louis, MO) was delivered by syringe pumps (KD Scientific, Boston, MA) and evaporated into the air stream. A microprocessor-based controller (Chron-Trol, San Diego, CA) turned syringe pumps on and off as necessary.
Gas sampling lines were constructed using Teflon tubing. Initial tests conducted prior to placement of activated carbon demonstrated that column components other than GAC had little or no adsorption capacity for toluene. All experiments were conducted at ambient laboratory temperature of 23±2°C.

4.3.2 Intermittent (8 hr/day) Toluene Loading at Various Relative Humidity Levels

Effects of various humidity levels on load equalization of toluene intermittently supplied in an air stream were assessed using columns containing 12.5 cm depth GAC (EBCT 1.5 sec). Influent toluene concentrations of 100, 400, and 1000 ppmv, were tested in separate columns. Toluene was supplied in the air stream 8 hr/day, and uncontaminated air flowed through the columns at the same rate and humidity level as during contaminant loading intervals for 16 hr/day. The intermittent loading regime began with dry air (<5% relative humidity). Subsequently, water vapor concentration in the influent air was progressively increased in step-wise fashion to approximately 30, 50, 60, 70, 80, and 90% relative humidity. At each humidity level tested, the loading condition was maintained until quasi-steady-state condition was observed for at least five days. Quasi-steady state, as used here, refers to the conditions when the total daily toluene mass entering and leaving the column were essentially the same and a consistent pattern of concentration variation was observed on a daily basis.

Actual feed concentration of toluene was verified for three days of loading before and after experiment for each of the columns.

4.3.3 Load Attenuation at 80% Relative Humidity for Various GAC Bed Depths and Influent Toluene Concentrations

Experiments to determine effects of water vapor on load equalization as a function of EBCT employed packed columns divided into four sections having GAC packed bed depths of
12.5, 20.8, 25, and 25 cm, respectively. Cumulative GAC depths from the top of the column were 12.5, 33.3, 58.3, and 83.3 cm, corresponding to GAC packed bed EBCTs of 1.5, 4.0, 7.0, and 10.0 sec, respectively, at a gas flow rate of 22.8 L/min. Monitoring ports located in a plenum between adjacent sections were used to measure toluene concentrations.

Syringe pumps were turned on 8 hr/day to achieve influent toluene concentrations of 100, 250, 400, or 1000 ppmv in each of the four columns tested. For the remaining 16 hr/day, uncontaminated air entered the columns. Relative humidity in the influent air was steady at 80% during both toluene loading and non-loading intervals. This loading regime was continued until quasi-steady state was achieved. The column receiving 100 ppmv toluene was maintained with intermittent contaminant loading (toluene supplied 8 hr/day) for more than 250 days to assess long-term performance of the GAC column.

4.3.4 Analytical Procedures

Toluene concentrations were measured using either a model 1312 photoacoustic multigas monitor (California Analytical, Orange, CA) or a model 600 HFID hydrocarbon analyzer (California Analytical, Orange, CA). Toluene data were recorded at 5.0 min intervals. Temperature and relative humidity recorded at 1.0 min intervals were measured using HiTemp102RH temperature and humidity data loggers (ERTCO, Dubuque, IA).

4.3.5 Pore and Surface Diffusion Modeling

The pore and surface diffusion model (PSDM) described by Crittenden et al. (1988) and Hand et al. (1997) was used for modeling GAC adsorption/desorption processes under intermittent (8 hr/day) toluene loading conditions. PSDM simulations were performed using the AdDesignSTM software package (Michigan Technological University). The PSDM is a dynamic
fixed-bed model that incorporates several assumptions (Mertz et al., 1999) enumerated in Chapter 2. Toluene and water co-adsorption at various toluene concentrations, relative humidity, and GAC packed bed depths was simulated by PSDM.

Dynamic adsorption calculations using this model require equilibrium parameters, kinetic parameters, physical properties of adsorbing compound(s) and adsorbent, fluid properties, influent concentrations, and column dimensions. A summary of parameter values and sources of data input to the model is presented in Table 4.1. Influent toluene and water vapor concentrations and air flow rates input to the model were identical to target experimental loading conditions tested.

4.4 Results

4.4.1 Load Attenuation of Toluene Supplied 8 hr/day at Various Relative Humidity Levels

Following start of intermittent toluene loading with dry air in GAC columns receiving toluene 8 hr/day, there was an initial period during which toluene accumulated in the GAC columns and no contaminant was detected in the effluent (data not shown). Eventually, breakthrough occurred and a consistent pattern of attenuated effluent toluene concentration was exhibited on a daily basis. Daily minimum ($C_{min}$) and maximum ($C_{max}$) toluene concentrations exiting the columns were consistently reproducible (within 5%) and mass balance calculations verified that contaminant mass entering and exiting the GAC columns on a daily basis were essentially equal (mass balance closure $\geq 95\%$). Hereafter, this condition is referred to as quasi steady-state behavior. Data were collected for a minimum of five days at quasi-steady state at each loading condition prior to increasing relative humidity to a higher level. Measured inlet
Table 4.1. Parameter values used in pore and surface diffusion model (PSDM) simulations of toluene-water co-adsorption using AdDesigns™.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
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<tr>
<td><strong>Fixed bed properties</strong></td>
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</tr>
<tr>
<td>Bed length</td>
<td>12.5 – 83.3 (^{a})</td>
<td>cm</td>
</tr>
<tr>
<td>Bed diameter</td>
<td>7.62 (^{a})</td>
<td>cm</td>
</tr>
<tr>
<td>Bed Mass</td>
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<td>kg</td>
</tr>
<tr>
<td><strong>Adsorbent properties (Calgon BPL 4\times6 mesh)</strong></td>
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<td></td>
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<tr>
<td>Particle apparent density ((p_a))</td>
<td>0.85 (^{b})</td>
<td>g/cm(^3)</td>
</tr>
<tr>
<td>Average particle diameter ((d_p))</td>
<td>0.372 (^{b})</td>
<td>cm</td>
</tr>
<tr>
<td>Particle void fraction ((\varepsilon_p))</td>
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<tr>
<td>Particle shape factor</td>
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<td><strong>Freundlich isotherm parameters for toluene</strong></td>
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<tr>
<td>K</td>
<td>305 (^{c})</td>
<td>((mg/g)(L/mg)^{1/n})</td>
</tr>
<tr>
<td>1/n</td>
<td>0.107 (^{c})</td>
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</tr>
<tr>
<td><strong>Freundlich isotherm parameters for water</strong></td>
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<tr>
<td>K</td>
<td>44.64 (^{d})</td>
<td>((mg/g)(L/mg)^{1/n})</td>
</tr>
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<td>1/n</td>
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<tr>
<td>Density</td>
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<td>Viscosity</td>
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<td><strong>Kinetic Parameters for toluene</strong></td>
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<tr>
<td>Film mass-transfer coefficient ((k_f))</td>
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<td>Pore diffusion coefficient ((D_p))</td>
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<tr>
<td>Surface to pore diffusion flux ratio</td>
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<td>dimensionless</td>
</tr>
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<td>Tortuosity</td>
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<td>dimensionless</td>
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<td><strong>Kinetic Parameters for water</strong></td>
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<td>cm(^2)/s</td>
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<tr>
<td>Surface diffusion coefficient ((D_s))</td>
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<td>Surface to pore diffusion flux ratio</td>
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</tr>
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<td>Number of radial collocation points</td>
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<td></td>
</tr>
</tbody>
</table>

\(^{a}\) Experimentally measured  
\(^{b}\) Data provided by Calgon Carbon Corp. (Pittsburgh, PA)  
\(^{c}\) Yaws et al., 1995  
\(^{d}\) Calculated by regression using experimentally determined adsorption data reported by Rudisill et al. (1992) for water vapor adsorption to BPL GAC at relative humidity range of 60 to 95% and T=25°C  
\(^{e}\) Calculated by correlation using the STEPP™ database (Mertz et al., 1999)  
\(^{f}\) Calculated by AdDesignS using Gnielinski correlation (Mertz et al., 1999)  
\(^{g}\) Calculated by AdDesignS using the Wilke-Lee modifications of the Hirschfelder-Bird-Spotz method (Mertz et al., 1999)  
\(^{h}\) Calculated by AdDesignS using Sontheimer correlation (Mertz et al., 1999) for toluene concentrations of 100 to 1000 ppmv or air RH of 30 to 90%.  
\(^{i}\) Assumed parameter based on experimental fit determined by Crittenden et al. (1988)
toluene and water vapor concentrations were found to closely match target concentrations (within 5% of target values, data not shown).

Experimental measurements of quasi-steady state toluene and water vapor breakthrough curves for GAC columns receiving 8 hr/day toluene loading in air with various relative humidity levels are shown in Figure 4.2. Each graph depicts data from a 48-hr period with toluene measured at 5.0 min intervals and water vapor measured at 1.0 min intervals. The $y$-axis of each graph is the dimensionless effluent concentration of toluene (left $y$-axis) or water (right $y$-axis) (effluent concentration, $C$, divided by corresponding influent concentration, $C_o$, entering during the loading interval). Time zero on the $x$-axis corresponds to the start of an 8-hr loading period during a 24-hr cycle. In each individual graph, the upper curves are for effluent water vapor concentration; bottom curves in each graph are for effluent toluene. Where the influent relative humidity was <5%, effluent water vapor concentrations were close to zero and hence, are not shown in the graphs. Results from model simulations are depicted as thin lines for influent relative humidity levels $\geq$60%.

For influent toluene concentrations of 100 and 400 ppmv, maximum toluene concentrations exiting the GAC columns at quasi-steady state were appreciably lower than influent concentration (i.e., $C/C_o < 1.0$) for all relative humidity levels tested. On the other hand, minimum toluene concentrations exiting the GAC columns were appreciably higher than influent concentration during 16 hours of no toluene loading (i.e., 0 ppmv). For 8 hr/day loading of 100 ppmv, toluene, toluene concentrations exiting the GAC column were quite uniform as a function of time near the “ideal buffering” level. “Ideal buffering” refers to the situation in which dynamically-varying concentrations of contaminants entering a GAC column are attenuated to such an extent that they exit the GAC column at a constant concentration equal to the time-
Figure 4.2. Effluent toluene (bottom curves) and water vapor concentrations (upper curves) from columns loaded 8 hr/day with toluene in air at various influent concentrations and influent relative humidity. Influent toluene concentrations, $C_o$, were 100 ppm, (left column), 400 ppm, (middle column) and 1000 ppm, (right column). Influent relative humidity, as indicated, varied from $< 5\%$ to $90\%$ relative humidity. Results of model simulations are also depicted as thin lines when influent relative humidity $\geq 60\%$. 

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weighted average of influent concentration (in this case, equal to one-third of the influent concentration during the loading interval, $C/C_o=0.33$, because influent toluene was provided 8 hr per 24 hr period).

For intermittent loading of toluene with an influent concentration of 1000 ppmv, maximum effluent toluene concentrations were slightly lower (by 31 ppmv only) than the influent concentration during the loading interval at relative humidity levels $\leq 70\%$. Appreciably lower maximum toluene concentrations were observed at higher relative humidity levels.

At a given influent relative humidity level, the degree of load attenuation for toluene decreased as the influent toluene concentration, $C_o$, increased. For example, at influent relative humidity of 60%, the dimensionless maximum daily effluent toluene concentration at quasi-steady state, $C_{\text{max}}/C_o$, was $0.34 \pm 0.003$, $0.53 \pm 0.01$, and $0.96 \pm 0.01$ for influent toluene concentrations of 100, 400, and 1000 ppmv, respectively. On the other hand, the trends for $C_{\text{max}}/C_o$ at increasing relative humidity were different for the various loading concentrations tested. For low toluene loading of 100 ppmv, increasing relative humidity in the gas stream tended to increase $C_{\text{max}}/C_o$ (decreased attenuation); at high toluene loading of 1000 ppmv, increasing relative humidity in the gas stream tended to decrease $C_{\text{max}}/C_o$ (increased load attenuation). For intermediate toluene loading of 400 ppmv, increasing the relative humidity to up to 90% did not generally alter degree of load attenuation, with most apparent exception when relative humidity=70%. There was a slight deviation in $C_{\text{max}}/C_o$ from the average value of $C_{\text{max}}/C_o=0.54$ (216 ppmv) at all other relative humidity levels, to $C_{\text{max}}/C_o=0.45$ (180 ppmv) at relative humidity=70%. This corresponds to a difference of 36 ppmv.

For a fixed influent toluene concentration, more pronounced maximum and minimum effluent water concentrations were observed when influent humidity concentration was higher.
For a fixed influent relative humidity level, larger difference between maximum and minimum effluent water concentrations was observed at higher toluene concentrations. For example, at 80% influent relative humidity and 100 ppmv influent toluene, the maximum water vapor concentration in the effluent deviated only slightly from the minimum (a difference of 0.70 mg/L between maximum and minimum water concentration). In contrast, at 80% relative humidity and 1000 ppmv influent toluene, the maximum water vapor concentration in the column effluent differed from the minimum by 2.04 mg/L. In columns receiving ≥80% relative humidity, experimentally measured water vapor concentrations exiting the GAC columns increased to levels higher than influent concentrations following the start of the 8 hr daily toluene loading intervals. This was most readily apparent for columns receiving higher influent toluene concentrations (e.g., 1000 ppmv) and higher relative humidity (e.g., 90%).

PSDM model simulations employing IAST to account for competitive adsorption effects were in good general agreement with experimentally observed measurements of both toluene and water vapor concentrations exiting the GAC columns receiving intermittent toluene loading in the continuous flow of humidified air. Differences between experimental measurements and model simulations were quite small, especially for experiments conducted using 100 ppmv toluene. Effluent water vapor concentrations were consistently over-predicted for influent toluene concentration of 1000 ppmv. Qualitatively, however, the model simulations were in agreement with the general trends that were experimentally observed. Simulations indicated that columns loaded with lower toluene concentrations (i.e., 100 ppmv) would achieve slightly worse load attenuation as relative humidity increased, consistent with what was experimentally observed. Simulations also indicated the trend that for higher influent toluene concentrations (i.e.,
1000 ppmv), the degree of toluene load equalization would increase while at the same time, peak effluent water vapor concentrations would also increase.

Plots of daily toluene maxima and minima (expressed as $C_{\text{max}}/C_o$ and $C_{\text{min}}/C_o$) at various influent toluene and relative humidity levels are shown in Figure 4.3. Each data point in the figure represents the average of daily values from at least five days of monitoring after quasi steady-state was reached. As depicted in the figure, for all levels of $C_o$, there was a relative humidity threshold below which water vapor did not have a discernable effect on GAC load attenuation of toluene in terms of $C_{\text{max}}$ and $C_{\text{min}}$. At relative humidity levels of 70% and higher, effects become more apparent. With 100 ppmv, there was a small but readily apparent increase in the daily maximum effluent toluene concentration and a decrease in the daily minimum effluent toluene concentration (i.e., high relative humidity had a negative effect on GAC load equalization). This difference, however, was less than 10 ppmv and still represents a large degree of load equalization. In somewhat of a contrast, for influent toluene concentrations of 1000 ppmv, at relative humidity levels ≥70%, lower $C_{\text{max}}$ values and higher $C_{\text{min}}$ values were observed. (i.e., high relative humidity improved load attenuation). For toluene loading of 400 ppmv, increased relative humidity did not effect discernable change in degree of load attenuation except at 70% relative humidity.

4.4.2 Impact of EBCT and Influent Toluene Concentration at 80% Relative Humidity

Experimentally measured quasi-steady state breakthrough curves for GAC columns receiving air flow containing 80% relative humidity and intermittent (8 hr/day) loading of toluene under various EBCTs (1.5, 4.0, 7.0, and 10 sec) and influent toluene concentrations (100, 250, 400, and 1000 ppmv) are shown in Figure 4.4. Each graph in the figure shows data from a 48-hour interval of loading after the system reached quasi-steady state. A consistent daily pattern
Figure 4.3. Average maximum (filled symbol) and minimum (open symbol) effluent toluene concentration from columns (EBCT 1.5 sec) loading toluene in air stream at various relative humidity and influent concentration of $C_o=100$ ppmv (top), $C_o=400$ ppmv (middle), and $C_o=1000$ ppmv.
Figure 4.4. Effluent toluene (bottom curves) and humidity (upper curves) profiles at various EBCT and influent toluene concentrations in a humid gas stream (80% relative humidity). Loading condition: 8 hr/day of toluene-contaminated air, 16 hr/day of toluene-free air. Model simulation results are shown as thin lines on the graphs. Time zero in each graph corresponds to the start of an 8-hr loading period after quasi-steady state was reached.
of concentration for both effluent toluene and water was exhibited. Daily maximum and minimum values were consistently reproducible (differing by ≤5% on a day to day comparison), and mass balance calculations verified that toluene and water masses entering test columns were essentially the same as those exiting on a daily basis (within 5%). Model simulation results for the various loading conditions are also depicted as thin lines in the graphs. In each individual graph, bottom curves correspond to those of effluent toluene concentrations while the upper curves correspond to effluent water vapor concentrations.

The degree of load attenuation (characterized by lower $C_{\text{max}}$ and higher $C_{\text{min}}$) increased as the EBCT increased. For example, the average $C_{\text{max}}/C_o$ and $C_{\text{min}}/C_o$ observed from a 1.5-sec EBCT column receiving 400 ppmv toluene were 0.54 and 0.21, respectively. For a 10-sec EBCT column with identical loading, the average $C_{\text{max}}/C_o$ and $C_{\text{min}}/C_o$ observed were 0.35 and 0.31, respectively. Smaller differences between maximum and minimum values at higher EBCT indicate a higher degree of load attenuation in taller columns. Degree of load attenuation also increased as the influent toluene concentration decreased. At each EBCT tested, the effluent toluene concentration was more attenuated at lower influent concentration of 100 ppmv than it was for a higher influent concentration of 1000 ppmv. For example, at 1.5 sec EBCT and 100 ppmv, effluent $C_{\text{max}}/C_o$ and $C_{\text{min}}/C_o$ observed were 0.42 and 0.30, respectively; while for the same column height and 1000 ppmv, experimentally observed effluent $C_{\text{max}}/C_o$ and $C_{\text{min}}/C_o$ were 0.77 and 0.14, respectively.

Similar trends were observed for water vapor, with effluent water vapor concentrations more attenuated with higher EBCT and when influent toluene concentrations were lower. These trends for both toluene and water were reasonably well captured in model simulations. Although the model over-predicted maximum toluene and water vapor concentrations at high toluene
concentration (i.e., 1000 ppmv) and model water vapor concentrations were out of phase with experimentally-determined daily peaks, the model qualitatively predicted the trends of toluene-water co-adsorption.

To further assess differences in GAC load attenuation between dry and humid air streams, experimentally determined values of toluene $C_{\text{max}}/C_o$ with air at 80% relative humidity were plotted as a function of column EBCT (Figure 4.5) along with lines representing $C_{\text{max}}/C_o$ and $C_{\text{min}}/C_o$ values determined in PSDM simulations using input parameters previously validated for dry air (Li and Moe, 2005). Each experimental data point in the figure represents the average of at least five replicate loading cycles determined after the columns reached quasi steady-state. At EBCTs $\geq$ 7.0 sec, $C_{\text{max}}/C_o$ values experimentally determined at 80% relative humidity (present study) were quite similar to base-line model curves for dry air (Moe and Li, 2005). At low EBCT (e.g., 1.5 sec), however, some deviations of $C_{\text{max}}/C_o$ and $C_{\text{min}}/C_o$ from the base-line model curves were observed. For example, at 1000 ppmv influent toluene, experimentally determined values of $C_{\text{max}}/C_o$ was 224 ppmv (22.4%) lower and $C_{\text{min}}/C_o$ was 59 ppmv (5.9%) higher at 80% relative humidity than was predicted by the model for dry loading conditions (i.e., the base-line model under-predicted degree of load equalization). On the other hand, at influent toluene concentration of 100 ppmv, experimentally determined $C_{\text{max}}/C_o$ at 80% relative humidity was 7.5 ppmv (7.5%) higher and $C_{\text{min}}/C_o$ was 2.1 ppmv (2.1%) lower than the base-line model (i.e., the base-line model over-predicted degree of load equalization) when EBCT=1.5 seconds.

For the column receiving 100 ppmv toluene 8 hr/day, loading was continued for more than 250 days to assess long-term performance. Toluene and water vapor concentration profiles observed after this long-term operation were essentially identical to profiles observed shortly after the system reached quasi-steady state.
Figure 4.5. Experimental $C_{\text{max}}/C_o$ (■) and $C_{\text{min}}/C_o$ (□) of effluent toluene from columns of various EBCTs loading toluene (8 hr/day, 80% relative humidity) at various influent concentrations, $C_o$, compared with model-generated curves from Moe and Li (2005).
4.5 Discussion

Data gathered from the present study demonstrated that toluene mass can temporarily accumulate in a GAC column during intervals when influent contaminant concentrations are high and desorb within a sufficiently short time interval (i.e., during each loading cycle) when influent concentrations are low, to be of practical benefit as a passively-operated load equalization system even when humidity in the gas stream is high. The only driving force necessary for contaminant desorption was the decrease in influent contaminant concentration imposed by the gas stream. Regeneration of the carbon through other means (e.g., heating as described by Emamipour et al., 2007) was not necessary.

The degree by which a GAC column can attenuate variability in contaminant loading concentration was assessed by comparing the differences in maximum ($C_{\text{max}}$) and minimum ($C_{\text{min}}$) concentration of contaminants in the GAC column effluent (i.e., the smaller the difference, the better is the load attenuation). Ideally, for certain conditions of loading (low contaminant loading in tall columns), the system approaches perfect load equalization when concentrations from the GAC column approach a constant value (i.e., $C_{\text{max}} - C_{\text{min}} = 0$) equivalent to the time-weighted average of the influent concentration. In this study, experimentally tested short columns achieved nearly perfect or ideal load attenuation for low toluene concentrations and low relative humidity. For example, at constant toluene loading of 100 ppm, during 8 hrs/day, ≤ 5% relative humidity, the concentration profile exiting the GAC column was almost a straight line at approximately constant concentration of 33 ppm, (i.e., time-weighted average for constant loading of 100 ppm, for 8 hrs/day and 0 ppm, for 16 hr/day).

During intermittent loading of toluene in the presence of water vapor, results of this study suggest that there is relative humidity threshold (~70% relative humidity) level below which the
effects of water vapor on GAC load attenuation are not readily apparent in terms of load
equalization performance. Above this threshold, the impact of high relative humidity on GAC
load attenuation varied from slightly reduced attenuation (higher $C_{max}/C_o$) when influent toluene
was low (i.e., 100 ppmv), to increased load attenuation (lower $C_{max}/C_o$) when influent toluene
was high (i.e., 1000 ppmv). The humidity threshold above which such effects were observed
correlates well with the relative humidity range previously reported as causing decreased
adsorption capacity for organic adsorbates in continuous-flow systems. Cal et al. (1996) reported
that water vapor had little effect on the adsorption capacity of benzene (500 ppmv) until 65%
relative humidity when rapid decrease resulted in the adsorption capacity of benzene. Russell and
Levan (1997) also observed significant effect of water on alkane adsorption starting at relative
humidity of 50%.

Water and toluene co-adsorption onto GAC is a case of competitive adsorption, which
had been previously observed with organic multi-component vapor-phase carbon adsorption
(Gong and Keener, 1993; Li and Moe, 2004). Earlier elution of the component with lower
affinity for activated carbon was usually observed. The displacement of the weakly adsorbed
component, while it is continuously supplied in the gas flow, results in an increased total effluent
concentration that is higher than the influent concentration. Hence the so-called “roll-over”
phenomenon for the component with lower affinity for the adsorbent. Competitive sorption
effects can be caused by differences in physical properties of the adsorbates and the adsorbent
(Ruthven, 1986; Yang, 1987). Such activated carbon (adsorbent) surface characteristics may
include pore volume, specific surface area, and polarity, while adsorbate properties may include
dipole moment, boiling point, and molecular weight (Chiang et al., 2001). Activated carbon has
a higher affinity for VOCs than for water vapor (Crittenden et al. 1988; Rudisill et al. 1992).
Because the surface of activated carbon is non-polar or slightly polar, it generally has higher affinity and higher adsorption capacity for non-polar organics (e.g., toluene, dipole moment of 0.36 debyes) than it does for polar organics (e.g., water, dipole moment of 1.85 debyes) (Gong and Keener, 1993). Furthermore, toluene has additional characteristics favoring adsorption over water, namely, higher boiling point than water (111°C vs 100°C, P= 1 atm), and higher molecular weight than water (92 vs 18 g/mol). Therefore, toluene is likely to outcompete water for adsorption onto GAC and displace adsorbed water from GAC. This is consistent with the results of continuous loading experiments described in Appendix A.

In this study, especially at high influent concentrations of toluene and water vapor, competitive adsorption during intermittent loading of toluene with continuous loading of water vapor was manifested in (1) cyclic daily patterns of increase and decrease of effluent water vapor; and (2) “roll-over” phenomenon observed with water vapor concentrations in the effluent. Observation of daily cyclic patterns of increase and decrease of effluent water vapor in columns supplied with intermittent toluene but steady relative humidity is consistent with the notion that there can be temporary adsorption of water vapor onto GAC when toluene is lean or absent in the gas flow and water displacement from GAC when toluene, present in the air stream at high concentration, adsorbs to GAC. When influent toluene concentration was zero, there was a driving force for desorption of toluene from GAC located near the packed bed depth inlet. As toluene desorbed, sites became available for adsorption of water. When the toluene concentration in the influent was subsequently increased at the start of the next loading interval, toluene displaced the water that had temporarily accumulated during the 16 hr period of no toluene loading.

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The “roll-over” phenomenon was evident in some concentrations of water in the effluent that were higher than the level of concentration in the influent (i.e., C/C₀ > 1.0). In continuously loaded columns receiving contaminant mixtures on a continuous basis, this phenomenon occurs when more strongly adsorbing compounds displace more weakly adsorbing components that initially accumulated in an adsorbent column at a time prior to when breakthrough is observed (Kapoor and Yang, 1987; Jedrzejak et al., 1989). In the present experiment, it likely reflects the fact that a portion of the water temporarily accumulating on the GAC during the 16 hr/day interval of no toluene loading was displaced by toluene during the 8 hr/day of toluene loading. The combination of this displaced water with that which continuously enters the column but was not adsorbed (because toluene was preferably adsorbing) would have resulted in higher water concentrations in the effluent than in the influent during some time intervals. During intervals when toluene was absent from the influent and there was a net driving force for toluene desorption, water was able to re-occupy adsorption sites vacated by toluene, leading to a net accumulation of water in the column and hence water vapor concentrations lower than the influent were present in the effluent. Thus, the competitive effects were observed each daily loading cycle rather than only once during initial breakthrough as would be the case for a column receiving a gas flow with two competitively adsorbing compounds on a continuous basis.

Among the most common approaches for predicting multi-component adsorption based on classical thermodynamic methods is the Ideal Adsorbed Solution Theory – IAST (Qi et al., 2000; Jorge and Seaton, 2003). IAST was the first major theory predicting mixed gas adsorption from pure component isotherms and remains the most widely accepted (Yang, 2003). Such an approach was successfully used to predict the degree of load equalization achieved by activated carbon for a binary contaminant mixture of toluene and acetone (Li and Moe, 2005). For
mixtures of water and hydrocarbons adsorbed on activated carbon, however, IAST may perform poorly because the system is far from ideal and the fundamental mechanisms of water adsorption are different from that of hydrocarbons (Doong and Yang, 1987; Huggahalli and Fair, 1996; Jorge and Seaton, 2003). While organic molecules are adsorbed on the adsorbent surface mainly by strong dispersion forces, water vapor adsorption occurs as water molecules are attracted to oxygen complexes on the carbon surface and to other adsorbed water molecules with which they hydrogen bond at low pressures, followed by the formation and coalescence of water clusters and capillary condensation at higher pressures (Qi and LeVan, 2005). In addition, water adsorption shows hysteresis on adsorption and desorption branches, which distinguishes it from organic adsorption. While the Freundlich isotherm equation generally well-describes adsorption of organics such as toluene to GAC (Chatzopoulos et al., 1993; Moe and Li, 2005), adsorption of water vapor to GAC generally follows a type V isotherm (i.e., S-shaped) in the International Union of Pure and Applied Chemistry (IUPAC) classification system (Lin and Nazaroff, 1996). As such, modified Langmuir isotherm equations have been used to describe the adsorption of water vapor over the entire range of relative humidity.

On the other hand, Qi and LeVan (2005), reported that toluene-water co-adsorption onto BPL activated carbon is well-described by IAST, better than is the MEK-water system. Results of the present study conform to this result and a qualitative prediction of trends of toluene and water concentrations in the gas phase during their co-adsorption onto BPL GAC was observed. At high relative humidity (≥ 80%), experimentally observed tendency of decreased load attenuation at low toluene loading (i.e., 100 ppmv) and increased load attenuation at high toluene loading (i.e., 1000 ppmv) were consistently predicted by the model. PSDM simulations
conducted employed the assumption of adsorption equilibrium for competitive adsorption of toluene and water described by the Ideal Adsorbed Solution Theory (IAST).

In the model simulations conducted using the AdDesignSTM software package, individual component’s adsorption equilibrium was described using Freundlich isotherms. These Freundlich parameters for toluene are readily available from the database provided in the package, but not for water. Instead, these parameters for water were approximated from regression analyses of adsorption and desorption data for water onto BPL granular activated carbon that are available in literature (Qi et al., 2005, Qi et al., 2006, Rudisill et al., 1992, Sullivan et al., 2007) for data within the range of 60-90% relative humidity. It is within this range that this study found significant effect of high relative humidity on GAC column performance. Of the various sets of Freundlich parameters calculated, that determined from Rudisill et al. (1992) conformed with the experimental data generally well. These parameters \(K=44.642 \text{ (mg/g)}(L/mg)^{1/n}; 1/n=0.7092; r^2=0.98\) were used in subsequent simulations and results shown indicate sufficiency of parameter values for prediction of dynamics of toluene-water co-adsorption as ideal mixtures (hence, validity of IAST) under the PSDM.

The present study at high relative humidity demonstrates that the degree of load attenuation is a function of both column EBCT and influent toluene concentration, consistent with results reported previously for dry air (Moe and Li, 2005). Overall, results indicate that effects of high relative humidity on toluene load attenuation become negligible at sufficiently long EBCT. Based on Figure 4.5, for influent toluene concentrations 100 ppmv to 1000 ppmv., a short column EBCT of about 4.0 sec could be sufficient to dampen off humidity effects (up to 80% relative humidity) to achieve similar column performance as when the gas stream is dry. For example, for toluene loading of 400 ppmv (8 hrs/day) through a column with equivalent
EBCT of 4.0 sec, the experimentally determined $C_{\text{max}}/C_o$ when air relatively humidity was at 80% was only slightly higher than the corresponding value when air was dry (0.45 vs 0.39). As such, design curves previously developed for the dry toluene-air gas stream may prove useful in preliminary design of GAC-biofilter systems subjected to high relative humidity.

Maximum effluent concentration, expressed as fraction of the influent concentration ($C_{\text{max}}/C_o$), was used to provide a useful tool for assessing performance of GAC load equalization systems. It was also suggested as a design parameter for GAC load equalization columns integrated with biofilters (Moe and Li, 2005; Moe et al., 2007). In conjunction with $C_{\text{max}}/C_o$, the minimum concentration exiting a GAC column at any time during the loading cycle ($C_{\text{min}}/C_o$), also provides useful information about the GAC load equalization process, because it allows assessment of whether starvation conditions would be imposed on a downstream biofilter during intervals when contaminant concentrations are low. Previous studies demonstrated that peak loading to a biofilter could be greatly reduced and starvation during periods of low or no contaminant loading could be minimized or entirely avoided at sufficiently long EBCTs and column heights (Moe and Li, 2005; Moe et al., 2007).

Experimental observations from this study show that although toluene could outcompete water for adsorption onto GAC, water effect on toluene adsorption could be significant at high relative humidity. To certain extent, GAC column performance with respect to equalizing transient concentrations of toluene was also influenced by the presence of high relative humidity in the air stream. Overall, however, the results gathered demonstrate that GAC columns can achieve equalization/attenuation of intermittently-loaded contaminants even in the case when humidity in the gas stream is high. These results are reasonably supported by model simulations conducted.
4.6 Conclusions

- At relative humidity $\leq 60\%$, the presence of water vapor did not have a discernable impact on load equalization by GAC columns subjected to intermittent (8 hr/day) toluene loading.

- At relative humidity levels $\geq 60\%$, the presence of water vapor tended to improve load attenuation by GAC column with high influent toluene concentration (e.g., 1000 ppmv) during intermittent (8 hr/day) contaminant loading. On the other hand, high humidity tended to worsen performance of GAC columns with respect to attenuating intermittent loading of toluene at low concentrations (e.g., 100 ppmv).

- Consistent with earlier research with dry air, load attenuation by GAC columns increased with increasing EBCT. For a given EBCT, load attenuation increased with decreasing influent toluene concentration.

- PSDM simulations performed using IAST to account for the competitive adsorption of toluene and water on GAC, conformed generally well to the experimental data obtained for relative humidity between 60 to 90\%.
CHAPTER 5
ACTIVATED CARBON LOAD EQUALIZATION OF TRANSIENT CONCENTRATION SPIKES OF GAS-PHASE TOLUENE

5.1 Introduction

Owing to the unsteady nature of industrial processes, many fixed-film bioreactors (e.g., biofilters) used for air pollution control) are subjected to temporary loading conditions in which spikes in influent concentration of volatile organic compounds (VOCs) occur over short time intervals. Temporary periods of high concentration loading can be problematic because they often result in a temporary decrease in biofilter treatment performance (Atoche and Moe, 2004; Cox and Deshusses, 2002; Kim et al., 2007; Marek et al., 2000; Moe and Irvine, 2001; Mohseni et al., 1998; Siegnez et al., 2004; Song and Kinney, 2005; Wani et al., 2000). Diminished treatment performance in biofilters subjected to large influent contaminant concentration spikes has been attributed to limitations in mass transfer rates and biological reaction capacity (Moe and Irvine, 2001; Wright, 2005).

Previous studies have demonstrated that passively-operated GAC load equalization columns can markedly attenuate peak loading to downstream air pollution control devices and that GAC columns can function effectively over long-term operation without the need for external regeneration or operator intervention (Li and Moe, 2005; Moe and Li, 2005; Moe et al., 2007). While promising in concept, previous studies on passively-operated GAC load equalization systems have investigated system performance under a rather limited range of potential loading conditions. In particular, studies have only dealt with what may be categorized as “regular” transient loading, conditions in which an identical loading pattern is observed on a recurring basis. Most studies have been conducted with contaminant loading to the system at a constant influent concentration for 8 hr/day and no contaminant loading for the rest of the day,
intended to simulate industrial operations with an 8 hr/day work schedule (Weber and Hartmans, 1995; Li and Moe, 2005; Moe and Li, 2005). One study explored the effect of cycle lengths and relative lengths of loading to non-loading periods, however, the influent contaminant concentration during loading intervals was constant (Moe et al., 2007). In contrast, contaminant loadings to biofilters in actual industrial operations are often highly dynamic with considerable variation over short time intervals. In this sense, the loading may be classified as “irregular,” because the loading conditions do not occur in identical fashion on a fixed, recurring interval.

The study reported in this chapter was conducted to explore the potential for using passively-operated GAC columns to attenuate irregular loading of VOCs characterized by short duration and high intensity relative to baseline loading concentrations. The experimental regime included testing of GAC columns subjected to isolated spikes in toluene concentration as well as complex loading patterns involving multiple spikes in series. A MATLAB code developed in the Mathematics Department at the Louisiana State University was used to implement the pore and surface diffusion model to allow simulation of transient loadings of varying intensity and short duration. Furthermore, GAC load equalization performance was also assessed through model simulations at various GAC column depths and empty bed contact times (EBCTs).

5.2 Materials and Methods

5.2.1. Granular Activated Carbon (GAC) and Experimental Apparatus

The adsorbent employed in this research was BPL 4×6 mesh GAC (Calgon Carbon Corp., Pittsburgh, PA), a bituminous coal-based activated carbon designed for use in vapor phase applications. GAC was rinsed with distilled water to remove fines, dried at 105°C, and stored in dessicators prior to use.
The configuration of the experimental apparatus used in initial fixed-bed adsorption/desorption experiments (Figure 5.1), included two air supply lines. Each supply line was connected to a three-way valve that allowed switching of flows to a common line that entered the GAC column. Each of the packed columns, constructed of 7.62 cm ID PVC pipe, contained a stainless steel support mesh at the bottom, 6-cm depth glass beads to distribute air flow, a thin layer of glass wool, a 10-cm layer of GAC (mass 200 g), another thin layer of glass wool, and another 6-cm glass beads.

Figure 5.1. Experimental apparatus used in conducting fixed-bed adsorption desorption experiments with transient concentration spikes of gas-phase toluene.
Electronic mass flow controllers (Aalborg Instruments, Orangeburg, NY) regulated air flow through the system. For all experiments, air flow rate through the GAC column was 22.8 L/min, corresponding to superficial gas velocity of 300 m/h in the packed columns. Liquid toluene (ACS reagent grade, Sigma, St. Louis, MO) was delivered by syringe pumps (KD Scientific, Boston, MA) and evaporated into the air stream.

Gas supply and sampling lines were constructed of Teflon tubing. Initial tests conducted prior to placement of activated carbon demonstrated that column components other than GAC had little or no adsorption capacity for toluene. All experiments were conducted at ambient laboratory temperature of 23±2°C.

5.2.2. Evaluation of Spike Intensity and Duration Effects

For initial experiments, toluene-contaminated air at a baseline influent concentration of 100 ppmv, toluene was loaded to each GAC column until breakthrough and a steady-state concentration of toluene was observed in the effluent. Thereafter, spikes of toluene up to ten times the baseline concentration were loaded to the column by temporarily diverting the air stream entering the column to a side vent, and replacing it with a parallel gas flow with the same flow rate but with the target spike concentration. At the end of the spike-loading interval, the higher toluene concentration gas flow was diverted to a side vent and the gas flow containing 100 ppmv, toluene was restored to the column influent. This allowed near instantaneous changes in the influent toluene concentration. The toluene concentration was monitored in the gas flow exiting the GAC column before, during, and after the spike loading to assess performance. Each transient loading was separated by at least two days, which was sufficient for the effluent toluene concentrations to return to the pre-spike baseline level.
To determine GAC column performance at various spike concentrations, toluene-contaminated air at constant toluene concentrations of 200, 500, 700 and 1000 ppmv (2, 5, 7, and 10× baseline concentration, respectively) were loaded to the column for 1.0 hr duration. To explore the effects of various durations of spike loading, a 1000 ppmv toluene-contaminated airflow was loaded to the column at spike durations of 4.0 hr, 2.0 hr, 1.0 hr, 30 min and 15 min. Half of the transient loading experiments were tested in duplicate to verify reproducibility of the results observed.

5.2.3. Multiple Spike Loading

Further experiments were conducted to investigate the performance of GAC load equalization systems under highly dynamic loading conditions intended to simulate industrial operations with wide variation in contaminant concentrations during an 8 hr/day work schedule. The loading scenario included four target influent concentrations, 100, 200, 500, and 1000 ppmv, (1, 2, 5, and 10× the baseline concentration of 100 ppmv) occurring for various durations (5, 10, 15, 30, 60 min) throughout an 8 hr/day loading interval (see Figure 5.2). During the remaining 16 hr/day, toluene-free air flowed through the column at the same flow rate as during loading intervals. The target time-weighted average influent toluene concentration was 250 ppmv during the 8 hr/day loading interval. The time-weighted average concentration calculated accounting for the 16 hr/day interval of no loading was 83 ppmv. The experimental apparatus used to test this loading scenario was identical to that employed in single-spike experiments (Figure 5.1) except that there were four parallel gas flows, which allowed introduction of gas with four different influent concentrations at different time intervals.
5.2.4. Analytical Procedures

Influent and effluent toluene concentrations were measured using a model 1312 photoacoustic multigas monitor (California Analytical, Orange, CA) as described previously (Moe et al., 2007) with concentrations recorded at 1.0 min intervals. A model 600 HFID hydrocarbon analyzer (California Analytical, Orange, CA) was used to measure toluene concentrations in the side-stream exhaust flow to verify stable influent toluene concentrations prior to changing the influent gas flow streams at the start of the spike-loading conditions.

Figure 5.2. Target toluene concentrations entering the GAC column during the 8 h/day loading interval of dynamic multi-spike loading experiments. During the remaining 16 hr/day, uncontaminated air flowed through the GAC column.
5.2.5. MATLAB Simulations of the Pore and Surface Diffusion Model

The pore and surface diffusion model (PSDM) described by Crittenden et al. (1988) and Hand et al. (1997) was used to simulate the dynamic toluene adsorption and desorption on granular activated carbon (GAC) under loading conditions characterized by spikes in concentrations occurring at various intensity and duration. MATLAB was utilized to implement a numerical approach to solve the system of PDEs describing the dynamics of adsorption in fixed-bed adsorbers based on PSDM (see Chapter 2). The solution methodology closely followed the numerical approach presented by Friedman (1984) and Crittenden et al. (1986). The PDEs, initial conditions, and boundary conditions in eqn. (2.1)-(2.8) describing adsorber dynamics were first converted into dimensionless form and then reduced to a system of ordinary differential equations (ODEs) by the method of orthogonal collocation as described previously (Friedman, 1984; Crittenden et al., 1988). The intra particle phase equation (Eqn. 2.4) was expanded using symmetric orthogonal polynomials with even powers of $x$ (Jacobi polynomials of the form shown in eqn. 5.1) and with weighting factor equal to $1-x^2$ (Finlayson, 1972).

$$y(x^2) = \sum_{i=1}^{N+1} d_i x^{2i-2}$$

(5.1)

The gas bulk phase equation (eqn. 2.1) was expanded using non symmetric orthogonal polynomials (shifted Legendre polynomials of the form shown in eqn. 5.2) with weighting factor equal to 1 (Finlayson, 1972).

$$y(x) = \sum_{i=1}^{N+2} d_i x^{i-1}$$

(5.2)
The collocation points are the roots of these polynomials and were used as a discrete approximation to the spatial variable. The first and second spatial derivatives at each interior collocation point were discretized as the matrix product of the terms from the solution at the collocation points. Boundary conditions were also approximated with the same procedure. Spatial discretization of the PDE produces a system of ODEs that evolves from each collocation point in the computational domain. The resulting system of ODEs was solved using the MATLAB solver ode15s, which is designed for stiff problems. The ode15s subroutine is a variable order solver based on the numerical differentiation formulas (NDFs); optionally, it uses the backward differentiation formulas (also known as Gear's method) that are usually less efficient (Shampine and Reichelt, 1997). Collocation matrices and the roots of Legendre polynomials were verified against tabulated values given in the literature (Finlayson, 1972; Figueroa et al., 2006). The computer program was validated by comparison of simulation results to results from the Adsorption Design Software package (AdDesignS, Mertz et al., 1999) for simulation conditions to which both apply (Friedman, 1984; Moe et al., 2007). Additional comparisons were made with experimental measurements from the present study.

Calculations using the PSDM require equilibrium parameters, kinetic parameters, physico-chemical properties of adsorbing compound(s) and adsorbent, gas properties, concentration data, and column dimensions. A summary of parameter values and sources of data input to the model is presented in Table 5.1. Constant influent air flow rates and time-varying influent toluene concentrations input to the model were identical to the target loading conditions that were experimentally tested.

To investigate the effects of EBCT on GAC column response to transient loading, the new MATLAB code was used to simulate transient loadings with GAC packed bed depths of
Table 5.1. Parameter values and data input to the MATLAB program to implement the pore and surface diffusion model.

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<th>Parameter</th>
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<td><strong>Fixed bed properties</strong></td>
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</tr>
<tr>
<td>Bed diameter</td>
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<tr>
<td>Number of radial collocation points</td>
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<td></td>
</tr>
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</table>

*a* Assumed values, other than the case of 10 cm GAC packed bed depth, which was experimentally measured.

*b* Experimentally measured.

*c* Experimentally measured by Moe and Li (2005) for GAC packed beds with bulk density identical to that experimentally tested in the present study.

*d* Data provided by Calgon Corp. (Pittsburgh, PA).

*e* Assumed parameter based on experimental fit determined by Moe and Li (2005).

*f* Calculated by correlation using the StEPP™ database (Mertz *et al.*, 1999).

*g* Calculated using the Wilke-Lee modifications of the Hirschfelder-Bird-Spotz method (Mertz *et al.*, 1999).

*h* Calculated by using Sontheimer correlation as described by Mertz *et al.* (1999).

2.5, 5.0, 7.5, 10.0, 25.0, and 50.0 cm, corresponding to GAC column EBCTs of 0.3, 0.6, 0.9, 1.2, 3.0, and 6.0 seconds, respectively, at a superficial gas velocity of 300 m/hr.

5.3 Results

5.3.1 GAC Column Performance at Various Spike Intensity and Duration

Prior to the start of dynamic loading experiments, the GAC columns were subjected to continuous loading with air containing 100 ppm, toluene to establish base-line conditions. Following the start of continuous loading of toluene-contaminated air, there was an initial period during which toluene accumulated in the GAC column and no contaminant was detected in the effluent (Appendix Figure B.1). Complete breakthrough was achieved after approximately five days of continuous loading, and a near constant concentration of toluene was observed in the effluent that was essentially equal to the influent concentration (≤5% difference). Transient spikes comprised of temporary step-increases in toluene varying in influent concentrations and duration were then introduced to the GAC columns. Measured influent toluene concentrations during each of the spike loading conditions were found to closely match target concentrations (within 5% of target values, Appendix Figures B.2 and B.3).

Experimental measurements of effluent toluene from GAC columns which received transient spikes of 1000 ppm, toluene for various durations are shown in Figure 5.3. Results obtained for loading conditions tested in duplicate (4.0, 2.0, 1.0 hr spike duration) showed excellent reproducibility, with maximum effluent toluene concentrations differing only by <3% (see Appendix Figure B.4). For loading conditions tested in duplicate, point-by-point averages from the duplicate tests are depicted in Figure 5.3. Each graph shows data from a 24-hr interval with toluene measured at 1.0-min intervals. Time zero on the x-axis corresponds to the start of a spike loading period. Results from model simulations are also depicted.
Figure 5.3. Toluene concentrations exiting a GAC column (10 cm packed bed depth; EBCT 1.2 sec) after spike loading of 1000 ppm, toluene (10× baseline concentration of 100 ppm, toluene) for various durations. Corresponding model simulation results are depicted as open symbols.
At the spike concentration of 1000 ppmv toluene (10× the baseline loading of 100 ppmv), longer spike durations resulted in higher peak effluent toluene concentrations. In all cases tested, however, the maximum toluene concentrations exiting the GAC columns were well below the inlet spike concentration (1000 ppmv). Maximum effluent toluene concentrations experimentally observed when the spike duration was 4.0 hr averaged 634 ppmv, while maximum effluent concentrations for spike durations of 2.0, 1.0, 0.50, and 0.25 hr were 282, 180, 130, and 115 ppmv, respectively. In all loading cases tested, effluent toluene concentrations decreased back to the pre-spike baseline level of 100 ppmv within two days. Mass balance calculations verified that total toluene mass loaded to the column was essentially equal to the total amount exiting the column (≤5% difference) over this time interval.

Effluent toluene concentrations measured from GAC columns which received spikes of various concentrations (10, 7, 5, and 2× the baseline loading level of 100 ppmv) for a fixed duration of 1.0 hr revealed that as the inlet spike concentration decreased, the maximum toluene concentration observed in the GAC column effluent also decreased (Figure 5.4). For all spike levels tested, maximum toluene concentrations exiting the GAC column were well below the influent spike concentration. For example, a 1.0 hr duration spike in loading of 1000 ppmv toluene (10×C₀) was dampened to a maximum effluent concentration of 180 ppmv, corresponding to an 82% decrease in maximum concentration that would enter a biofilter or other downstream air pollution control device. For 1.0 hr spike loadings of 700, 500, and 200 ppmv toluene, maximum toluene concentrations exiting the GAC columns were 146, 130, and 108 ppmv, respectively.

For single spike loadings of varying duration (Figure 5.3) and intensity (Figure 5.4), model simulations were in close agreement with experimental measurements; however, the
Figure 5.4. Toluene concentrations exiting a GAC column (10 cm packed bed depth; EBCT 1.2 sec) after spike loading of various toluene concentrations for a 1.0 h duration. The baseline influent toluene concentration before and after spike loading was 100 ppmv. Model simulation results are depicted as open symbols.
model slightly under-predicted the degree of load equalization in comparison to experimental measurements (i.e., experimentally determined maximum effluent toluene concentrations were lower than model simulations). The largest difference was observed for spike loading of 1000 ppm$v$ toluene for duration of 4.0 hr, where the maximum experimentally observed effluent toluene concentration was 634 ppm$v$, while model simulations reflected a maximum effluent toluene concentration of 752 ppm$v$. This difference, however, was comparatively small (and measured values differing by 19%), especially considering that the input parameter values utilized in model simulations were not adjusted to calibrate the model in this study.

5.3.2 Multiple Spike Loading

The GAC column subjected to multiple-spikes of toluene loading during the course of an 8 hr/day loading period was operated for eleven days. The target influent toluene concentrations during the daily 8-hr loading interval were as shown in Figure 5.2, and for the remaining 16 hr/day, uncontaminated air flowed through the column at the same flow rate as during the toluene loading interval. Measured influent toluene concentrations for the multiple-spike loading scenario were reasonably close to the target concentrations (see Appendix Figure B.5). Largest variations between target and measured influent concentrations occurred during short intervals (<5 min) immediately following switching of gas flows.

Following the initial start of the 8.0 hr/day multi-spike loading, there was an initial period of approximately two days during which toluene accumulated in the GAC column and no contaminant was detected in the effluent. Eventually, breakthrough occurred and a consistent pattern of attenuated effluent toluene concentration was exhibited on a daily basis by day 5. Thereafter, daily minimum and maximum toluene concentrations exiting the GAC column were consistently reproducible (within 5%) and mass balance calculations verified that contaminant
mass entering and exiting the GAC column on a daily basis were essentially equal (mass balance closure $\geq 95\%$). Hereafter, this condition is referred to as quasi steady-state behavior.

Experimentally measured toluene concentrations exiting the GAC column receiving 8 hr/day multiple-spike loading in the interval after reaching quasi-steady state are shown in Figure 5.5, along with model simulations. Time zero on the x-axis corresponds to the start of an 8-hr loading period. The experimentally observed effluent concentration exhibited diurnal variation with a single daily peak of toluene; there was little or no evidence of the individual spikes present in the influent loading. The maximum daily effluent toluene concentration was $117\pm3$ ppmv (mean $\pm$ standard deviation, n=5), appreciably lower than the maximum daily spike concentration (1000 ppmv). The minimum daily effluent toluene concentration was $69\pm2$ ppmv (mean $\pm$ standard deviation, n=5), appreciably higher than the minimum daily influent concentration, which was 0 ppmv for 16 hr/day.

Results from model simulations of the 8 hr/day multi-spike target loading are quite similar to the experimental observations (Figure 5.5) both qualitatively and quantitatively. Model simulations indicated daily maximum toluene concentrations of 126 ppmv and daily minimum toluene concentrations of 52 ppmv at quasi-steady state. As with the experimental observations, there was little or no evidence of the individual spikes present in the influent during the daily 8 hr/day loading intervals.

Additional model simulations were conducted to compare GAC load attenuation for multiple-spike loadings with different patterns of spike concentrations and durations, but with the same time weighted average toluene concentration (250 ppmv) over daily 8.0 hr/day loading periods (Figure 5.6). Each graph on the right depicts modeled toluene concentrations exiting
Figure 5.5. Experimental measurements and model simulation of quasi-steady-state toluene concentrations exiting a 10-cm packed bed depth GAC column (EBCT 1.2 sec) subjected to target loading comprised of a series of concentration spikes as shown in Figure 5.2 for 8 hr/day and uncontaminated air 16 hr/day. The start of the first 8 hr/day toluene loading interval was designated as time zero.

GAC columns during five day intervals after reaching quasi-steady state for the respective daily multiple-spike loading pattern shown in the left column. The first three rows depict variations of multiple-spike loading pattern with influent toluene concentrations ranging from 100 to 1000 ppmv at intervals distributed throughout the daily 8.0 hr loading period. The fourth row depicts a loading scenario in which the highest spike concentration, 1000 ppmv, would occur during the
Figure 5.6. Model simulations of five-day quasi-steady state effluent toluene concentrations (right column) from 10-cm GAC (EBCT 1.2 sec) column receiving various patterns of spikes in toluene concentration during 8 hr/day loading intervals (left column) and uncontaminated air 16 hr/day. All loading patterns have time-weighted average influent toluene concentrations of 250 ppm over the 8 hr/day toluene loading interval. Time zero in each plot corresponds to the start of a daily toluene loading interval after the system reached quasi-steady state.
first 1.33 hr loading interval, and the influent concentration was 100 ppmv for the remainder of an 8-hr/day loading interval. The fifth row depicts a scenario in a spike concentration that would occur during the last 1.33 hr of the 8.0 hr/day loading period. The sixth row represents loading with a constant concentration of 250 ppmv throughout the 8.0 hr/day toluene loading interval. For all six loading conditions, model simulations of the effluent toluene concentrations were nearly identical. At quasi-steady state, the largest maximum daily effluent toluene concentration (128 ppmv for Case 2) differed from the smallest maximum daily effluent toluene concentration (117 ppmv for Cases 4 and 5) by only 11 ppmv. These were also quite close to the maximum daily effluent toluene concentration resulting from simulation of uniform loading at a rate of 250 ppmv throughout the course of the daily 8 hr/day loading interval, 126 ppmv (Case 6).

5.3.3 Model Simulations of GAC Column Performance at Various EBCTs

To further explore the range of load equalization performance expected from GAC columns subjected to various spike loading conditions, model simulations were performed for 8 hr/day multi-spike loadings as depicted in Figure 5.2 but for various GAC column heights shorter or taller than what was experimentally tested. Because the superficial gas velocity was maintained constant, this corresponds to simulation of GAC columns with various EBCTs. Results of these model simulations are shown in Figure 5.7. Consistent with previous experimental studies for transient loading of GAC columns with constant toluene concentration during intermittent loading intervals (Li and Moe, 2005; Moe and Li, 2005; Moe et al., 2007), model simulations suggest that intermittent loading (e.g., toluene present in the influent 8 hr/day) with highly dynamic conditions characterized by multiple spikes will be more attenuated as the GAC packed bed depth (and correspondingly, EBCT) increases.
Figure 5.7. Model simulations of quasi-steady state effluent toluene concentrations from GAC columns of various lengths receiving the multiple-spike toluene loading pattern shown in Figure 5.2 during 8 hr/day loading intervals and uncontaminated air flow 16 hr/day. Air flow was at the same rate during toluene loading and non-loading intervals. Corresponding EBCTs were 0.3, 0.6, 0.9, 1.2, 3.0, and 6.0 sec, respectively, at a superficial gas velocity of 300 m/hr. Time zero in each plot corresponds to the start of a daily toluene loading interval after the system reached quasi-steady state.
At very short GAC column bed depth (i.e., 2.5 cm, EBCT 0.3 sec), the multiple spikes in the influent loading were readily evident in the GAC column effluent toluene profile. For GAC packed bed depths of 5.0 cm and greater (EBCT ≥ 0.6 sec), appreciable smoothing of the effluent profile characterized by only a single daily of toluene concentration peak was observed. At the longest GAC bed depth considered (50.0 cm; EBCT 6.0 sec), the multiple spikes of the influent loading were completely attenuated; effluent toluene concentration was constant as a function of time.

For further analysis, simulations with single spike loading of various concentrations at 1-hr duration were also conducted for various GAC column EBCTs. Results summarized in Appendix Figure B.6 show that maximum concentrations from columns with as short as 2.0 sec EBCT (i.e., 16.7 cm GAC bed depth) did not exceed 200 ppmv, even when spikes in concentrations went up to 1000 ppmv (10 x baseline). Consistent with results for multi-spike loading, increased attenuation was observed with longer EBCT. Simulation results shown in the figure even suggest that at an EBCT = 6.0 sec., irrespective of spike concentrations (up to 1000 ppmv), same degree of load attenuation characterized by near constant concentration can be achieved.

### 5.4 Discussion

Results from the single-spike loading experiments (Figures 5.3 and 5.4) demonstrated that passively-operated GAC columns can temporarily accumulate contaminants during intervals of high influent concentration and desorb contaminants during intervals of lower loading (i.e., influent toluene concentration of 100 ppmv). This resulted in appreciable load equalization without need for external GAC regeneration by heating or other means as employed in other load equalization strategies (Kim et al., 2007; Hashisho et al., 2008).
Load attenuation such as that shown in Figures 5.3 and 5.4 would be of obvious practical benefit in operation of a downstream biofilter or other air pollution control device because peak contaminant loading would be markedly reduced compared to a system without load equalization. For example, Wright et al. (2005a) studied the transient responses of biofilters subjected to baseline loading of 107 ppm, toluene. After achieving stable treatment performance (essentially 100% contaminant removal efficiency) at this baseline loading level, the biofilters were subjected to various step increases in influent toluene concentration (e.g., 2.5, 5, 10× the baseline level) for duration of 1.0 hr. While the biofilters were able to remove essentially all of the contaminant loading when the step increase was comparatively low (e.g., 2.5× baseline loading, 268 ppmv), considerable contaminant breakthrough was observed when toluene concentrations entering the biofilters during the 1.0 hr period of elevated loading were higher. A best fit line to experimental data suggested that for a 1.0 hr spike loading, influent toluene concentrations above threshold values of 3.3× and 4.2× the baseline level resulted in contaminant breakthrough for biofilters operated with conventional unidirectional air flow and biofilters operated with a flow-direction-switching scheme, respectively. Above the thresholds, contaminant removal efficiency decreased in non-linear fashion as inlet toluene concentration increased.

The biofilter loading conditions experimentally tested by Wright et al. (2005a) are quite similar to the loading conditions imposed on the GAC column for which results are depicted in Figure 5.4 in the present study. Data presented in Figure 5.4 demonstrate that a relatively small GAC column (bed depth of 10-cm, EBCT 1.2 sec) could attenuate 1.0-hr spikes in loading concentrations at least as high as 1000 ppmv to levels below the thresholds causing toluene breakthrough in the biofilters reported by Wright et al. (2005a).
The threshold concentrations above which appreciable toluene breakthrough has been reported to occur from biofilter systems subjected to temporary step increases in loading varies widely (Wright et al., 2005). Developing generalizations about the magnitude of spike loadings that biofilters can treat without decrease in removal efficiency based on studies reported in literature is somewhat complicated due to widely varying packing media, nutrient concentrations, base-line loading conditions, and varying intensity and duration of spike loadings imposed. Although design parameters regarding the degree of load equalization desired prior to biofilter treatment are not yet well established, data reported here indicate that the GAC column sizes needed to achieve a substantial degree of load equalization would generally be small (EBCT on the order of seconds) in comparison to sizes of typical biofilters (EBCT on the order of a minute).

In addition to decreasing the peak contaminant concentration that would enter a downstream biofilter during spike loading events, GAC columns also redistribute the temporary surge in concentration over a time interval longer than the duration of the imposed spike. For example, with an influent spike of 1000 ppm, for a duration of 1.0 hr, the toluene concentration exiting the 10 cm column tested here was within the range of 125 to 180 ppm, for a duration of 13.6 hr. A sustained duration of modestly higher concentration would be expected to be more readily handled by a biofilter than a short-duration high-concentration loading. This results from the fact that the short-term microbial response to increases in contaminant loading (on the order of minutes) is largely limited to changes in physiological state, while longer term responses (on the order of hours) can include both changes in physiological state as well as growth (Wright et al., 2005b; Irvine and Moe, 2001).

The redistribution in time when temporary surges in pollutant loading exit a GAC column relative to the time when they enter may be particularly advantageous in applications with
biofilter systems receiving waste gases with temporary periods in which contaminants are absent from the gas stream at regular (e.g., daily) or irregular (i.e., unevenly spaced) intervals. Experimental data demonstrated that a small GAC column (10 cm, EBCT 1.2 sec) receiving a series of spikes (target concentrations ranging from 100 to 1000 ppmv, Figure 5.2) during 8 hr/day loading intervals could decrease peak effluent concentrations to 117±3 ppmv, well below the time-weighted average of the loading interval (250 ppmv), while also maintaining a relatively stable contaminant concentration in the effluent during the 16 hr/day interval when the influent toluene concentration was zero (minimum daily effluent concentration 69±2 ppmv, Figure 5.5). In biofilter operation, this could serve the purpose of decreasing peak loading while also minimizing or eliminating periods of no contaminant loading, a condition which can result in poor performance following resumption of contaminant loading due to excessive starvation of the microbial community (Cox and Deshusses, 2002; Moe and Qi, 2004, Devinny et al., 1999).

The PSDM model well described performance of the GAC load equalization process. This is consistent with previous work using the same governing equations and assumptions but using the ADesignsS software package (Li and Moe, 2005; Moe and Li, 2005; Moe et al., 2007). Use of the MATLAB code and solution methodology employed here, however, allowed simulation of short duration spikes (e.g., 5 min) and longer overall operation intervals (e.g., months) that are not possible using the previously employed software package because of limitations on the number of input data points and time steps used for integration.

Model simulations conducted using the PSDM implemented using the MATLAB code were in close agreement with experimental measurements even for the case of multiple, short-duration spikes. This modeling approach allows simulation of a variety of loading scenarios,
particularly those characterized by complex loading patterns characterized by appreciable short-term variation in pollutant concentrations and may prove useful in future studies.

Model simulations indicated that the toluene concentrations exiting a 10 cm packed bed depth GAC column (EBCT 1.2 sec) subjected to a variety of multiple-spike loading scenarios would be similar or identical to that from an equal size column receiving constant toluene loading at a level of 250 ppmv, the time-weighted average of the 8 hr/day toluene loading interval. This suggests that various dynamic loading scenarios of the same time-weighted average may result in similar degrees of load attenuation by GAC columns, provided that the maximum, minimum, and average influent concentrations are within a reasonably close range (i.e., maximum spike concentrations no more than $10 \times$ minimum concentrations or $4 \times$ average influent concentrations during the loading interval). Model simulations of multi-spike loading of GAC columns with very short packed bed depths (e.g., 2.5 cm column results in Figure 5.7); however, suggest that at very low EBCTs, the time-course of influent spike loading concentrations may influence the load equalization process in a manner that is not well approximated by time-weighted average influent concentration approximations.

### 5.5 Conclusions

- Passively operated GAC columns can appreciably dampen temporary spikes in contaminant loading. Peak toluene concentrations exiting the GAC load equalization system were markedly lower than peak influent concentrations, with the influent contaminant mass exiting the GAC columns more evenly distributed over longer period of time. Such systems have the potential to serve as load attenuation devices for biofilters or other air pollution control devices.
- An equivalent total-weighted average value for the multiple spike loading over the loading period can be conveniently and conservatively used in place of actual loading scenario to predict GAC column performance.

- The MATLAB code used to implement the PSDM was successful in simulating GAC column performance under loading conditions characterized by single spikes of varying intensity and duration as well as complex loading scenarios involving multiple spikes of various intensity and duration. The modeling approach described here may prove useful for simulating a variety of unsteady state loading scenarios of interest.
CHAPTER 6
EFFECT OF GAS FLOWRATE TURNDOWN ON LOAD ATTENUATION BY GAC COLUMNS FOR BIOFILTER APPLICATIONS

6.1 Introduction

The dynamically varying nature of many waste gas stream contaminant concentrations imposes unsteady loading conditions on air pollution control equipment. As described in previous chapters, columns filled with granular activated carbon (GAC) can serve as passively operated load equalization devices, resulting in more steady contaminant loading rates to downstream air pollution control devices. Previous research on the GAC load equalization process, however, has been limited to cases where airflow through the system has been constant during contaminant loading and non-loading intervals. While effective, this would require constant operation of a blower to supply gas to the system. In some cases, it may be desirable to decrease airflow rates during contaminant non-loading intervals as a means of minimizing power consumption and therefore treatment costs. Research described in this chapter was conducted to evaluate the effects of decreasing gas flow rates during contaminant non-loading intervals on GAC load equalization performance.

6.2 Background

As described in earlier chapters, biofilters may be subjected to temporary periods of high influent contaminant concentrations, a loading condition which can result in diminished treatment performance because of limitations in mass transfer rates and biological reaction capacity. Likewise, contaminants may be present at very low concentrations or may be completely absent in the gas stream for certain durations. Such transient periods of low or zero contaminant loading can impose starvation conditions on the microbial processes in a biofilter.
and result in diminished treatment capacity during resumption of “normal” contaminant loading levels.

There are three basic alternatives in operation of a biofilter when periods of low or no influent contaminant loading occur: (1) Airflow rate may be held constant, supplied at the same rate during contaminant loading and non-loading periods; (2) Air flow during non-loading periods may be totally shutdown, such that no air stream passes through the biofilter; or (3) Air flow may be continued but at a lower flow rate during the non-loading period than during loading intervals.

With regard to the first operating option, continued air flow during periods of no contaminant loading maintains aerobic conditions within the biofilter bed; however, if the duration of the interval of no contaminant loading is sustained for a sufficiently long time, starvation conditions are imposed on the microbial population. Because of endogenous decay, the size of the microbial population able to degrade contaminants can decrease, resulting in a period of time when the biofilter exhibits diminished contaminant removal efficiency when pollutant loading resumes. In general, longer durations of non-loading intervals have been reported to require longer time for biofilter performance recovery (Park and Kinney, 2001; Cox and Deshusses, 2002; Dirk-Faitakis and Allen, 2003; Moe and Qi, 2004). Because a blower is required to maintain gas flow during intervals of no pollutant loading, power consumption can be considerable. For example, if an industrial facility operates a pollutant generating process only 8 hr/day but continues air flow 24 hours per day, then they will use three times as much power to operate a blower compared to a system that operates the blower only during intervals when pollutants are being generated. Because costs associated with electricity to maintain blower
operation can comprise a relatively large fraction of total operating costs (Devinny et al., 1999), this can have a large influence on total operating costs.

The second operating option during periods of no contaminant loading, halting all airflow during non-loading periods, has the advantage of minimizing power costs associated with operating blowers. The effects of totally shutting down airflow to biofilters/biotrickling filters have been investigated previously (Marek et al., 2000; Martin and Loehr, 1996; Wani et al., 1998; Cox and Deshusses, 2002; Kim et al., 2005). Most of these studies were concerned with the reacclimation period after complete shutdown of airflow through the bioreactor. Short-term shutdown (in the order of hours, < 24 hours) had small effect on removal efficiency, while longer shutdowns resulted in longer time for recovery of biofilters. Martin and Loehr (1996) reported recovery period of 43 hours and 66 hours for toluene and benzene removal, respectively, after 14 days of complete shutdown. Longer duration of shutdown lasting to about 3 months was reported by Wani et al., 1995. Three biofilters of different packing media (hog fuel, compost, mixture of hog fuel and compost) treating H₂S-laden air regained full acclimation in 122-142 hours after 3 months of idle phase without airflow. Starvation condition resulting from halting airflow through a biotrickling filter was observed to have resulted in decreased biomass content, though not to the levels where biodegradation rates would be limited by the amount of biomass (Cox and Deshusses, 2002). Hence, loss of toluene removal after starvation was instead attributed to diminished activity of the remaining biomass. In addition, Cox and Deshusses (2002) suggested that anaerobic conditions in the biofilm could be a potential problem when no gas flow enters the biotrickling filter due to generation of odors or corrosion. It has been recommended that sufficient airflow should be maintained even during down times to prevent development of anaerobic conditions in the biofilter (Devinny et al., 1999).
The third scenario, continuing air flow but at a lower flow rate during the non-loading period than during loading intervals, is the least explored in spite of the fact that it may be a good operational strategy during intermittent pollutant loading to biofilters. Reduction of gas flow rate during times when contaminants are not being generated could result in savings on operating costs (due to decreased power consumption associated with blowers) while still supplying sufficient oxygen to maintain aerobic conditions.

For GAC columns intended to supply equalized loading to a downstream biofilter, operating strategies involving reduction in gas flow rates during the non-loading periods have not been reported previously. The objective of research described in this chapter was to characterize the effects of decreasing gas flow rates on GAC load equalization and assess the potential benefits of using GAC load equalization in cases where gas flow rates are decreased during intervals of no contaminant loading. A series of fixed-bed sorption experiments was conducted, with intermittent loading of toluene and varying air flow rate. During contaminant non-loading periods, air flow rates were reduced to various fractions (e.g., 50%, 10%) of the base-line full flow rate maintained during contaminant loading periods. The durations of contaminant loading tested were 12, 8, and 4 hr/day (with associate non-loading intervals of 12, 16, and 20 hr/day, respectively). A simple theoretical relationship based on mass balance calculations was developed to determine the maximum GAC column load equalization performance that can be achieved at various loading durations and air flow rate reductions during non-loading intervals.

6.3 Materials and Methods

6.3.1. Granular Activated Carbon (GAC) and Experimental Apparatus

The configuration of the GAC columns (7.62 cm ID, 33.3 cm GAC packed bed depth, 716 g GAC per column) and experimental apparatus employed in the fixed-bed adsorption/
desorption experiments was as described in Chapter 5 and depicted graphically below in Figure 6.1. The system included two air supply lines alternately turned on during experimental runs. One provided air flow during periods of toluene loading and the other provided contaminant-free gas flow during periods of no toluene loading. Airflow from each of the supply lines was controlled by a solenoid valve (Asco Valve Inc., NJ), which was turned on and off as necessary using a microprocessor-based controller (Chron-Trol, San Diego, CA). Air flow rate in each

Figure 6.1. Experimental apparatus used in fixed-bed adsorption-desorption experiments with turndown of gas flow rate during non-loading period.
supply stream was controlled using an electronic mass flow controller (Aalborg Instruments, Orangeburg, NY). For all experiments, flow rate through the GAC columns during toluene loading intervals was 22.8 L/min, corresponding to superficial gas velocity of 300 m/hr in the packed columns. During toluene non-loading intervals, gas flow rates were 0.50 times the baseline level (i.e., 11.4 L/min, corresponding to superficial gas velocity of 150 m/hr in the packed columns) or 0.10 times the baseline level (i.e., 2.28 L/min, corresponding to superficial gas velocity of 30 m/hr in the packed columns). During toluene loading intervals, liquid toluene (ACS reagent grade, Sigma, St. Louis, MO) was delivered by syringe pumps (KD Scientific, Boston, MA) and evaporated into one of the air supply lines.

Gas supply and sampling lines were constructed of Teflon tubing. Initial tests conducted prior to placement of activated carbon demonstrated that components of the experimental set-up other than GAC had little or no adsorption capacity for toluene. All experiments were conducted at ambient laboratory temperature of 23±2°C.

6.3.2. Turndown of Gas Flow Rate During Non-Loading Period

To evaluate GAC column performance with varying air flow rate, three columns, each containing 33.3 cm of GAC packed depth (empty bed contact time, EBCT = 4.0 sec when air flow rate was 22.8 L/min), were constructed. The columns were supplied with toluene contaminated air for 4 hr/day, 8 hr/day, and 12 hr/day, respectively, at influent toluene concentration of 250 ppm,. Initially, each column received air at full flow of 22.8 L/min during both loading and non-loading period until quasi-steady state was reached. After at least five days of data were gathered during quasi-steady state at this initial loading condition, the air flow rate during non-loading periods was then sequentially reduced to 50% and 10% of full flow (i.e., 11.4 or 2.28 L/min) while maintaining full flow rate during the toluene loading periods. An
illustrative example of a 48-hr loading scenario with intermittent loading of toluene (8 hr/day) and reduced flow rate during the non-loading period is shown in Figure 6.2. Each time flow rate was reduced during the non-loading period, the system was allowed reach quasi-steady state and five days worth of effluent toluene data were gathered before loading conditions were changed.

Figure 6.2. Illustrative example of a 48-hr loading scenario with intermittent toluene loading and reduced air flow rate during contaminant non-loading intervals. Shown is loading of toluene (250 ppmv) in air flowing at full flow of 22.8 L/min for 8 hrs/day. During toluene non-loading intervals (0 ppmv, influent toluene), air flows at the reduced flow rate of 11.4 L/min (50% of full flow rate).

6.3.3. Analytical Procedures

Influent and effluent toluene concentrations were measured using a model 1312 photo-acoustic multi-gas monitor (California Analytical, Orange, CA), with concentrations recorded at
1.0 min intervals. A model 600 HFID hydrocarbon analyzer (California Analytical, Orange, CA) was used to monitor toluene concentrations from columns undergoing transition from one turndown of flow rate to another.

### 6.3.4. Mass Balance Calculation of Ideal Load Equalization for Cases of Contaminant Supply During a Fraction of Each Day and Air Flow Turndown During Contaminant Non-Loading Intervals

A simple mass balance analysis was employed to determine the daily average toluene concentration that would exit GAC columns subjected to flow rate turndown during periods when no toluene was present in the airflow. In this approach, it was assumed that full baseline air flow rate, $Q_o$, will occur during toluene loading intervals, while a fraction of the baseline airflow would occur during toluene non-loading periods. Ideal load equalization would be observed if the toluene concentration exiting the GAC column were to be constant as a function of time at a level equal to the flow-weighted average influent concentration (including toluene loading and non-loading intervals). At quasi-steady state, the toluene mass entering a GAC column on a daily basis equals the mass exiting the column on a daily basis. The total toluene mass exiting the GAC column on a daily basis includes mass exiting during intervals of full flow (interval when toluene is present in the influent) and intervals of partial flow (when toluene is absent from the influent) as indicated in eqn. 6.1.

\[
C_o Q_o t_o = C_{avg} Q_o t_o + C_{avg} f_Q Q_o t_p
\]  

(6.1)

Where:

$C_o$ = influent toluene concentration during the loading interval

$C_{avg}$ = the flow-weighted average effluent toluene concentration at quasi-steady state, assuming perfect buffering

$Q_o$ = volumetric flow rate during toluene loading intervals (full flow)
\( f_Q \) = fraction of the baseline volumetric flow rate maintained during toluene non-loading intervals (partial flow)

\( t_o \) = daily duration of toluene loading at full volumetric flow rate  
(i.e., \( Q=Q_o \))

\( t_p \) = daily duration of no toluene loading with air at partial flow 
(i.e., \( Q=f_Q Q_o \))

Dividing all terms in eqn. 6.1 by the air flow rate during toluene loading intervals (\( Q_o \)) and grouping terms results in eqn. 6.2.

\[ C_o t_o = C_{avg} (t_o + f_Q t_p) \quad (6.2) \]

The ratio of the duration of no toluene loading (or when flow is turned down) to the duration of the toluene loading period (at full baseline air flow rate) can be defined as shown in eqn. 6.3:

\[ r_t = t_p/t_o, \quad (6.3) \]

Substituting eqn. 6.3 into eqn. 6.2 and rearranging terms results in definition of the ideal load equalization, expressed in terms of dimensionless effluent toluene concentration, as shown in eqn. 6.4.

\[ \frac{C_{avg}}{C_o} = \frac{t_o}{t_o + f_Q t_p} = \frac{1}{1 + f_Q r_t} \quad (6.4) \]
6.4 Results

6.4.1 GAC Column Performance at Various Turndown Rate of Airflow During Non-Loading Period

Toluene was loaded daily at 250 ppmv, for durations of 12, 8, and 4 hr/day for each of the three columns. For the remainder of each day, the columns were supplied with toluene-free air at the same flow rate as during toluene loading intervals (i.e., 22.8 L/min). Following the start of loading to each of the columns, there was an initial period during which toluene accumulated in the GAC columns and no contaminant was detected in the effluent (see Figure 6.3). Eventually, breakthrough occurred, and then a consistent pattern of effluent toluene concentrations was observed on a daily basis. As shown in Figure 6.3, appreciable toluene breakthrough was observed after approximately 9 days and quasi-steady state was achieved after about 14 days of intermittent toluene loading. Longer time to reach initial breakthrough and quasi-steady state was observed for loading conditions in which there was a shorter interval of toluene loading on a daily basis (approximately 20 days and 40 days for daily toluene loading of 8 hrs/day and 4 hrs/day, respectively) (data not shown).

After breakthrough was achieved (e.g., as shown in Figure 6.3), a consistent pattern of effluent toluene concentration was observed on a daily basis in all three column experiments (i.e., with toluene loading interval last 12, 8, or 4 hr/day). In all columns, daily maximum and minimum effluent toluene concentrations were consistently reproducible (differing by <3%), and mass balance calculations verified that the toluene mass entering and exiting the columns on a daily basis were essentially equal (mass balance closure ≥95%). Hereafter, this is referred to as a quasi-steady state. After effluent toluene concentrations were measured for a minimum of five days after reaching quasi-steady state, the air flow rate during toluene non-loading periods was decreased by 50% (i.e., to 11.4 L/min), while keeping the flow rate during toluene loading at full
Figure 6.4 depicts experimental effluent toluene measurements from GAC columns subjected to various durations of loading period, $t_l$, and various air flow rates during toluene non-loading (partial flow, $Q = f_Q Q_o$). Each graph shows data from a 5-day interval with toluene measured at 1.0-min intervals. Time zero on the x-axis corresponds to the start of a loading period after quasi-steady state was achieved.

Figure 6.3. Toluene breakthrough from GAC column (33.3 cm packed bed depth; EBCT=4.0 sec) loaded with 250 ppmv, toluene, 12 hrs/day at full flow rate of 22.8 L/min (no turndown of flow rate during non-loading period).
Figure 6.4. Toluene concentrations exiting GAC column (33.3 cm packed bed depth) loaded with 250 ppm, toluene at full flow rate ($Q_0=22.8$ L/min) during a portion of each day and at various fractional flow rates, $f_0Q_0$, during non-toluene loading periods. Left: full flow (i.e., $f_0=1$) of 22.8 L/min during toluene non-loading periods; Middle: 50% full flow (i.e., $f_0=0.50$, $Q=f_0Q_0=11.4$ L/min) during toluene non-loading periods; Right: 10% full flow (i.e., $f_0=0.10$, $Q=f_0Q_0=2.28$ L/min,) during toluene non-loading periods. Duration of toluene loading period, $t_o$, 12 hr/day (top); 8 hr/day (middle); 4 hr/day (bottom).
Four trends are apparent from the graphs of Figure 6.4. First, for a given daily duration of toluene loading, $t_o$, average concentrations observed during quasi-steady state increased as flow rate during the toluene non-loading period decreased. For example, for the GAC column loaded with toluene for 12 hr/day (first row of figures), daily average effluent concentrations increased from 125 ppmv, to 168 ppmv, to 219 ppmv, as the air flow rate during toluene non-loading intervals was consecutively reduced from 22.8 L/min, to 11.4 L/min, to 2.28 L/min, respectively.

Second, for a given duration of toluene loading, $t_o$, reducing air flow rate during the non-loading period resulted in a small increase in variation between the maximum concentration ($C_{max}$) and minimum concentration ($C_{min}$). For example, at 12 hr/day of toluene loading, $C_{max}$ and $C_{min}$ differed roughly by 11.6, 11.9, and 17.6 ppmv when non-loading flow rate was 22.8, 11.4, and 2.28 L/min, respectively.

Third, for a given flow rate during toluene non-loading period, $f_Q Q_o$, a shorter duration of daily toluene loading resulted in lower effluent toluene concentrations. For example, when the flow rate during non-loading interval was reduced to 11.4 L/min (50% of full flow), the average effluent toluene concentrations ($\pm$ standard deviations) determined during five days of quasi-steady-state were 168±1.7 ppmv, 120±2.3 ppmv, and 70±0.5 ppm, for loading durations of 12 hrs, 8 hrs, and 4 hrs, respectively.

Fourth, for a given $f_Q$, increased load equalization was observed for decreasing daily duration of toluene loading interval, $t_o$. This is consistent with the work of Moe et al. (2007) who reported an increased load equalization when fraction of time during which toluene was supplied decreased. For the shortest duration of loading tested here (i.e., $t_o = 4$ hr/day) the profiles were almost straight lines with little variations between daily maximum and minimum concentrations; hence, the highest degree of load equalization for the same $f_Q$. 

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While the toluene concentrations shown in Figure 6.4 were relatively constant with time even when flow rates during non-loading interval were reduced to 50% and 10%, the actual mass flux of toluene varied considerably with time. Corresponding toluene mass flux rates during five days of quasi-steady state are depicted in Figure 6.5. As shown, maximum fluxes were observed during period of loading (full flow rate) while minimum fluxes were observed during intervals of non-loading (i.e., when flow rate was reduced to a fraction of the full flow). The calculated maximum mass flux was higher when for a given duration of loading, the flow rate during non-loading interval was lower. For example, when the column received toluene loading 4 hr/day, daily maximum toluene mass fluxes averaged over five days of quasi-steady state varied from 49.7 g/m²-hr to 82.9 g/m²-hr and 187.0 g/m²-hr when flow rate during the 20-hr interval of non-loading was reduced from full flow to 50% and 10% of full flow rate, respectively. Toluene mass flux rates, however, decreased with decreased duration of loading for the same flow rate during non-loading period. For example, when flow rate during non-loading was reduced to 50% of full flow rate (\(f_Q=0.50\)), maximum flux rates were 197.1 g/m²-hr, 142.1 g/m²-hr, and 82.9 g/m²-hr for durations of loading of 12 hr/day, 8 hr/day, and 4 hr/day, respectively.

### 6.4.2 Maximum Potential Load Equalization in Columns Subjected to Intermittent Loading of Toluene with Air Flow Rate Decrease during Non-loading Period

Dimensionless effluent toluene concentrations expected for ideal load equalization conditions, as calculated by Equation 6.4 for loading scenarios comprised of various durations of daily toluene loading (\(t_o\)) and various fractions of air flow rate turn-down (\(f_Q\)) during toluene non-loading intervals, are shown in Figure 6.6. As shown in the figure, mass balance considerations demonstrate that toluene concentrations exiting a GAC column load equalization device once quasi-steady state conditions are achieved have an upper limit that approaches the
Figure 6.5. Toluene mass flux rates exiting GAC column (33.3 cm packed bed depth) loaded with 250 ppm, toluene at full flow rate ($Q_o=22.8$ L/min) during a portion of each day and at various fractional flow rates, $fQQ_o$, during non-toluene loading periods. Left: full flow (i.e., $fQ=1$) of 22.8 L/min during toluene non-loading periods; Middle: 50% full flow (i.e., $fQ=0.50$, $Q=fQQ_o=11.4$ L/min) during toluene non-loading periods; Right: 10% full flow (i.e., $fQ=0.10$, $Q=fQQ_o=2.28$ L/min,) during toluene non-loading periods. Duration of toluene loading period, $t_o$, 12 hr/day (top); 8 hr/day (middle); 4 hr/day (bottom).
Figure 6.6. “Ideal” GAC column load equalization for various durations of toluene loading and various airflow turn-down rate during toluene non-loading periods. Full rate flows through the column during toluene loading of 250 ppmv. Average concentrations determined from 5 days of experimental measurements are shown as filled symbols.
level of concentration in the influent (i.e., $C_{avg}/C_o=1$) as the fraction of air flow during the toluene non-loading interval ($f_Q$) approaches zero. This results from the fact that as the volume of clean air passing through the GAC column decreases, there is less volume for toluene temporarily accumulated in the column to be distributed into. For example, if the air flow rate during toluene non-loading intervals is zero, in the absence of net accumulation in the GAC column (i.e., a necessary condition for quasi-steady state), the effluent toluene concentration will equal the toluene concentration entering during the loading interval (i.e., if toluene concentration in the influent is 250 ppmv for 12 hours, then air flow is completely turned off for 12 hours, when loading with 250 ppmv, toluene resumes, the effluent toluene concentration will be equal to 250 ppmv if there is no net daily accumulation in the column (i.e., the system is at quasi-steady state)). There would be no accumulation of toluene on even a temporary basis; the flux rate of toluene entering and exiting the column would be equal during the loading interval and there would be no net adsorption or desorption during the toluene non-loading interval. Alternately, if the flow rate during the toluene non-loading rate is greater than zero, then the mass of toluene exiting the column is diluted into a larger volume of air, resulting in a lower average effluent toluene concentration. At $f_Q=1$ (the case of constant air flow during loading and non-loading intervals) and constant pollutant concentration during loading intervals, ideal load equalization results in a dimensionless effluent pollutant concentration ($C=C/C_o$) equal to the fraction of time pollutants are present in the influent. For pollutant loading durations of 12, 8, and 4 hr/day as was experimentally tested here, this corresponds to levels of dimensionless effluent pollutant concentrations of 0.50, 0.33, and 0.17, respectively.

Experimentally measured data from 33 cm packed bed depth GAC columns are depicted in Figure 6.6 as filled symbols. Each data point represents the average toluene concentration
exiting the GAC column during five days of quasi-steady state. Error bars represent the average dimensionless minimum ($C_{\text{min}}/C_o$) and maximum ($C_{\text{max}}/C_o$) daily toluene concentrations. As shown, the experimental data was in close agreement with the ideal load equalization levels represented by average effluent concentrations calculated based on mass balances for GAC columns subjected to intermittently varying flow rates. This demonstrates that comparatively small columns (packed bed depth 33.3 cm, EBCT of 4.0 sec during full-flow conditions) can achieve close to the maximum theoretical degree of load equalization.

For further analysis, maximum flux ($N_{\text{max}}$) and minimum flux ($N_{\text{min}}$) rates of toluene were calculated for various duration of loading and turndown rates during non-loading period for a GAC column (33.3 cm. packed bed height) loaded with 250 ppm, toluene at full flow rate and 0 ppm, at reduced flow rates during the daily non-loading intervals. Results are summarized in Figure 6.7. Fluxes calculated from experimental effluent data are also shown as filled symbols in the graphs. Mass flux rates are expressed in dimensionless form as the ratio of the maximum or minimum flux to the flux rate during toluene loading ($N_o$) when toluene concentration is at 250 ppmv in air flowing at full flowrate. As depicted in the figures, maximum flux rates have an upper limit that approaches the level during loading period (i.e., $N_{\text{max}}/N_o=1.0$) as flow rate during the non-loading interval is turned down to zero. Minimum fluxes, on the other hand, have a lower limit that approaches the level when no toluene enters the column due to the absence of air passing through the column (i.e., $N_{\text{min}}/N_o=0$). For a given duration of loading, the curves of maximum and minimum fluxes approach each other when non-loading flowrate is equal to the flowrate during loading period (i.e., $f_Q = 1.0$, no turndown in flowrate).
Figure 6.7. Maximum and minimum toluene mass fluxes at various duration of toluene loading and various turndown rate of airflow during the non-loading period. Full rate flows through the column during toluene loading of 250 ppm. Average daily maximum and minimum flux rates determined from 5 days of experimental measurements are shown as filled symbols.
6.5 Discussion

GAC columns subjected to reduced flow rates during contaminant non-loading periods can achieve concentrations lower than the influent concentration but would approach the influent concentration during the toluene loading interval if the flow rate during the non-loading period is reduced to extremely low levels. The GAC columns temporarily accumulated toluene during intervals when it was present in the airflow and desorbed toluene during intervals of no pollutant loading (i.e., influent toluene concentration of 0 ppm,) at reduced flow rate. Again, this shows the potential of the GAC column to achieve load equalization during intermittent loading, even with intermittently varied flow rate. When toluene was absent in the influent, previously adsorbed toluene in GAC desorbed and redistributed in the effluent during non-loading periods when the airflow was at reduced flow rate. The result was an increased toluene concentration in the effluent during what would have otherwise been a non-loading period for a downstream bioreactor. At quasi-steady state, an equalized effluent concentration profile was observed, with an average value that was higher than what would be observed if no turndown in flow rate was imposed during the non-loading period. For a given duration of loading, the lower the flow rate during non-loading, the higher the resulting average concentration of toluene in the effluent and the more variations in concentrations were observed. There was an overall reduction in GAC load equalization when flow rate during the non-loading period was reduced.

For the particular GAC column EBCT (4.0 seconds at full flow) experimentally tested in this study, toluene concentrations in the effluent were relatively constant, close to ideal load equalization. However, mass flux of toluene through the column dynamically varied with the change in gas flow rate. Maximum toluene mass fluxes were observed during the loading interval (when air flow rates were highest) while minimum fluxes were observed during the
toluene non-loading intervals when flow rate was reduced. It is important to note that the minimum fluxes were not equal to zero even when no toluene was being supplied from the system, as long as at least some air flow was continuously supplied to the system. Toluene which accumulated in the GAC during the loading period redistributed in the reduced airflow. In an integrated system comprised of a GAC column followed by a biofilter, this could be used to achieve the practical advantage of continuously supplying substrate to meet the requirements of microorganisms in the biofilter to maintain induction of degradative enzymes and minimize starvation. Park and Kinney (2001) demonstrated that supplemental feed at a contaminant mass loading rate equal to a relatively small fraction of that during “normal loading” (e.g., 12%) could markedly decrease the length of time required for a biofilter to regain high removal efficiency following shut-down periods as long as 7 days when no contaminant was generated for the biofilter. As already discussed in Chapter 2, however, there are two disadvantages in providing supplemental contaminant feed to biofilters. One disadvantage is the additional cost of the supplemental feed, and the other is the risk of directly increasing the overall contaminant mass emitted by the facility if the supplement itself is not completely degraded in the biofilter. In a biofilter with a GAC column load equalization device, the minimal contaminant flux that occurs during the non-loading period may be sufficient to maintain the biofilter while realizing savings in cost due to the reduced flow rate, without the risk of increasing overall emissions.

Experimental results demonstrated that for cases of short duration of daily pollutant loading (e.g., 4 hr) a relatively low EBCT (e.g., 4.0 sec at full flow rate) could achieve close to the maximum theoretical load equalization potential calculated using the mass balance approach when the influent toluene concentration was 250 ppmv. It is important to note that at much higher concentration (e.g., 1000 ppmv) there could be larger difference between $C_{\text{max}}$ and $C_{\text{min}}$, and the
degree of load equalization could markedly deviate from the maximum theoretical level for an equivalent size GAC column. Likewise, previous studies (Li and Moe, 2005; Moe and Li, 2005; Moe et al., 2007; chapter 4 of this dissertation) have demonstrated that the degree of load attenuation is a function of packed bed depth, and for shorter columns (with corresponding lower EBCT), the degree of load equalization may be considerably less than the maximum theoretical level. Longer columns tend to result in more complete GAC load attenuation.

Results of this study suggest some implications on the design and performance of bioreactor systems which employ GAC column as load equalization device. For new systems that will still have to be put in place, a design plan that incorporates a GAC load equalization device with the option to reduce gas flow rates during non-loading has the potential of saving costs due to lower electricity costs compared to what would be expected from the intermittently reduced flow rate during fraction of the day when no contaminant is generated. Such a system is likely to be especially attractive for processes that experience a low fraction of time with contaminant loading. As a means of demonstrating this point, a simple economic analysis was conducted to compare the costs associated with two biofilter system configurations that could be employed to treat a hypothetical waste gas stream—(1) a stand alone biofilter; and (2) an integrated GAC column-biofilter system subjected to various turndown in flow rate during intervals of no contaminant loading. The hypothetical waste gas stream to be treated was assumed to contain 250 ppmv toluene for a duration of 4 hr/day. A design loading rate of 50 g/m³-h was assumed in sizing biofilters with and without load equalization. A 33.3-cm GAC bed depth (EBCT=4.0 sec at full flow rate) was assumed for the load equalization component of the integrated system. Operating costs were calculated as electrical costs arising from the blower or
fan to move air through the system (Devinny, 1999). Assumptions and detailed calculations are described in Appendix C.

Annualized costs over the assumed 20 years of equipment service life for the two treatment schemes are depicted in Figure 6.8 (tabulated values appear in Appendix C). As shown in the figure, the option to reduce flow rates during the non-loading period would result in reduced annual cost of electricity for either case of biofilter configuration. For the stand-alone biofilter without GAC load equalization, the lowest total annual cost, $36,441 per year, corresponds to the case in which air flow is totally shutdown during toluene non-loading periods, because this minimizes electricity consumption (and therefore operating cost) while not affecting capital costs. In practice, however, this option may not be attractive due to the risks of anaerobic condition in the biofilter during shutdown of airflow and the potential for denitrification to deplete the supply of nitrogen nutrients which can be problematic because nitrogen limitations can limit biofilter performance (Jorio et al., 2000; Moe and Irvine, 2001).

Conversely, for the case of an integrated GAC column-biofilter system, reducing the flow rate to zero during the non-loading period would result in a larger total cost. This results from the fact that although electricity cost would be minimized, there would be a larger capital cost due to the cost for the GAC column and the larger volume requirement for the biofilter at very low air flow rate during contaminant non-loading intervals. More annual savings can be realized with the integrated system than with the stand-alone biofilter when flow rate during the non-loading period is turned down to no lower than 20% of full rate (i.e., \( f_Q > 0.2 \), see Figure C.1. in Appendix C). For example, for a flow rate turndown to 50% of the full flow rate (i.e., \( f_Q=0.50 \)), a stand-alone biofilter would have an annual cost of $40,459, while a biofilter with GAC load equalization would have an annual cost of $32,299 over the 20-year life span assumed for the
Figure 6.8. Annual costs associated with a stand-alone biofilter system (top) and an integrated GAC column-biofilter system (bottom) over 20 years of equipment service life for treatment of toluene-contaminated air (250 ppm). Biofilter design loading rate is assumed at 50 g/m$^3$-h. Operating cost is attributed only to electricity costs while capital cost is the cost of biofilter for the stand-alone system or the cost of biofilter and GAC column for the integrated system. Annual interest rate at 8%; annual inflation rate at 3.5%.
treatment system. This represents a potential annual savings of $8,160. Cost savings associated with load equalization would be even larger for a 10 year planning horizon. A stand-alone biofilter lacking load equalization would have an estimated total annual cost of $55,635 while a biofilter including load equalization with 50% flow rate turn-down would have an estimated total annual cost of $35,951 (see Appendix C), representing a potential annual savings of $19,685 over the 10-year planning period. If the cost of electricity were higher than assumed in the present analysis, then use of a load equalization process in conjunction with gas flow rate turndown during contaminant non-loading intervals would be even more attractive than use of GAC load equalization without flow rate turndown or use of biofilters without any load equalization at all.

6.6 Conclusions

- Overall, results from this study demonstrated that load equalization can be achieved by GAC columns which receive intermittent toluene loading in combination with intermittent reduction of air flow rates during toluene non-loading intervals. As the reduction of flow rate during the non-loading period increased, the maximum degree of load equalization that can be achieved by GAC columns decreases.

- GAC column performance under conditions studied with intermittently reduced gas flow rates in columns of packed GAC bed depth of 33.3 cm (4.0 sec EBCT at full-flow) were able to achieve load equalization close to the theoretical maximum calculated based on a simple overall mass balance approach.

- Reduction of flow rate during non-loading period to a biofilter system which employs GAC load equalization has the potential to reduce costs due to reduced electricity costs.
CHAPTER 7
OVERALL CONCLUSIONS AND RECOMMENDATIONS

7.1 Overall Conclusions

Overall results gathered from both experiments and model simulations conducted in the study reported in this dissertation indicate that the potential of GAC adsorption columns to serve as passively-controlled load equalization devices upstream of biofilters or other pollution control processes treating contaminated gas streams is valid over a wide range of conditions of unsteady loading. A GAC column can accumulate toluene during periods of high contaminant loading and subsequently desorb contaminants to the gas flow when the influent concentration is low or zero generally resulting in equalized contaminant concentrations and consequent steady loading to a downstream biofilter. Depending on the scenario of unsteady loading investigated, specific GAC column performance and capability were observed. These are summarized in the following discussions.

(1) During shutdown conditions (discussed in Chapter 3), when no contaminant loading may occur for relatively long period of time, such as during weekend (i.e., two days) and extended period (e.g. one week), model simulations conducted to assess minimum loading conditions that would be imposed by the GAC column on a biofilter indicate that this minimum is not necessarily equal to zero. Small amount of contaminant will be available to provide supplemental feed to a biofilter during periods of no contaminant loading (i.e., process shutdowns). Consequently, GAC adsorption columns in series prior to biofilters may prove useful in alleviating the adverse impacts of starvation during periods of operational shutdown when no contaminants would otherwise be supplied to the biofilter. The performance and re-
acclimation after shutdown of a biofilter in a coupled system is expected to be better than what may be observed with a stand-alone or an unbuffered biofilter subjected to shutdown conditions.

(2) Investigations on the effect of gas humidity on GAC load equalization discussed in Chapter 4 revealed that there is a threshold level of relative humidity when its effects manifest on performance of GAC columns subjected to intermittent loading condition. High humidity tended to improve load attenuation by GAC columns with high influent toluene concentration, but tended to worsen performance of GAC columns with respect to attenuating intermittent, low loading of toluene. Overall, however, these effects are relatively small and significant load equalization can still be achieved using sufficiently tall columns. For practical purposes, curves developed earlier for dry loading case can be used to predict performance and design for sufficiently short columns (corresponding to at least 4 second EBCT) receiving high-humidity, toluene-containing air stream. Competition between water and toluene adsorbing onto GAC was satisfactorily described by IAST, although some previous research indicate otherwise.

(3) For a typical loading characterized by spikes in concentrations, passively operated GAC columns were found to appreciably dampen temporary spikes in contaminant loading. Peak toluene concentrations exiting the GAC load equalization system were markedly lower than peak influent concentrations, with the influent contaminant mass exiting the GAC columns more evenly distributed over longer period of time. The relevance of using an equivalent total-weighted average value in place of actual multiple-spike loading scenario to predict GAC column performance was also shown. The MATLAB program code used to implement the PSDM was successful in simulating GAC column performance under loading conditions characterized by single spikes of varying intensity and duration as well as complex loading
scenarios involving multiple spikes of various intensity and duration, which may prove useful for simulating a variety of unsteady state loading scenarios of interest.

(4) Experimental and modeling efforts conducted to determine the effects of reducing flow rate to GAC columns during non-loading period (reported in Chapter 6) show that reduction of flow rate during the non-loading period reduces the degree of load equalization that can be achieved by GAC columns. This was manifested in increased variation in concentrations (e.g., larger difference between $C_{\text{max}}$ and $C_{\text{min}}$) and increased level of average effluent toluene concentrations. Overall, significant load equalization was achieved by GAC columns which received intermittent toluene loading, and intermittent reduction of flow rate during non-loading.

A general observation gathered from all different conditions of unsteady-state loading is that the degree of load equalization by GAC columns increase with increase in GAC column depth (increase in EBCT). Thus in all of the tests conducted, column performance was generally better with taller GAC columns (longer EBCTs). Another general observation is that GAC columns can reduce concentrations well below the influent level, hence the benefit from reduced construction cost for the biofilter.

Adsorption of toluene onto GAC can be satisfactorily described by the pore and surface diffusion model (PSDM) at various conditions of loading tested. Nonetheless, in sufficiently tall columns, effluent concentrations from GAC columns tend to achieve constant concentrations and a simple mass balance on toluene was sufficient to predict/describe GAC column performance. This was particularly the case with intermittently reduced gas flow rates in columns of packed GAC bed depth (33.3 cm, 4.0 sec EBCT).
7.2 Recommendations for Further Research

Although this research was set-up on the basis of the need to explore GAC column performance under various conditions of unsteady loading, there are still some other facets of this aspect that can be explored. In particular, GAC column performance under fluctuating flow rate may earn merit for further study. Few studies in this area were conducted such that even known understanding of variable flow rate effects on biofilter performance is limited. Therefore, a recommended study of GAC performance during conditions of intermittently varying flow rates may also include a downstream biofilter.

GAC column performance should also be evaluated for contaminants other than toluene or MEK (as previously studied) to assess the range of contaminants and process applications that it can be successfully operated. Such other contaminants may include H$_2$S, which has been a first major application of biofilters and a common component of gas streams that create odor nuisance to the environment. Other compounds which have the tendency to react on GAC surfaces or whose reaction may be triggered by the presence of humidity or other components present in the gas streams may also be worthy for consideration.

This study suggests the potential of GAC load equalization device over a widely varying loading conditions that are unsteady in nature. To date however, its applications were explored only for biological systems used in air pollution control. Various other applications should also be explored such as the case with process systems requiring steady loading of process feeds.
REFERENCES


APPENDIX A
EXPERIMENTS INVOLVING CONTINUOUSLOADING OF TOLUENE IN DRY AND WET AIR STREAMS

INTRODUCTION

Reported effects of water vapor on carbon adsorption are generally with continuous loading. Background literature about these effects are presented in Chapter 4. To provide additional baseline understanding that would aid evaluation of GAC column performance during intermittent loading condition at high relative humidity, fixed-bed adsorption experiments were conducted under steady loading. Continuous toluene loading experiments were conducted using dry (0-5% RH) and humid (80 % RH) air to allow comparison of GAC adsorption capacity, and determine the ability of toluene to displace water initially adsorbed to GAC.

METHODOLOGY

Experimental Apparatus

The GAC columns used in the adsorption/desorption experiments were constructed of PVC (ID=7.62 cm) pipes filled with BPL 4×6 mesh GAC (Calgon Carbon Corp., Pittsburgh, PA). Details of column construction and preparation of the GAC are as described in Chapter 4.

The general configuration of the experimental set-up used is similar to the one used in Chapter 4 (depicted in Figure 4.1). Contaminant-free compressed air flowed through an electronic mass flow controller (Aalborg Instruments and Controls, Inc., Orangeburg, New York) which measured and regulated total air flow through the system. A portion of the total air flow was passed through an aeration stone submerged in a 20 L glass carboy filled with deionized water to provide air humidification to 80% relative humidity. For dry loading experiments, the
carboy was bypassed and all the flow was directed to the column. Liquid toluene (ACS reagent grade, Sigma, St. Louis, MO) was delivered continuously by syringe pumps (KD Scientific, Boston, MA) and evaporated into the air stream. Gas sampling lines were constructed using Teflon tubing. Initial tests conducted prior to placement of activated carbon demonstrated that column components other than GAC had little or no adsorption capacity for toluene. All experiments were conducted at ambient laboratory temperature of 23±2°C.

**Analytical Procedures**

Toluene concentration was measured using either a model 1312 photo-acoustic multi-gas monitor (California Analytical Instruments, Orange, CA) or a model 600 FID/HFID (high-flame ionization detector) hydrocarbon analyzer (California Analytical Instruments, Orange, CA).

Temperature and relative humidity of the air were measured using HiTemp102RH temperature and humidity data loggers (ERTCO, Dubuque, IA).

**Fixed-Bed Continuous Loading Experiments**

Fixed-bed adsorption experiments were conducted under steady loading condition using “conditioned” GAC columns. Twelve columns were constructed (as detailed in Chapter 4) and filled with known amount of virgin GAC to a column height of 7.5 cm. (corresponding EBCT = 0.90 second for air flowing at 22.8 li/min). These columns were “conditioned” by subjecting each to one conditioning cycle with continuous loading of air at steady toluene concentration of 1000 ppmv until complete breakthrough. The columns were then desorbed by passing continuous flow of uncontaminated air. Desorption was continued until effluent toluene was below detection level.
The conditioned carbon columns were subsequently used in fixed-bed continuous loading adsorption studies on two conditions of loading: dry loading (air stream humidity of 0-5% RH) and wet loading (80% RH). For the case of wet loading studies, the conditioned carbon columns were preloaded with continuous flow of toluene-free air stream at 80% RH until the humidity of the air stream exiting the column was approximately equal to the influent humidity. Loading was then continued with toluene injected to the wet air stream. Experiments were conducted at target influent toluene concentrations of 50, 100, 250, 400, 750, and 1000 ppmv. Breakthrough curves were generated, and the mass of toluene reversibly adsorbed to the conditioned carbon was calculated.

RESULTS AND DISCUSSION

Adsorption of Toluene during Continuous Loading with High Humidity Gas Stream

The effect of high humidity on the adsorption of toluene onto GAC was explored at different influent toluene concentrations, $C_o$, ranging from the lowest at 50 ppmv, to the highest concentration of 1000 ppmv. Actual concentrations tested were within 5% of these target concentrations. Continuous loading experiments were conducted using “conditioned” GAC that would allow quantification of the “working capacity” of the carbon during repeated adsorption/desorption - the case with GAC columns receiving intermittent loading or unsteady concentrations of toluene. Previous research (Li and Moe, 2005) has demonstrated that when virgin carbon is first used for adsorption processes, it is likely to have higher adsorption capacity than it does following subsequent regeneration. In a passively-operated GAC column loading unsteady contaminant flows, regeneration may occur during the time when contaminant concentration in the gas flow is low.
Columns used for wet air experiments were initially loaded with toluene-free air at 80% RH. Breakthrough curves for water adsorption in three of these columns prior to start of toluene loading were monitored and are shown in Figure A.1. Breakthrough of water from the columns occurred shortly (less than an hour) after humid air was introduced into the columns. Mass of water initially adsorbed to GAC was determined two ways – gravimetric method and area integration method. By gravimetric method, the difference between the GAC column weight before and after water adsorption to equilibrium approximates the amount of water initially adsorbed prior to toluene loading. Integration of the area under the breakthrough curve for water, on the other hand, gives the total amount of water in the effluent; when subtracted from the actual total water in the influent, the difference gives the amount of water adsorbed. Corresponding masses of water (mass of water per unit mass of virgin GAC) calculated to be adsorbed at equilibrium between conditioned GAC and air at 80% RH in the absence of toluene are shown in Table A.1. The masses approximated by gravimetric and integration methods are in close agreement with each other. These values show some small, but significant amount of water adsorbed onto GAC that was pre-loaded with toluene which remained sorbed even after continuous desorption by continuous flow of contaminant-free air. Toluene was not detected in the effluent of conditioned column even when humid air was introduced to the column.

Toluene breakthrough curves at different influent toluene concentrations, $C_o$, determined during dry loading (0-5% RH) and wet loading (80% RH) are shown in Figure A.2. Also depicted in the figures are effluent humidity profiles for the wet loading case only. Effluent relative humidity profiles during dry loading, which ranged from 0 to 5% RH and were similar to the influent RH, are not shown.
Figure A.1. Breakthrough curves for water from three of the columns loaded with toluene-free air at 80% RH (GAC column height corresponds to EBCT = 0.90 second).
During wet loading of toluene in air containing 80% relative humidity, effluent RH was also initially at around 80% - the humidity of pre-loaded toluene-free air. As soon as toluene loading commenced, effluent water vapor in the effluent started to increase to certain concentrations higher than the influent water vapor concentration; hence, the observed “humps” in the effluent humidity profiles, particularly for influent toluene concentrations of 250 ppmv and higher. This “roll-over” of water vapor concentrations is a phenomenon previously observed with organic multi-component vapor-phase carbon adsorption processes (Gong and Keener, 1993; Li and Moe, 2004). In this study, the humps observed could be due to pre-loaded water vapor displaced by toluene in the GAC. The amount of displaced water is proportional to the area under the “hump” in the curve. By integration of this area, the amount of water displaced was calculated and are summarized in Table A.2. As shown, more water was displaced when higher concentration of toluene was present in the airflow.

Effluent toluene was initially close to zero. From the commencement of toluene loading (time= 0) an initial section of the toluene breakthrough curves shows negligible to no toluene in

<table>
<thead>
<tr>
<th>Column #</th>
<th>Mass of Water adsorbed (g/g-GAC)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gravimetric Method $^b$</td>
</tr>
<tr>
<td>1</td>
<td>0.26</td>
</tr>
<tr>
<td>2</td>
<td>0.30</td>
</tr>
<tr>
<td>3</td>
<td>0.27</td>
</tr>
<tr>
<td>Average</td>
<td><strong>0.28</strong></td>
</tr>
</tbody>
</table>

$^a$ gram of water per gram virgin GAC  
$^b$ weight measurements were done after 70 hours of continuous loading  
$^c$ integration over the duration of 25 hours of loading
Figure A.2. Toluene breakthrough curves and effluent RH from columns (EBCT=0.90 second) loading toluene at various influent concentrations, $C_o$, in air. Dry loading at 0 to 5% RH; Wet loading at 80% RH.
the effluent until breakthrough occurs. At breakthrough, toluene begins to be detected in the effluent, increasing in concentration until the value becomes approximately equal to the influent concentration (within 5% difference). At this point, a complete breakthrough is assumed and the loading is continued for at least 4 hours to ascertain this point. Complete breakthrough was achieved after a relatively short period of time (1 to 2 days) for higher influent toluene concentrations ($C_0 \geq 250$ ppmv) and after 5 to 6 days for lower influent toluene concentrations ($C_0 = 50$ ppmv and 100 ppmv); hence the difference in time-scale shown.

Comparison of toluene breakthrough curves between the dry and the wet loading case shows two apparent effects of high RH on the breakthrough curves of toluene – 1) broadening

Table A.2. Mass of water displaced from columns containing “conditioned” GAC pre-adsorbed with water vapor during loading of toluene at various concentrations in humid air (80% RH). Mass calculations were made on the area under “humps” in the effluent water vapor curves observed during loading of toluene-contaminated air at 80% RH.

<table>
<thead>
<tr>
<th>Influent Toluene Concentration (ppmv)</th>
<th>Mass of water displaced (mg/g*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>~0.0</td>
</tr>
<tr>
<td>100</td>
<td>~0.0</td>
</tr>
<tr>
<td>250</td>
<td>20.5</td>
</tr>
<tr>
<td>400</td>
<td>51.7</td>
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<tr>
<td>750</td>
<td>91.1</td>
</tr>
<tr>
<td>1000</td>
<td>96.4</td>
</tr>
</tbody>
</table>

* milligram water per gram “virgin” GAC
shape of the breakthrough curve; and 2) earlier time to breakthrough. Breakthrough curves of toluene at higher RH resulted in wider and broader profiles for all toluene concentrations tested. Gong and Keener (1993) attributed their similar result to the increased thickness of the moving mass transfer zone of adsorption. The mass transfer zone is a finite layer in the adsorbent column described by a distribution of adsorption velocities among the adsorbate molecules. A wider mass transfer zone may be associated with wider distribution of adsorption velocities of adsorbate molecules. An increase in thickness of the mass transfer zone may be a consequence of reduced kinetics due to an increase in resistance for mass transfer. Water vapor, at high concentration in the gas stream, can fill up spaces and use up adsorption sites in the GAC, making them not readily available for toluene adsorption. The rate of adsorption may be significantly slowed down as water molecules have to be displaced off these sites and spaces first before subsequent toluene adsorption may occur. In addition, an increased resistance to mass transfer can also result from counter diffusion of water molecules being desorbed from GAC. Hence, the presence of high humidity in the gas stream would have increased resistance to mass transfer for toluene adsorption resulting in longer mass transfer zones that were manifested in the observed broadening of the breakthrough curves.

Breakthrough of toluene occurred earlier in the case of wet loading than in the case of dry loading for all levels of toluene concentration in the influent. This effect was more pronounced at lower concentration as shown by the difference in time to breakthrough between the two cases. For example, at the lowest influent concentration, $C_o=50$ ppmv, the time to breakthrough to 20% was reduced from 3.75 days for the dry loading to about 1.25 days for the case of wet loading (a reduction of about 2.5 days). At the highest concentration, $C_o=1000$ ppmv, time to breakthrough to 20% was reduced from about 0.25 day to about 0.10 day (a reduction of about 0.15 day).
These results can also be attributed to reduced potential for toluene adsorption due to the presence of water. Water vapor molecules competing for adsorption onto GAC could have limited available adsorption sites in the GAC for toluene adsorption and slowed down toluene adsorption resulting in toluene distributed earlier in the airflow. It is important to note, however, that complete breakthrough was reached generally earlier with dry loading than with wet loading. Breakthrough curves for the dry loading case were generally steeper (for \( C_0 \geq 250 \text{ ppm}_v \)) than those for the wet loading case. The presence of water vapor would have resulted in earlier breakthrough of toluene but not necessarily earlier approach to complete breakthrough.

Mass of toluene adsorbed per unit mass of activated carbon in each of the columns, calculated for both dry and wet loading cases are summarized in Table A.3. Mass of toluene adsorbed was calculated from the difference between the total mass of toluene in the influent and the mass of toluene in the effluent. The latter was determined from the area under the toluene breakthrough curve. Gravimetric measurements were also attempted but were challenging because of the difficulty posed by water simultaneously desorbing with toluene from the GAC column. Results summarized in Table A.3 show that mass of toluene adsorbed during wet (80% RH) loading was significantly reduced for most levels of influent toluene when compared with mass of toluene adsorbed during dry loading (0-5% RH). Highest reduction in the amount of toluene adsorbed was observed at low influent concentrations of 50 ppm\(_v\) and 100 ppm\(_v\). For a given condition (wet or dry) of loading, GAC adsorption capacity decreased with decrease in influent toluene concentration.

Further processing of these data was done to determine the Freundlich parameters that would describe the equilibrium of adsorption onto GAC for toluene under dry and wet loading conditions. 

\[
q = KC^{1/n}
\]
The amount of toluene adsorbed on virgin carbon, $q$ (mg toluene/g carbon), and concentration of toluene in the gas phase, $C$ (mg/L), obtained from the present study were plotted on a log-log scale shown in Figure A.3. A linear relationship between these two variables, was obtained, with slope defined by the Freundlich parameter, $K$. The dry and the wet loading curves behave not so differently at high influent toluene concentrations and deviate from each other most at the lowest concentration. This indicates the stronger influence of high RH on toluene adsorption at lower concentration than at higher toluene concentrations. For comparison, data points determined from Freundlich parameters reported by Li and Moe (2005) and Calgon are also shown. Calgon data are for virgin GAC while Moe and Li’s (2005) data are for dry loading with conditioned GAC.

Table A.3. Comparison of adsorption capacity between GAC columns subjected to dry (0-5% RH) and wet (80% RH) continuous loading of toluene at various influent concentrations.

<table>
<thead>
<tr>
<th>Influent Toluene Concentration (ppm)</th>
<th>Mass of toluene adsorbed (mg/g*)</th>
<th>Reduction in Adsorbed Toluene (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dry Loading</td>
<td>Wet Loading (80% RH)</td>
</tr>
<tr>
<td>50</td>
<td>153.86</td>
<td>87.13</td>
</tr>
<tr>
<td>100</td>
<td>198.83</td>
<td>111.41</td>
</tr>
<tr>
<td>250</td>
<td>219.60</td>
<td>173.98</td>
</tr>
<tr>
<td>400</td>
<td>230.36</td>
<td>206.26</td>
</tr>
<tr>
<td>750</td>
<td>257.97</td>
<td>244.17</td>
</tr>
<tr>
<td>1000</td>
<td>265.95</td>
<td>263.39</td>
</tr>
</tbody>
</table>

* milligram water per gram “virgin” GAC
Data sets for all six challenge concentrations fit the Freundlich equilibrium equation well, as satisfactorily justified by the regression coefficients obtained for both the dry and the wet loading ($r^2=0.9417$ and $r^2=0.9896$, respectively). Freundlich parameters obtained from regression analysis are summarized in Table A.4. For the present study, lower Freundlich parameter, $K$, was obtained during wet loading than during dry loading, indicating lower adsorption capacity of GAC under highly humid condition (80% RH). Calgon data for the parameter, $K$, is relatively higher compared to the other dry loading data due to the fact that Calgon data are for adsorption on virgin GAC, while other data presented are for previously.

Figure A.3. Freundlich parameter calculations for dry (0-5% RH) and wet (80% RH) loading of toluene-contaminated air.
adsorbed and desorbed GAC (conditioned GAC). For both dry loading studies using conditioned GAC, the present dry (0-5% RH) loading study reports of a higher adsorption capacity than previous dry loading study at 20% RH. Although there was a difference in levels of influent humidity, the differences in trends observed may be attributed at least in part to different lots of carbon used in the studies.

CONCLUSIONS

Results from the continuous loading experiments suggest the capability of toluene to displace water during co-adsorption onto GAC. However, significant effects of high water vapor concentration on toluene adsorption were observed in at least some cases. Overall, the effects of high humidity on the adsorption process can be grouped into two general categories:

(1). effect on the adsorption kinetics; and

<table>
<thead>
<tr>
<th>Condition of loading</th>
<th>K (mg/g)(L/mg)^{1/n}</th>
<th>1/n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry loading, 0-5% RH (Present study)</td>
<td>218</td>
<td>0.162</td>
</tr>
<tr>
<td>Wet loading, 80% RH (Present study)</td>
<td>170</td>
<td>0.367</td>
</tr>
<tr>
<td>Dry loading, 20% RH (Li and Moe, 2005)</td>
<td>152</td>
<td>0.249</td>
</tr>
<tr>
<td>Virgin GAC (Calgon)</td>
<td>305</td>
<td>0.107</td>
</tr>
</tbody>
</table>

Table A.4. Table of Freundlich parameter values obtained from various studies.
The consequences of these two effects were manifested in the broadening of the breakthrough curves and the early breakthrough of toluene during continuous loading. While both effects may be manifested in the case of low toluene loading, only the first effect was observed with high (1000 ppmv) toluene loading.

**CITED REFERENCES**


Figure B.1. Experimentally measured toluene concentrations exiting from a 10-cm packed bed depth GAC column (EBCT 1.2 sec) during continuous loading of 100 ppmv toluene. Time zero in the plot indicates the start of toluene loading.
Figure B.2. Experimentally measured influent concentrations for spike loading of toluene at target influent concentration 1000 ppm\textsubscript{v} for durations of 0.25, 0.50, 1.0, 2.0, and 4.0 hr. The start of the spike loading interval was designated as time zero. Base-line toluene concentration before and after the spike loading was 100 ppm\textsubscript{v}, toluene.

Figure B.3. Experimentally measured influent concentrations for 1.0 hr duration spike loadings of toluene at target influent concentrations of 1000, 700, 500, and 200 ppm\textsubscript{v}. The start of the spike loading interval was designated as time zero. Base-line toluene concentrations before and after the spike loading was 100 ppm\textsubscript{v}, toluene.
Figure B.4. Data from individual replicates for some spike loading scenarios (various spike concentrations and durations) tested showing good replication of data.
Figure B.5. Comparison of target and actual concentrations of toluene during a series of spikes of loading to a 10-cm (EBCT=1.2 seconds) GAC column. Actual loading concentrations depicted are point-by-point average of data obtained from four separate 8-hour loading tests.
Figure B.6. Maximum toluene concentrations exiting GAC columns of various EBCTs receiving 1.0-hr duration step increases in toluene concentrations to levels of 200, 500, and 1000 ppm, as determined from model simulations. Baseline toluene concentration was 100 ppm, before and after spike loading.
APPENDIX C

COMPARISON OF COSTS ASSOCIATED WITH DIFFERENT CONFIGURATIONS OF BIOFILTER SYSTEMS SUBJECTED TO VARIOUS TURN DOWN OF FLOW RATE DURING NON-LOADING PERIOD

**Problem Statement**
An industry emits an air stream with constant flowrate \( Q_G \) of 150 m\(^3\)/min, temperature of 23\(^\circ\)C. Toluene is present as a contaminant in the waste gas for 4 hr/day at a concentration \( C_o \) of 250 ppmv, (0.95 g/m\(^3\)), and during the remainder of the day, no contaminant is present in the airflow. Assuming a biofilter loading rate \( L \) of 50 g/m\(^3\)-h, compare associated costs with a stand-alone biofilter, and a biofilter with GAC load equalization when flow rate during non-loading period is turned down to various fractions of the full flow rate \( f_{Q} \).

**Assumptions:**

i). The GAC column to be used in the integrated system will contain GAC column depth of 33.3 cm – EBCT =4.0 seconds (similar to the one experimentally tested in this study). For this column size, load equalization is almost perfect or close to ideal and hence,

\[
\frac{C_{max}}{C_o} = \frac{C_{avg}}{C_o} = \frac{t_o}{t_o + f_{Q}t_p} = \frac{1}{1 + f_{Q}r_t}
\]

(see Equation 6.4)

where, \( r_t = t_p/t_o \) (see Equation 6.3)

ii). Annual Interest Rate = 8%

iii). Annual Inflation Rate = 3.5%

iv). Capital costs are associated primarily with the biofilter, including labor to build and install the biofilter.

v). Biofilter Cost = $2000 /m\(^3\)
(Note: Costs per unit volume vary greatly. Reactor costs for small design (100 m\(^3\)) have been estimated at $1000 to $3500 per m\(^3\) of filter bed. Larger designs (300 m\(^3\)) become more cost effective at $300 to $1000 per m\(^3\) (Devinny et al., 1999).)

vi). Operating costs are primarily attributed to the energy consumption by the biofilter. It is a substantial part of the operating costs with the majority of electrical costs arising from the blower or fan (Devinny et al., 1999).


viii). Cost of GAC = $ 6.00/lb; (Calgon Corp.); $ 11,220/m\(^3\)
**Solution:**

A. Capital Cost

i). Biofilter Volume, \( V_{bio} = \frac{C_{avg}/C_o \times C_o \times Q_o}{L} \)

For a biofilter that lacks a GAC load equalization, biofilter size would be designed based on the maximum concentration of toluene which is equal to the influent concentration (i.e., \( C_{max}/C_o = C_{avg}/C_o = 1.0 \)); hence is constant for a stand-alone biofilter. Solving for the conditions given:

\[
V_{bio} = \frac{1.0 \times 0.95 \text{ g/m}^3 \times 150 \text{m}^3 / \text{min} \times (60 \text{min/hr})}{50 \text{g/m}^3 - h} = 171 \text{m}^3
\]

For a biofilter with GAC load equalization, \( C_{avg}/C_o \) depends on the fraction of flow rate during the non-loading period \( (f_Q) \) as shown in Equation 6.4. Therefore, biofilter size in an integrated system is a function of \( f_Q \). To illustrate for \( f_Q = 0.50 \),

\[
\frac{C_{max}}{C_o} = \frac{C_{avg}}{C_o} = \frac{t_o}{t_o + f_Q t_p} = \frac{1}{1 + f_Q r_i} = \frac{1}{1 + (0.5 \times \frac{20}{4})} = 0.286
\]

\[
V_{bio} = \frac{0.286 \times 0.95 \text{ g/m}^3 \times 150 \text{m}^3 / \text{min} \times (60 \text{min/hr})}{50 \text{g/m}^3 - h} = 48.9 \text{m}^3
\]

ii). GAC Volume, \( V_{GAC} = Q_G \times \text{EBCT} \)

\[
V_{GAC} = 150 \text{m}^3 / \text{min} \times 1 \text{min/60s} \times 4.0s = 10 \text{m}^3
\]

Total Capital Costs= \( $2,000 \times V_{bio} + $11,220 \times V_{GAC} \)

**Annualized Capital Cost**, \( A = \frac{\text{Total Capital Cost} \times 0.08(1 + 0.08)^n}{(1 + 0.08)^n - 1}; \)

\( n = \text{number of years} \)

B. Annual Operating Cost, \( C_{electricity} \) ($/yr), 10-hp blower

For operation at constant flow rate,

\[
C_{electricity} = 10hp \times 0.75kW / hp \times 365days / yr \times 24hrs / day \times $0.069 / kW - h
\]
For an operation of varying flow rate, cost of electricity is a function of the fraction of time and turndown rate of flow. For example, at 50% turndown of flow rate during 20 hrs of non-loading,

\[ C_{electricity} = 10 hp \times 0.75 kW / hp \times 365 days / yr \times (4 \times 1.0 + 20 \times f_Q) hrs / day \times $0.069 / kW - h \]

\[ C_{electricity} = 10 hp \times 0.75 kW / hp \times 365 days / yr \times (4 \times 1.0 + 20 \times 0.5) hrs / day \times $0.069 / kW - h \]

\[ C_{electricity} = $3,844 / yr \]

Annualized Operating Cost, \( B = \frac{\sum_{i=1}^{n} C_{electricity} \times (1 + 0.035)^i}{n}; \)

\( n = \) number of years

**Total Annual Cost = A + B**

**Results:**

Results of the above calculations are summarized in the tables below. Comparison of the total costs for a biofilter with and without GAC load equalization subjected to various turndown rate of flow during the non-loading interval is shown in the figure below.

**Figure C.1. Total annualized costs for a stand-alone biofilter and for an integrated GAC column-biofilter system treating toluene-contaminated air (250 ppmv) generated 4 h/day.**
Table C.1. Summary of costs associated with a stand-alone biofilter treating toluene-contaminated air. Based on 8% interest rate over 10 and 20 years of equipment service life.

### 10-year planning

<table>
<thead>
<tr>
<th>A. Capital Cost (Biofilter)</th>
<th>Volume (m$^3$)</th>
<th>Cost ($)</th>
<th>Annualized Cost ($)</th>
<th>Total Annualized Cost ($) (Biofilter + Electricity)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>171</td>
<td>342,000</td>
<td>50,968.09</td>
<td></td>
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<table>
<thead>
<tr>
<th>B. Operating Cost (Electricity)</th>
<th>$f_Q$</th>
<th>Annual Cost ($)</th>
<th>Annualized Cost ($)</th>
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<tr>
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<td>0.1</td>
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<td>1,098.29</td>
<td>1,333.54</td>
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</table>

### 20-year planning

<table>
<thead>
<tr>
<th>A. Capital Cost (Biofilter)</th>
<th>Volume (m$^3$)</th>
<th>Cost ($)</th>
<th>Annualized Cost ($)</th>
<th>Total Annualized Cost ($) (Biofilter + Electricity)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>171</td>
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<td>34,833.46</td>
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</table>

<table>
<thead>
<tr>
<th>B. Operating Cost (Electricity)</th>
<th>$f_Q$</th>
<th>Annual Cost ($)</th>
<th>Annualized Cost ($)</th>
</tr>
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<tbody>
<tr>
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<td>1.0</td>
<td>6,589.71</td>
<td>9,643.87</td>
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<td>0.9</td>
<td>6,040.57</td>
<td>8,840.21</td>
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<td>8,036.56</td>
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<td>4,942.28</td>
<td>7,232.90</td>
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<td>4,393.14</td>
<td>6,429.24</td>
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<td>5,625.59</td>
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<tr>
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<td>4,018.28</td>
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<td>2,196.57</td>
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<td>1,607.31</td>
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</table>
Table C.2. Summary of costs associated with an integrated GAC column-biofilter system treating toluene-contaminated air. Based on 8% interest rate over 10 years of equipment service life.

10-year planning

<table>
<thead>
<tr>
<th></th>
<th>A. Capital Cost (Biofilter + GAC)</th>
<th></th>
<th>B. Operating Cost (Electricity)</th>
<th>Total Annualized Cost, $</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$f_Q$</td>
<td>Volume (m³)</td>
<td>Cost ($</td>
<td>Annualized Cost ($)</td>
</tr>
<tr>
<td>GAC Column</td>
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<td></td>
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<tr>
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<td>342,000.00</td>
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</tr>
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</table>

Based on 8% interest rate over 10 years of equipment service life.
Table C.3. Summary of costs associated with an integrated GAC column-biofilter system treating toluene-contaminated air. Based on 8% interest rate over 20 years of equipment service life.

<table>
<thead>
<tr>
<th>20-year planning</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A. Capital Cost (Biofilter + GAC)</strong></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>GAC Column</td>
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<tr>
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<td></td>
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<tr>
<td></td>
</tr>
</tbody>
</table>
CITED REFERENCES


VITA

Marilou Montevirgen Nabatilan is the first child born to Mr. And Mrs. Marcos Romulo Montevirgen in July, 1969, in Zambales, Philippines. She took up her bachelor of science in chemical engineering studies from the University of the Philippines, Los Baños (UPLB), and graduated in 1992. Since graduation from college, she had been in the teaching profession – having served as instructor in physics (1991-1992), as graduate teaching assistant in chemistry (1996-1997), and as assistant professor in chemical and environmental engineering in UPLB (1997-2002). The gap in time was spent either or both raising a family and attending graduate school. With her husband Larry Nabatilan, she tended to her three children – Arielle, Joshua, and Miguel, while doing her master’s degree in environmental engineering at the University of the Philippines.

She came to LSU in Fall, 2002, and obtained the Master of Science in Chemical Engineering in December, 2005. She started her doctoral program in civil engineering in August, 2005, which is to be conferred on her during the Summer Commencement, in August, 2009.