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Activated carbon load equalization of transient concentration spikes of gas-phase toluene

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ABSTRACT

Biofilters used for air pollution control often experience diminished treatment performance when subjected to transient periods of elevated contaminant concentrations. In research reported here, the potential for using granular activated carbon (GAC) columns to attenuate peak loading of highly variable toluene concentrations was investigated through a combination of experimental testing and numerical modeling. 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 short duration. Collectively, experimental and modeling results demonstrate that passively operated GAC columns with short contact times can accumulate toluene present in waste gases when influent concentrations are temporarily high and later desorb and redistribute the toluene at comparatively lower concentrations over a longer time period when influent concentrations are lower. Such processes have the potential to dampen shock loading to a downstream biofilter or other air pollution control device, and thereby improve treatment performance.

1. Introduction

Owing to the unsteady nature of industrial processes, many biofilters (fixed-film bioreactors 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 [1–9]. 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 [5–10].

Various design approaches and operational strategies have been proposed to address problems associated with transient loading to biofilters [3,11–18]. One particularly promising approach is to employ an integrated system comprised of a passively operated load equalization device consisting of a column packed with granular activated carbon (GAC) located in series prior to the biofilter. The rationale for such a system is that during periods of high contaminant loading, the GAC adsorbent can temporarily accumulate contaminants and then subsequently desorb contaminants during intervals when concentration in the waste gas is lower. This has the potential to decrease peak contaminant loading to biofilters subjected to transient conditions, can prevent starvation conditions during periods when influent contaminant concentrations are low or absent, and it provides a means of incorporating a safety factor in system design [12,15,16]. 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 [12,15,16].

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 h/day and no contaminant loading for the rest of the day, intended to simulate industrial operations with an 8 h/day work schedule [12,15,19]. 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 [16]. In contrast, contaminant loading to biofilters in actual industrial

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Nomenclature

$C_{0,i}i$	initial influent concentration (M/L^3)
$C_i(z, t)$	adsorbent concentration in bulk phase (M/L^3)
$C_{p,i}(r, z, t)$	adsorbate concentration in adsorbent pores (M/L^3)
$D_{p,i}$	pore diffusivity (L^2/T)
$D_{s,i}$	surface diffusivity (L^2/T)
$k_{f,i}$	film transfer coefficient (L/T)
L	bed length (L)
m	number of components
$q_i(r, z, t)$	adsorbent phase concentration (M/M)
R	average adsorbent particle radius (L)
V	loading rate (L/T)

Greek letters

ε_p	particle void fraction
ρ_a	apparent adsorbent density (M/L^3)
ε	bed void fraction

Subscript

i	component number i

operations is 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 here 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 was used to implement a 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).

2. Materials and methods

2.1. Granular activated carbon 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 desiccators prior to use.

The configuration of the experimental apparatus used in initial fixed-bed adsorption/desorption experiments (Fig. 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 a GAC column. Each packed column, 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.

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.

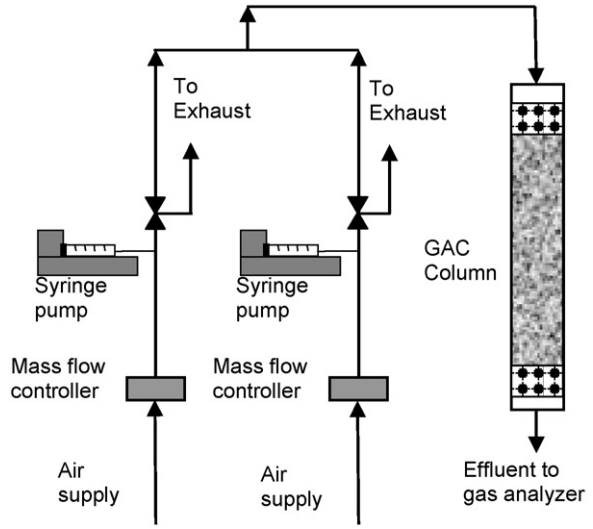

Fig. 1. Experimental apparatus used in conducting fixed-bed adsorption/desorption experiments.

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.

2.2. Evaluation of spike intensity and duration effects

For initial experiments, toluene contaminated air at a baseline influent concentration of 100 ppm$_v$ 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 ppm$_v$ 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 2 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 ppm$_v$ (2, 5, 7, and 10× baseline concentration, respectively) were loaded to the column for 1.0 h duration. To explore the effects of various durations of spike loading, a 1000 ppm$_v$ toluene-contaminated airflow was loaded to the column at spike durations of 4.0 h, 2.0 h, 1.0 h, 30 min and 15 min. Half of the transient loading experiments were tested in duplicate to verify reproducibility of the results observed.

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 h/day work schedule. The loading scenario included four target influent concentrations, 100, 200, 500, and 1000 ppm$_v$ (1, 2, 5, and

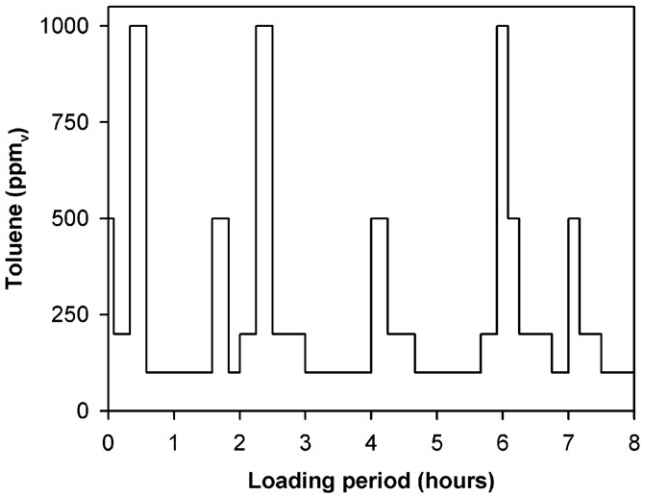

Fig. 2. Target toluene concentrations entering the GAC column during the 8 h/day loading interval of dynamic multi-spike loading experiments. During the remaining 16 h/day, uncontaminated air flowed through the GAC column.

10× the baseline concentration of 100 ppm$_v$) occurring for various durations (5, 10, 15, 60 min) throughout an 8 h/day loading interval (see Fig. 2). During the remaining 16 h/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 ppm$_v$ during the 8 h/day loading interval. The time-weighted average concentration calculated accounting for the 16 h/day interval of no loading was 83 ppm$_v$. The experimental apparatus used to test this loading scenario was identical to that employed in single-spike experiments (Fig. 1) except that there were four parallel gas flows, which allowed introduction of gas with four different influent concentrations at different time intervals.

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 [16] 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.

2.5. Pore and surface diffusion model

The pore and surface diffusion model (PSDM) described by Crittenden et al. [20] and Hand et al. [21] 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. The PSDM is a dynamic fixed-bed model that incorporates several assumptions [22]: (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; and (6) adsorption equilibrium of an individual compound can be represented by the Freundlich isotherm equation.

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 [22,23].

The bulk gas phase mass balance for component i (in this case, toluene) is given by (see Nomenclature section for definition of variables) Eq. (1).

$$\frac{\partial C_i}{\partial t}(z,t) + V\frac{\partial C_i}{\partial z}(z,t) + 3\frac{k_{f,i}(1-\varepsilon)}{\varepsilon R}[C_i(z,t) - C_{p,i}(r=R,z,t)] = 0 \quad (1)$$

The initial and boundary conditions are respectively:

$$C_i(z,t) = 0 \quad \text{at } 0 \le z \le L,\ t = 0 \quad (2)$$

$$C_i(z,t) = C_{0,i}(t) \quad \text{at } z = 0,\ t > 0 \quad (3)$$

In the adsorbent, the intraparticle phase mass balance for component i in an assumed spherical particle is given by:

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2 D_{s,i}\frac{\partial q_i}{\partial r}(r,z,t) + \frac{r^2 D_{p,i}\varepsilon_p}{\rho_a}\frac{\partial}{\partial r}C_{p,i}(r,z,t)\right] = \frac{\partial}{\partial t}\left[q_i(r,z,t) + \frac{\varepsilon_p}{\rho_a}C_{p,i}(r,z,t)\right] \quad (4)$$

The initial condition and boundary conditions are, respectively:

$$q_i(r,z,t) + \frac{\varepsilon_p}{\rho_a}C_{p,i}(r,z,t) = 0 \quad \text{at } 0 \le r \le R,\ t = 0 \quad (5)$$

$$\frac{\partial}{\partial r}\left[q_i(r,z,t) + \frac{\varepsilon_p}{\rho_a}C_{p,i}(r,z,t)\right] = 0 \quad \text{at } r = 0,\ t \ge 0 \quad (6)$$

$$D_{s,i}\,\rho_a\frac{\partial q_i}{\partial r}(r=R,z,t) + D_{p,i}\varepsilon_p\frac{\partial C_{p,i}}{\partial r}(r=R,z,t) = k_{f,i}[C_i(t) - C_{p,i}(r=R,z,t)] \quad (7)$$

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

$$C_{p,i}(r,z,t) = \frac{q_i(r,z,t)}{\sum_{k=1}^{m} q_k(r,z,t)}\left[\frac{\sum_{k=1}^{m} n_k q_k(r,z,t)}{n_i K_i}\right]^{n_i} \quad (8)$$

MATLAB was utilized to implement a numerical approach to solve the system of PDEs describing the dynamics in a fixed-bed adsorber. The solution methodology closely followed the numerical approach presented by Friedman [23] and Crittenden et al. [24]. The PDEs, initial conditions, and boundary conditions in Eqs. (1)–(8) describing adsorber dynamics were first converted into dimensionless form [23,24] and then reduced to a system of ordinary differential equations (ODEs) by the method of orthogonal collocation as described previously [23,24]. The intraparticle phase equation (Eq. (4)) was expanded using symmetric orthogonal polynomials with even powers of x (Jacobi polynomials of the form shown in Eq. (9)) and with weighting factor equal to $1 - x^2$ [26].

$$y(x^2) = \sum_{i=1}^{N+1} d_i x^{2i-2} \quad (9)$$

The gas bulk phase equation (Eq. (1)) was expanded using non-symmetric orthogonal polynomials (shifted Legendre polynomials of the form shown in Eq. (10)) with weighting factor equal to 1 [26].

$$y(x) = \sum_{i=1}^{N+2} d_i x^{i-1} \quad (10)$$

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 [25]. Collocation matrices and the roots of Legendre polynomials were verified against tabulated values given in the literature [26,27]. The computer program was validated by comparison of simulation results to results from the Adsorption Design Software package (AdDesignS [22]) for simulation conditions to which both apply [16,23]. 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 Supplementary Table S1. 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 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 s, respectively, at a superficial gas velocity of 300 m/h.

3. Results

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_v 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 (Supplementary Fig. S1). Complete breakthrough was achieved after approximately 5 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, Supplementary Figs. S2 and S3).

Experimental measurements of effluent toluene from GAC columns which received transient spikes of 1000 ppm_v toluene for various durations are shown in Fig. 3. Results obtained for loading conditions tested in duplicate (4.0, 2.0, 1.0 h spike duration) showed excellent reproducibility (maximum effluent toluene concentrations differing <3%). For loading conditions tested in duplicate, point-by-point averages from the duplicate tests are depicted in Fig. 3. Data are shown from a 24-h 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.

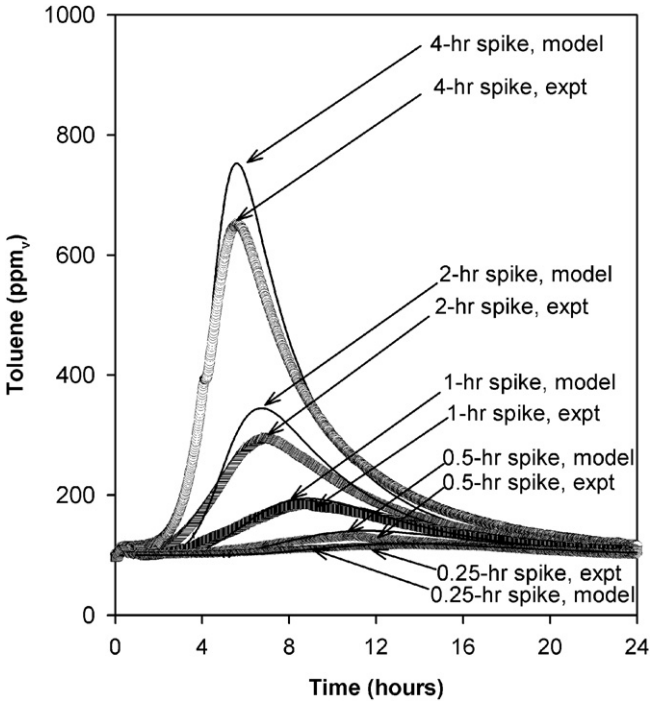

Fig. 3. Experimental measurements and model simulations of toluene concentrations exiting a GAC column (10 cm packed bed depth; EBCT 1.2 s) after spike loading of 1000 ppm_v toluene (10× baseline concentration of 100 ppm_v toluene) for various durations ranging from 0.25 to 4.0 h. Time zero indicates the start of the spike loading interval.

At the spike concentration of 1000 ppm_v toluene (10× the baseline loading of 100 ppm_v), 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 ppm_v). Maximum effluent toluene concentrations experimentally observed when the spike duration was 4.0 h averaged 634 ppm_v, while maximum effluent concentrations for spike durations of 2.0, 1.0, 0.50, and 0.25 h were 282, 180, 130, and 115 ppm_v. In all loading cases tested, effluent toluene concentrations decreased back to the pre-spike baseline level of 100 ppm_v within 2 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 ppm_v) for a fixed duration of 1.0 h revealed that as the inlet spike concentration decreased, the maximum toluene concentration observed in the GAC column effluent also decreased (Fig. 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 h duration spike in loading of 1000 ppm_v toluene ($10 \times C_0$) was dampened to a maximum effluent concentration of 180 ppm_v, corresponding to an 82% decrease in maximum concentration that would enter a biofilter or other downstream air pollution control device. For 1.0 h spike loadings of 700, 500, and 200 ppm_v toluene, maximum toluene concentrations exiting the GAC columns were 146, 130, and 108 ppm_v, respectively.

For single spike loadings of varying duration (Fig. 3) and intensity (Fig. 4), model simulations were in close agreement with experimental measurements; however, the model slightly under-predicted the degree of load equalization in comparison

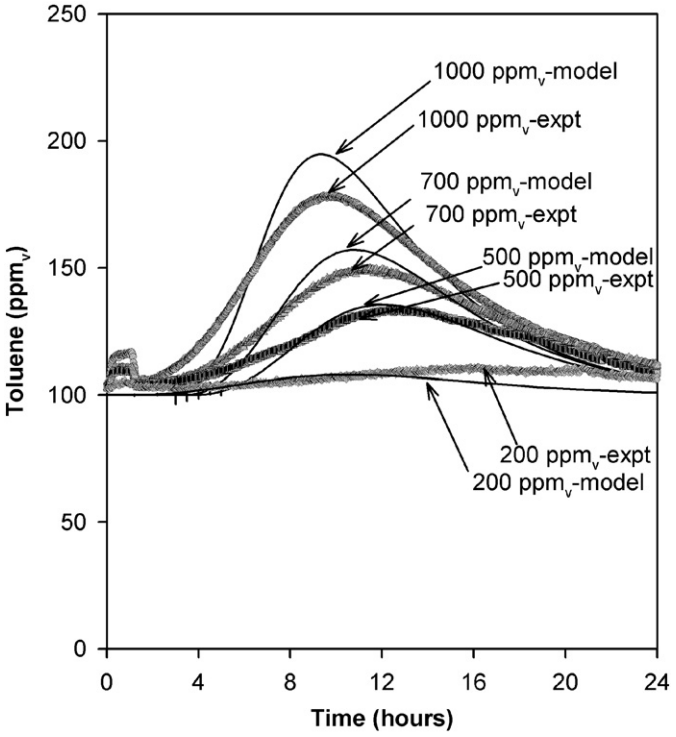

Fig. 4. Experimental measurements and model simulations of toluene concentrations exiting a GAC column (10 cm packed bed depth; EBCT 1.2 s) after spike loading of various toluene concentrations for a 1.0 h duration. The base-line influent toluene concentration before and after spike loading was 100 ppm_v. Time zero indicates the start of the spike loading interval.

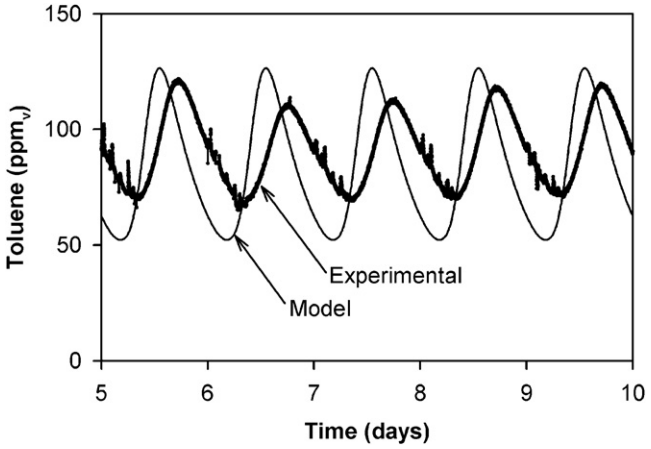

Fig. 5. Experimental measurements and model simulation of quasi-steady-state toluene concentrations exiting a 10-cm packed bed depth GAC column (EBCT 1.2 s) subjected to target loading comprised of a series of concentration spikes as shown in Fig. 2 for 8 h/day and uncontaminated air 16 h/day. The start of the first 8 h/day toluene loading interval was designated as time zero. Quasi-steady state was reached by day 5 as shown in Supplementary Fig. S5.

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 h, 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 (model 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.

3.2. Multiple spike loading

The GAC column subjected to multiple-spikes of toluene loading during the course of an 8 h/day loading period was operated for 11 days. The target influent toluene concentrations during the daily 8-h loading interval were as shown in Fig. 2, and for the remaining 16 h/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 (Supplementary Fig. S4). 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 h/day multi-spike loading, there was an initial period of approximately 2 days during which toluene accumulated in the GAC column and no contaminant was detected in the effluent (Supplementary Fig. S5). 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 ≥95%). Hereafter, this condition is referred to as quasi-steady-state behavior.

Experimentally measured toluene concentrations exiting the GAC column receiving 8 h/day multiple-spike loading in the interval after reaching quasi-steady state are shown in Fig. 5 along with model simulations. 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 ± 3 ppm_v (mean ± standard deviation, $n = 5$), appreciably lower than the maximum daily spike concentration (1000 ppm_v). The minimum daily effluent toluene concentration was 69 ± 2 ppm_v (mean ± standard deviation, $n = 5$), appreciably higher than the minimum daily influent concentration, which was 0 ppm_v for 16 h/day.

Results from model simulations of the 8 h/day multi-spike target loading are quite similar to the experimental observations (Fig. 5) both qualitatively and quantitatively. Model simulations indicated daily maximum toluene concentrations of 126 ppm_v and daily minimum toluene concentrations of 52 ppm_v 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 h/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 ppm_v) over daily 8.0 h/day loading periods (Fig. 6). Each graph on the right depicts modeled toluene concentrations exiting GAC columns during 5-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 ppm_v at intervals distributed throughout the daily 8.0 h loading period. The fourth row depicts a loading scenario in which the highest spike concentration, 1000 ppm_v, would occur during the first 1.33 h loading interval, and the influent concentration was 100 ppm_v for the remainder of an 8-h/day loading interval. The fifth row depicts a scenario in a spike concentration that would occur during the last

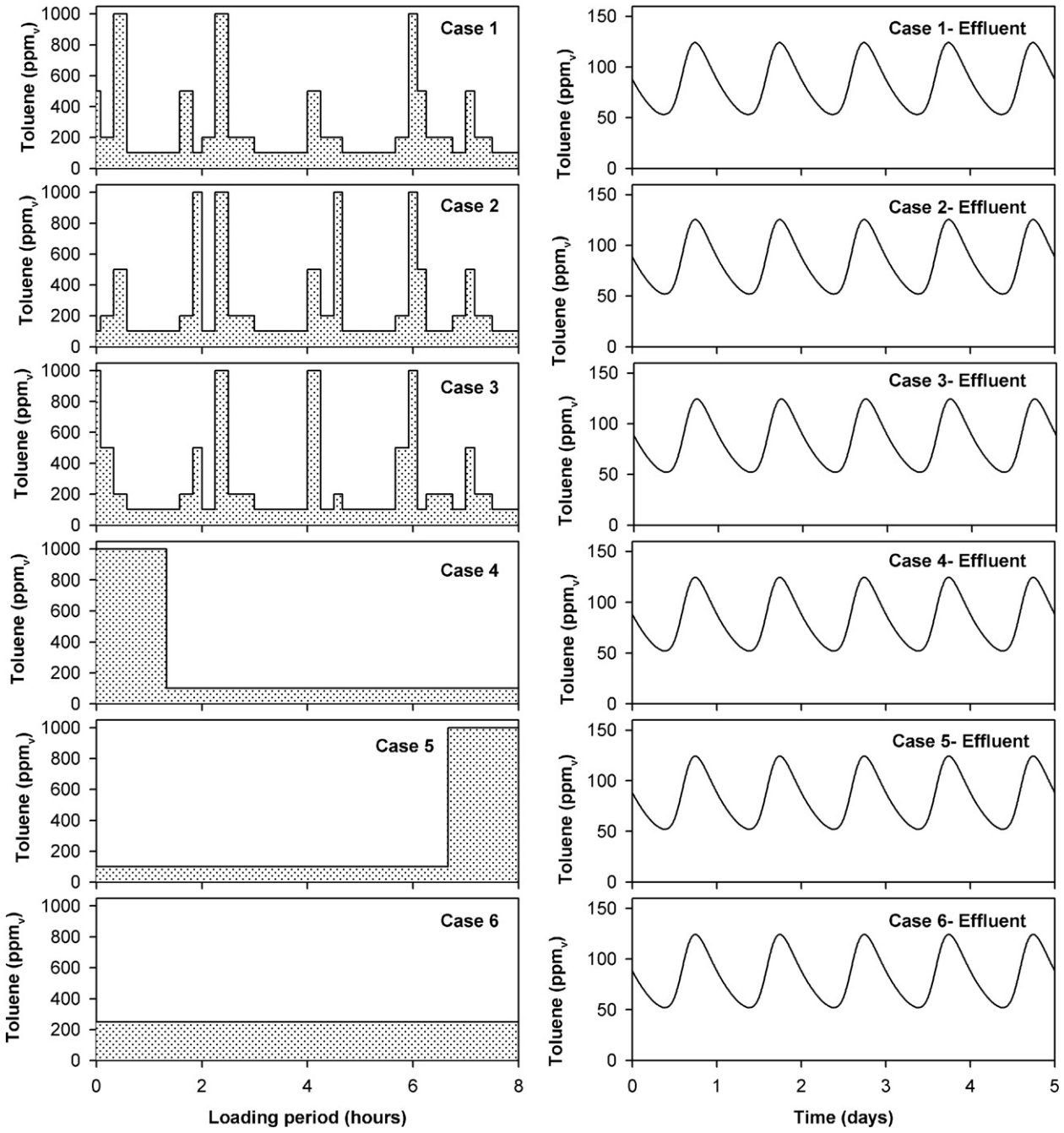

Fig. 6. Model simulations of 5-day quasi-steady state effluent toluene concentrations (right column) from 10-cm GAC (EBCT 1.2 s) column receiving various patterns of spikes in toluene concentration during 8 h/day loading intervals (left column) and uncontaminated air 16 h/day. All loading patterns have time-weighted average influent toluene concentrations of 250 ppm_v over the 8 h/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.

1.33 h of the 8.0 h/day loading period. The sixth row represents loading with a constant concentration of 250 ppm_v throughout the 8.0 h/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 ppm_v for Case 2) differed from the smallest maximum daily effluent toluene concentration (117 ppm_v for Cases 4 and 5) by only 11 ppm_v. These were also quite close to the maximum daily effluent toluene concentration resulting from simulation of uniform loading at a rate of 250 ppm_v throughout the course of the daily 8 h/day loading interval, 126 ppm_v (Case 6).

3.3. Model simulation 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 h/day multi-spike loadings as depicted in Fig. 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 Fig. 7. Consistent with previous experimental studies for transient loading of GAC columns with

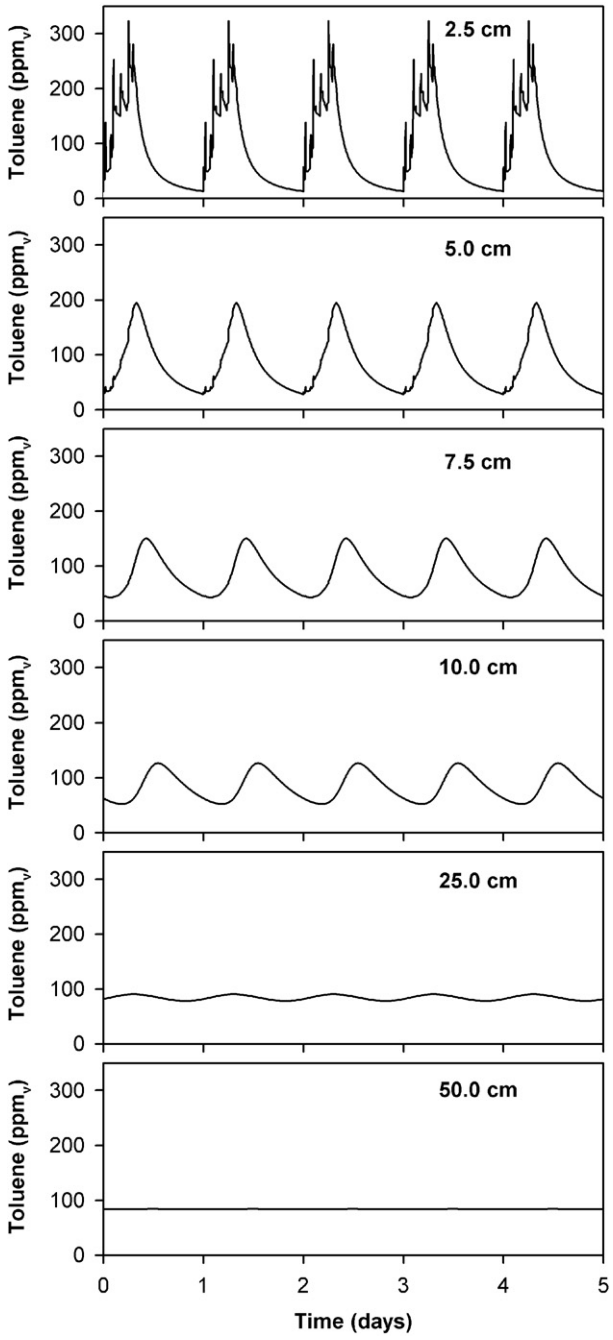

Fig. 7. Model simulations of quasi-steady state effluent toluene concentrations from GAC columns of various lengths receiving the multiple-spike toluene loading pattern shown in Fig. 2 during 8 h/day loading intervals and uncontaminated air flow 16 h/day. Air flow was at the same rate during toluene loading and non-loading intervals. Corresponding EBCTs were 0.3, 0.6, 0.9, 1.2, 3.0, and 6.0 s, respectively, at a superficial gas velocity of 300 m/h. Time zero in each plot corresponds to the start of a daily toluene loading interval after the system reached quasi-steady state.

constant toluene concentration during intermittent loading intervals [12,15,16], model simulations suggest that intermittent loading (e.g., toluene present in the influent 8 h/day) with highly dynamic conditions characterized by multiple spikes will be more attenuated as the GAC packed bed depth (and correspondingly, EBCT) increases.

At very short GAC column bed depth (i.e., 2.5 cm, EBCT 0.3 s), 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 $\geq$ 0.6 s), appreciable smoothing of the effluent profile characterized by only a single daily peak in toluene concentration was observed. At the longest GAC bed depth considered (50.0 cm; EBCT 6.0 s), the multiple spikes of the influent loading were completely attenuated; effluent toluene concentration was constant as a function of time.

4. Discussion

Results from the single-spike loading experiments (Figs. 3 and 4) demonstrated that passively operated GAC columns can temporarily accumulate contaminants during intervals of high influent concentration (e.g., 200–1000 ppm_v) and desorb contaminants during intervals of lower loading (i.e., influent toluene concentration of 100 ppm_v). This resulted in appreciable load equalization without need for external GAC regeneration by heating or other means as employed in other load equalization strategies [3,11].

Load attenuation such as that shown in Figs. 3 and 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. [28] studied the transient responses of biofilters subjected to base-line loading of 107 ppm_v 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$\times$ the baseline level) for duration of 1.0 h. While the biofilters were able to remove essentially all of the contaminant loading when the step increase was comparatively low (e.g., 2.5$\times$ baseline loading, 268 ppm_v), considerable contaminant breakthrough was observed when toluene concentrations entering the biofilters during the 1.0 h period of elevated loading were higher. A best fit line to experimental data suggested that for a 1.0 h spike loading, influent toluene concentrations above threshold values of 3.3$\times$ and 4.2$\times$ 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. [28] are quite similar to the loading conditions imposed on the GAC column for which results are depicted in Fig. 4 in the present study. Data presented in Fig. 4 demonstrate that a relatively small GAC column (bed depth of 10-cm, EBCT 1.2 s) could attenuate 1.0-h spikes in loading concentrations at least as high as 1000 ppm_v to levels below the thresholds causing toluene breakthrough in the biofilters reported by Wright et al. [28].

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 [10]. 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_v for a duration of 1.0 h, the toluene concentration exiting the 10 cm column tested here was within the range of 125–180 ppm_v for a duration of 13.6 h. 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 [29,30].

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 s) receiving a series of spikes (target concentrations ranging from 100 to 1000 ppm_v, Fig. 2) during 8 h/day loading intervals could decrease peak effluent concentrations to 117 ± 3 ppm_v, well below the time-weighted average of the loading interval (250 ppm_v), while also maintaining a relatively stable contaminant concentration in the effluent during the 16 h/day interval when the influent toluene concentration was zero (minimum daily effluent concentration 69 ± 2 ppm_v, Fig. 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 [2,31].

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 [12,15,16]. 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 and implementation scheme is sufficiently flexible to simulate a wide 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 s) subjected to a variety of multiple-spike loading scenarios (Fig. 6) would be similar or identical to that from an equal size column receiving constant toluene loading at a level of 250 ppm_v, the time-weighted average of the 8 h/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× minimum concentrations or 4× 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 Fig. 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. Conclusions

- Passively operated GAC columns can appreciably dampen temporary spikes in gas-phase 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.
- 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.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2009.05.006.

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