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MULTICOMPONENT ADSORPTION OF POLYCYCLIC AROMATIC HYDROCARBONS IN MANUFACTURED GAS PLANT SOILS

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ABSTRACT

Adsorption is an important process in the bioremediation of Manufactured Gas Plant (MGP) soils contaminated with high levels of polycyclic aromatic hydrocarbons (PAH). Over 2,000 sites nationwide exist that are contaminated with complex mixtures of PAH and other pollutants. Many PAH are classified as EPA priority pollutants. The adsorption properties of weathered contaminated soils are difficult to measure using pulse or step perturbations due to heterogeneous contaminant distributions and heterogeneous soil physical structure. This study compares the use of cyclical perturbations with step change perturbations to analyze these complex soil systems. The sinusoidal method proved to be more robust than the step perturbation method. Sinusoidal response was easier to interpret and was continuous. The step change method produced a transient response that was more difficult to interpret. Two parameters, period and amplitude, were available when using sinusoidal perturbation methods while only one parameter, magnitude of the step function, was available for dynamic studies using traditional step perturbation methods. Displacement behavior was observed with both sinusoidal and step experiments. Simulations are presented using favorable isotherms for an adsorption system using a sinusoidal feed input. Automated on-line high performance liquid chromatography and capillary gas chromatography systems developed for analysis are also described.

INTRODUCTION

Disposal of byproducts from pyrolytic production of synthetic natural gas (town gas) has resulted in thousands of sites contaminated with PAH which are recalcitrant to degradation (1). These PAH contaminated sites, termed MGP soils, range in size from less than one acre to over 100 acres, with contamination exceeding 15 feet in depth. Much concern exists over these sites since many PAH compounds such as benzo(a)pyrene, benzo(j)fluoranthene, benzo(b)fluoranthene, benzo(e)pyrene and others are believed to be carcinogenic (2). Bioremediation is an attractive potential remediation technology because of potential cost savings over many conventional technologies.

The effective use of bacteria for restoration of PAH contaminated sites depends upon a number of important factors including availability of contaminants (3). PAH readily adsorb to soils (4) and become unavailable for liquid phase biodegradation. Adsorption of hydrophobic organic compounds correlates best with soil organic matter content and is usually described by favorable type isotherms (5). Analysis of MGP isotherms is complicated by the heterogeneous physical structure of soils and by the presence of multiple sorbates with interfering isotherms. Removal of contaminates from the soil for many conventional analysis schemes substantially changes the character of the soil (due to high concentrations of the contaminants in the soils) and may significantly bias results. Robust protocols are needed for analysis of these extremely complex soil systems.

This paper compares the use of cyclical and classical step perturbation methods for analysis of adsorption in soils and describes developed on-line analytical systems for component measure in real time. Blackburn (6) proposed the use of sinusoidal perturbations for determining critical time constants of biological and physical processes affecting biological degradation in soils. Because of the robust nature of sinusoidal perturbation methods, they are further investigated as a tool for analysis of adsorption. Solutions for binary and ternary multicomponent adsorption systems (assuming a step change in feed concentration, and negligible mass transfer and dispersion) have been discussed by a number of researchers (7-9, and others). Prediction of front velocities, wave front types, and displacement using a simple geometric approach, derived

TABLE 1: COMPONENTS AND CONCENTRATIONS OF CONTAMINATES IN MGP SOIL.

Component	Concentration (mg/kg soil)	Component	Concentration (mg/kg soil)
Benzene	1.1	Ethylbenzene	2.9
Styrene	1.1	Toluene	1.8
Xylenes	15	Carbazole	89
Naphthalene	1200	Acenaphthylene	540
Acenaphthene	120	Fluorene	190
Anthracene	320	Phenanthrene	240
Fluoranthene	266	Pyrene	220
Benzo(b)-floranthene	39	Benz(a)-anthracene	170
Benzo(a)-pyrene	86	Chrysene	100
Benzo(k)-fluoranthene	56	Dibenzo(a,h)-anthracene	210
Indeno(123-cd)pyrene	125	Benzo(g,h,i)-perylene	59
2-methyl-naphthalene	510		

Adapted from M. A. Cushy and D. J. Morgan, Biological Treatment of Soils Containing Manufactured Gas Plant Residues, Topical Report, 1990, Gas Research Institute, Contract No. 5086-254-1334.

using the Method of Characteristics (7-9), was suggested by Coroyannakis (9). If dispersion and mass transfer are significant, the Coroyannakis method provides qualitative results.

MATERIALS AND METHODS

The adsorber design used has been previously described (10-11). Sinusoidal substrate input concentrations were produced by operating two Gilson 301 HPLC pumps 180° out of phase. A personal computer controlled pump operation. Feed rates of 0.05 to 0.40 mL/min were used to approach normal fluid transport rates through sandy soils (12). The adsorber systems were equipped with bypass lines to allow direct analysis of feed streams.

Soils were obtained from a PAH contaminated site, were sieved and then washed with 1 % sodium pyrophosphate solution. Soil particle sizes ranged between 0.175 and 1.0 mm. This minimal treatment prevented excessive pressure buildup during operation (11). The soil was characterized as a coal tar soil contaminated with high concentrations of PAH. Approximate contaminant concentrations in the soil are listed in Table 1. Soil was added to the adsorber in a slurry. Soil microbial activity was inhibited by continuous addition of 0.05 % $HgCl_2$ and maintenance of anaerobic conditions.

Naphthalene solution was produced by adding naphthalene crystals (Sigma) to boiling distilled water. The solution was allowed to cool slowly with stirring for at least several weeks before use.

A high performance liquid chromatography (HPLC) gradient program was optimized for resolving compounds leaching from a sample of MGP soil. The HPLC system consisted of a model 5560 liquid chromatograph (Varian, Palo Alto, CA), a 25 cm Vyadac 201TP5 column (Sep-ar-a-tions Group, Hesparia, CA) an LS-4 fluorescent spectrophotometer (Perkin Elmer, Norwalk, CT) and an LC 90 UV absorbance detector (Perkin Elmer). An eluant flow rate of 1.5 mL/min was used. The HPLC program consisted of a gradient from 100 % water to 50 % acetonitrile the first min and then a gradient from 50 to 100 % acetonitrile from 9 min to 18 min after injection. The column was equilibrated with water for 3.5 min prior to injection. This column has previously been shown to be very effective for separating PAH isomers (13). Eluants were continually sparged with helium to remove oxygen and other gases which could adversely effect chromatography and detection.

A previously described Gas Chromatography-Mass Spectroscopy method was used to identify compounds leaching from the soil (10-11). An on-line gas chromatography (GC) method was also available for analysis of volatile PAH which were less easily resolved by the HPLC method (10-11).

Potassium bromide tracer was introduced to the adsorber through a six-port HPLC valve for hydrodynamic characterization. Effluent samples were analyzed for tracer using a Waters Ion chromatography system with a series 510 HPLC pump, IC-PAK anion exchange column and 431 conductance detector (Waters, Cambridge, Mass.). The adsorber temperature was controlled by a Lauda RMT-6 recirculating bath with heat exchanger coil.

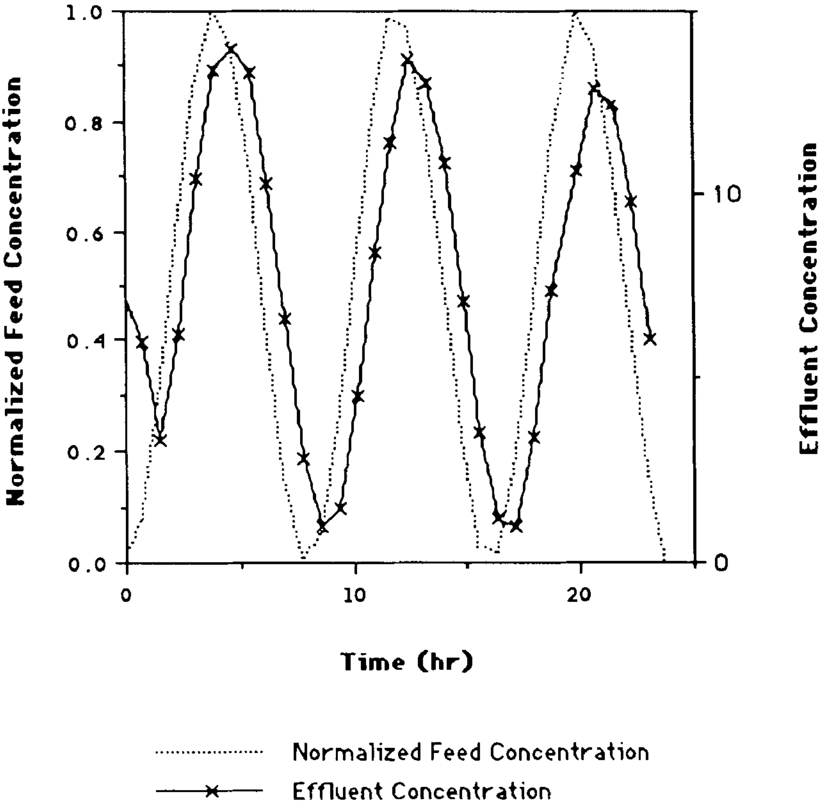

Figure 1. Response to sinusoidal perturbation in adsorber bypass mode.

RESULTS AND DISCUSSION

Residence time distribution analysis indicated that the dispersion coefficient, 4 X 10^{-4} cm^2/s, approached minimal values and that the feed was evenly distributed to the soil wafer.

Initial experiments indicated that adsorption to structural parts of the adsorber was negligible. The adsorber effluent concentration tracked the inlet when feed was diverted through the adsorber bypass valve while varying the feed concentration in a sinusoidal manner (Fig. 1).

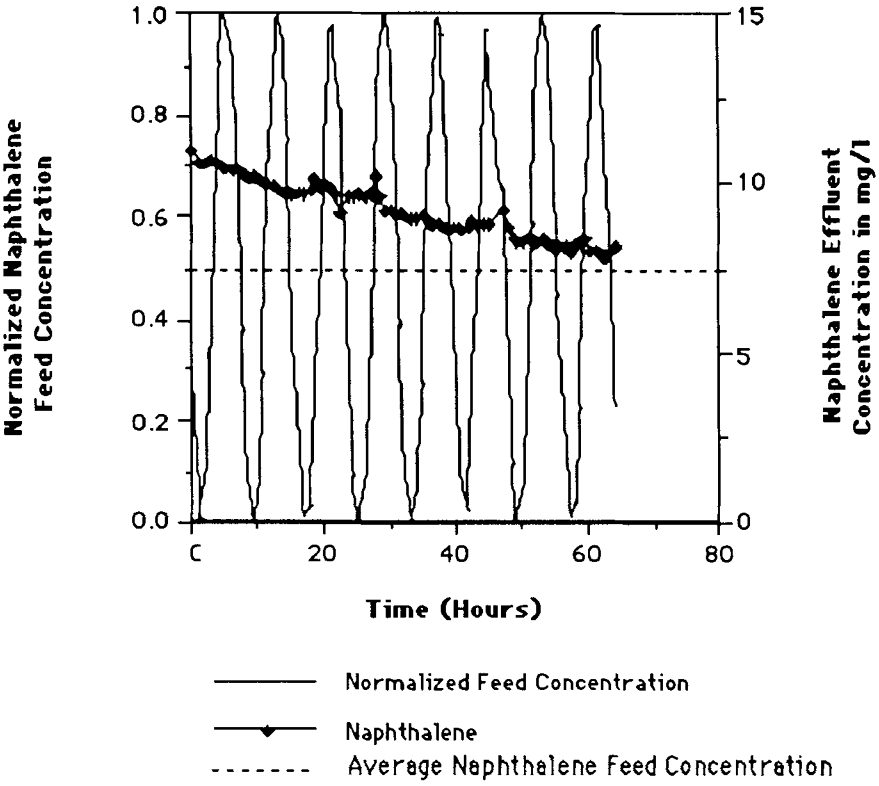

Figure 2. Naphthalene response to perturbations. Naphthalene feed and effluent concentrations from an adsorber packed with 16.2 mL of PAH contaminated soil.

Soil leachates identified using GC-MS and retention times from Standard Reference Material (SRM) 1491 (National Institute of Standards and Technology, Gaithersburg, MD) were biphenyl, naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, acenaphthalene, acenaphthene, 9-h-flourene, phenanthrene, and benzo(e)pyrene. 1,3,5-trimethylbenzene, ethenylmethylbenzene, 1,6-Dimethylnaphthalene, and dibenzofuran were identified using GC-MS only. Two ring compounds and benzene derivatives were generally volatile enough to be detected by the on-line GC method.

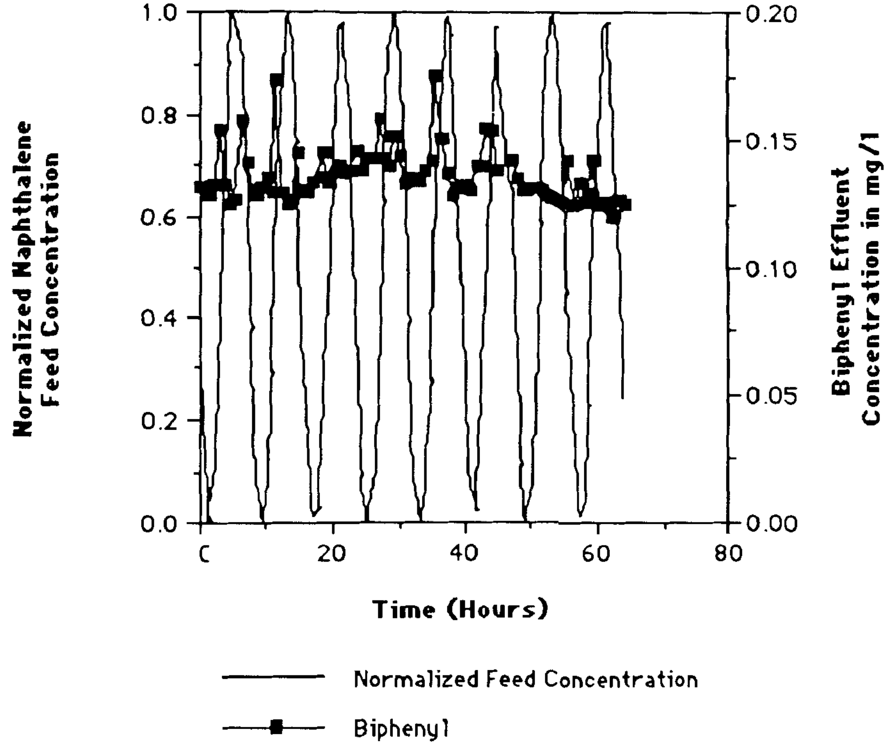

Figure 3. Biphenyl response to perturbations. Naphthalene feed and biphenyl effluent concentrations from an adsorber packed with 16.2 mL of PAH contaminated soil. *The biphenyl was not present in the feed* and leached from the soil.

Naphthalene solution was fed to the adsorber in a sinusoidal or step-wise manner. Leachate and naphthalene responses to the naphthalene feed concentration are shown in Figs. 2-10. Only naphthalene was present in the feed. The frequency of the input sine wave was 8 hr with a maximum naphthalene concentration of 14 mg/L. The feed concentration for the naphthalene step perturbation was 16 mg/L. Normalized naphthalene feed concentration, experimental time, and effluent concentrations are shown on the left hand, horizontal and right hand axis, respectively. The HPLC method was not developed

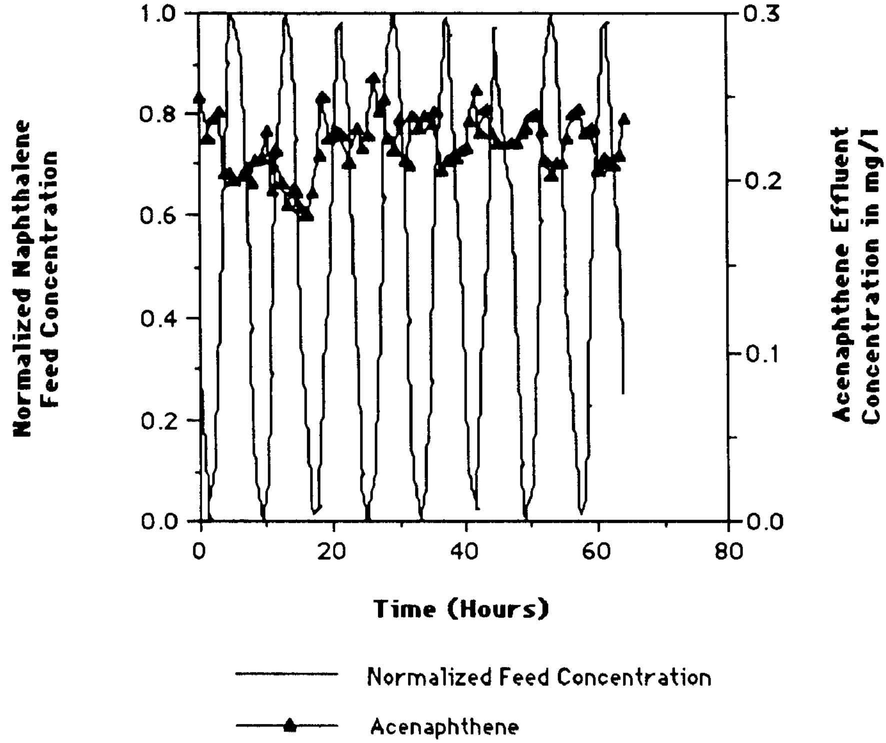

Figure 4. Acenaphthene response to perturbations. Naphthalene feed and acenaphthene effluent concentrations from an adsorber packed with 16.2 mL of PAH contaminated soil. The acenaphthene was not present in the feed and leached from the soil.

for on-line use at the time of initial sinusoidal perturbation experiments. Later the HPLC method was used to verify that the effluent leachate concentrations were affected by perturbations in the naphthalene feed concentration. The normalized FID response for leachates using SRM 1491 ranged from 9.12 X 10^{-1} to 1.00.

Fig. 2 illustrates the differences between input and output naphthalene concentration waves from the MGP soil. Initial naphthalene effluent concentrations were above average feed levels indicating leaching of pre-existing naphthalene from the soil matrix. The output naphthalene sine wave was

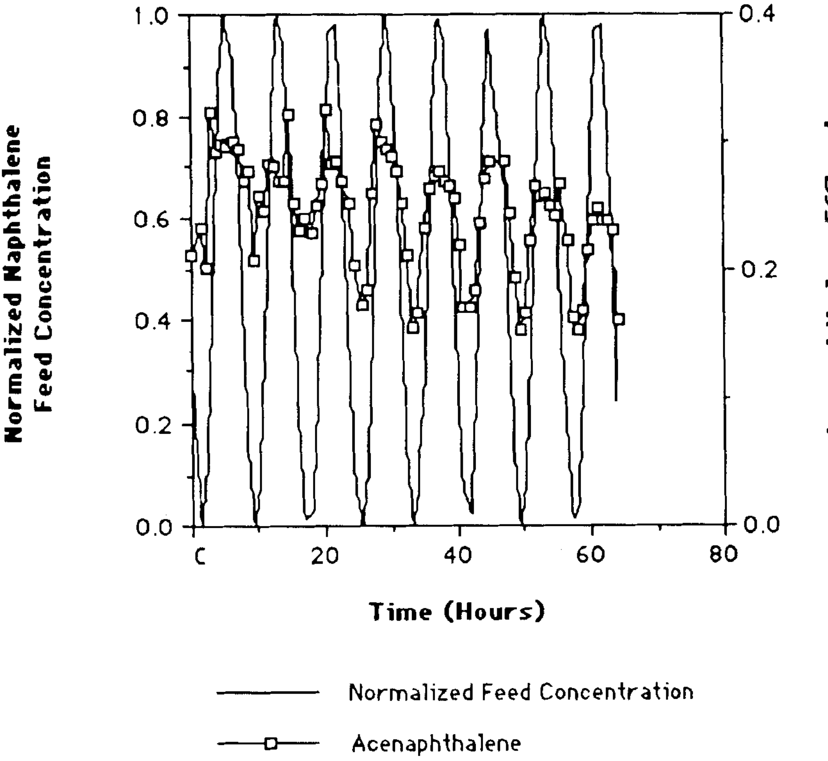

Figure 5. Acenaphthalene response to perturbations. Naphthalene feed and acenaphthalene effluent concentrations from a adsorber packed with 16.2 mL of PAH contaminated soil. The acenaphthalene was not present in the feed and leached from the soil.

severely damped by leaching of preexisting naphthalene and was always greater than the mean concentration of the feed. In other experiments where water was passed through the column, naphthalene was a major component in the adsorber effluent. Adsorption processes and leaching of preexisting naphthalene from the soil dampened the effluent concentration response.

Figs. 3 and 4 depict the effluent biphenyl and acenaphthene concentrations when the adsorber was pulsed with the sinusoidal naphthalene feed. The effluent

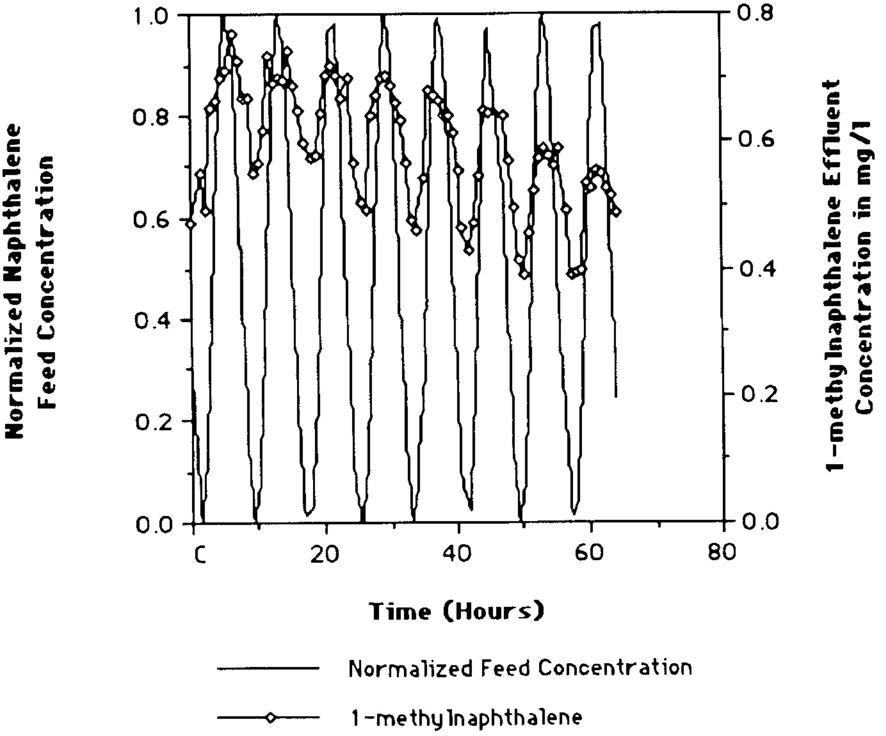

Figure 6. 1-methylnaphthalene response to perturbations. Naphthalene feed and 1-methylnaphthalene effluent concentrations from an adsorber packed with 16.2 mL of contaminated soil. The 1-methylnaphthalene was not present in the feed and leached from the soil.

concentrations are the result of leaching and sorption processes occurring in the soil. Peak areas were well above noise levels. Some scattering of data occurred although the effluent concentrations of acenaphthene and biphenyl were approximately constant. The effluent concentration of biphenyl and acenaphthene were not greatly influenced by the addition of naphthalene.

Figs. 5-8 depict the respective effluent concentrations of acenaphthalene, 1-methyl, 2-methylnaphthalene and fluorene concentrations as the adsorber was

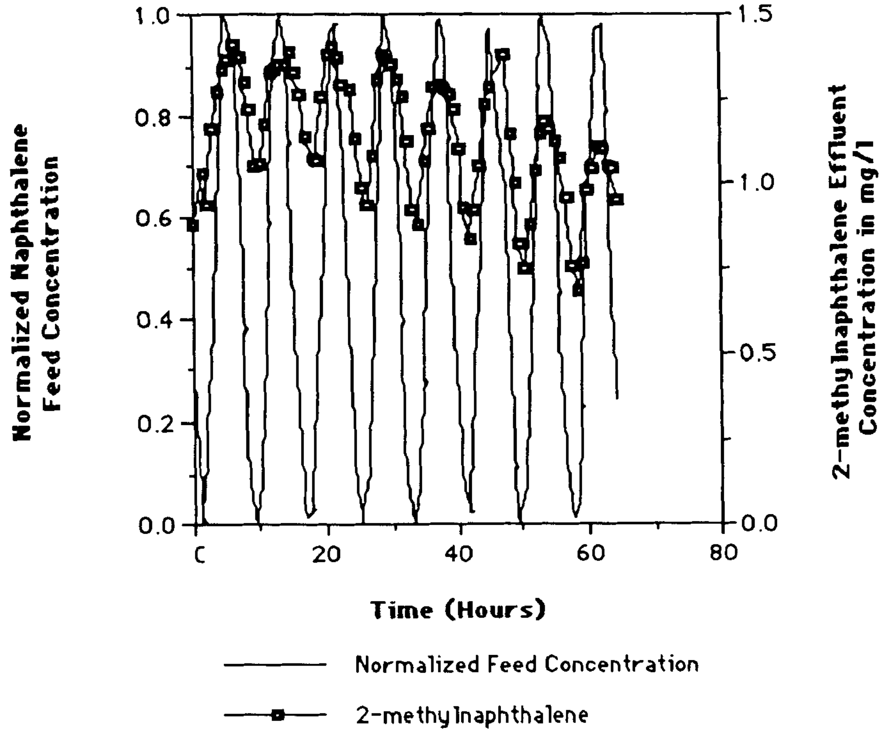

Figure 7. 2-methylnaphthalene response to perturbations. Naphthalene feed and 2-methylnaphthalene effluent concentrations from an adsorber packed with 16.2 mL of Town Gas Soil. The 2-methylnaphthalene was not present in the feed and leached from the soil.

pulsed with a sinusoidal naphthalene feed (constant hydrodynamic flow). In contrast to acenaphthalene and biphenyl, the effluent concentrations exhibited periodicity similar to the naphthalene feed concentration perturbations and were the result of leaching and adsorption processes. Peak areas for calculation of the acenaphthalene and alkylated naphthalene concentrations were well above noise levels. Fluorene concentrations at noise levels were not included in Fig. 8. Figs. 5-8 indicated that acenaphthalene, 1 and 2-methylnaphthalene and fluorene concentrations were affected by the naphthalene feed concentration.

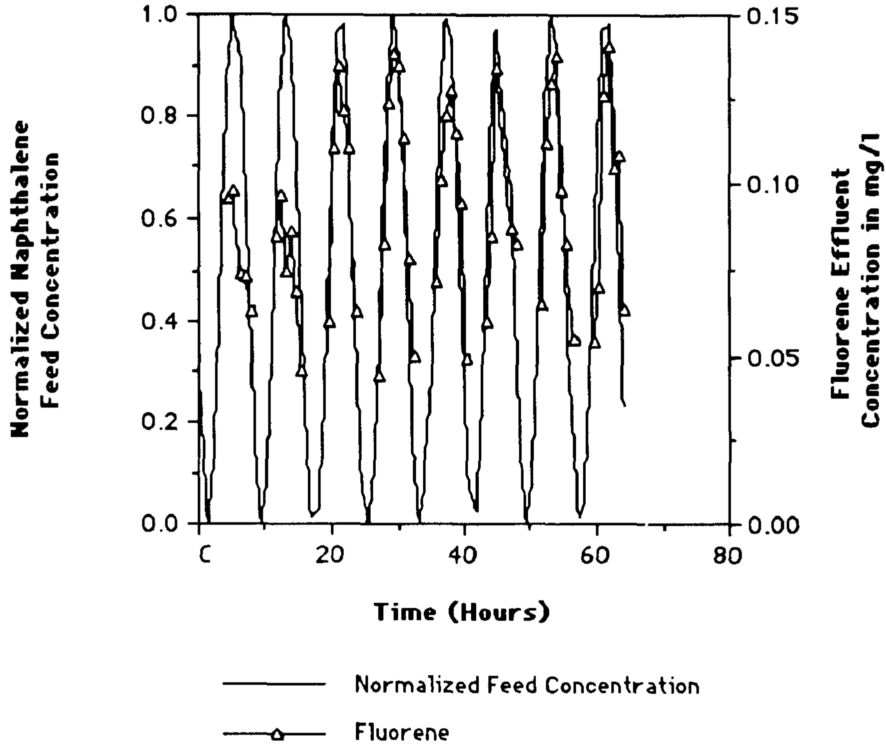

Figure 8. Fluorene response to perturbations. Naphthalene feed and fluorene effluent concentrations from an adsorber packed with 16.2 mL of MGP soil. The fluorene was not present in the feed and leached from the soil.

Step perturbation experiments were conducted to compare the sinusoidal response to the step change response and to further investigate the effect of naphthalene on the desorption process of PAH in the MGP soil. The experiments were conducted by running distilled water through the reactor bed followed by a constant input of aqueous naphthalene solution at a flow rate of 0.3 mL/min. The experiment was conducted at 20° C. The feed concentration for the naphthalene step perturbation was 16 mg/L. Naphthalene and several leachate responses to the step change in naphthalene feed concentration are shown in Figs. 9-11.

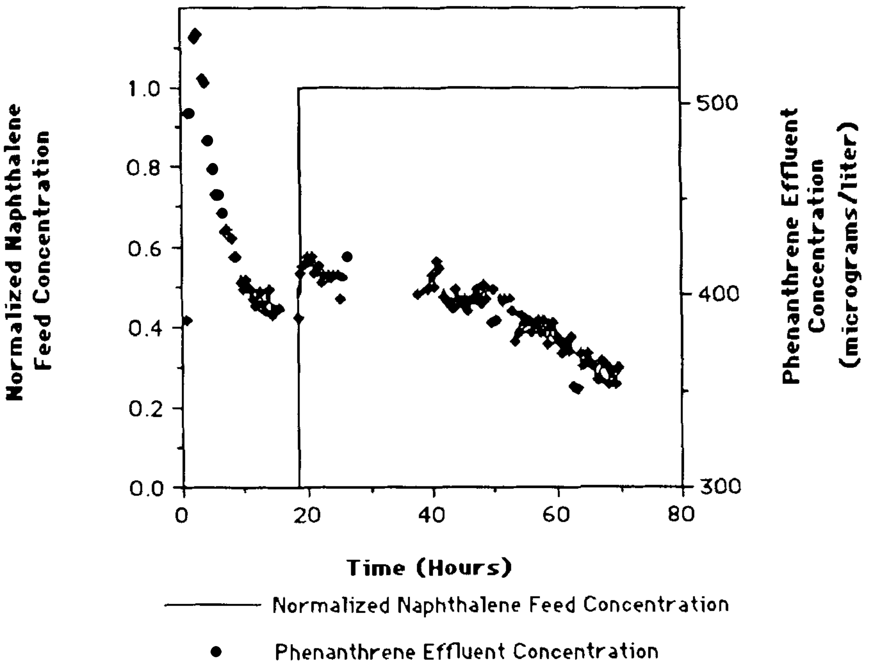

Figure 9. Phenanthrene response to step perturbation. Phenanthrene effluent concentrations from an adsorber packed with PAH contaminated soil.

Normalized naphthalene feed concentration, experimental time and effluent concentrations are shown on the left hand, horizontal and right hand axis, respectively.

Fig. 9 illustrates the response of phenanthrene to the step perturbation in naphthalene feed. The left hand axis is the normalized concentration of the naphthalene feed with the experiment time shown on the horizontal axis. The right axis is the effluent phenanthrene concentration. Because only naphthalene was present in the feed, the effluent concentration was the result of leaching and sorption processes occurring in the soil. The phenanthrene concentration initially reached a maximum when distilled water was passed through the reactor bed and then displayed a continuous decay pattern. When naphthalene solution

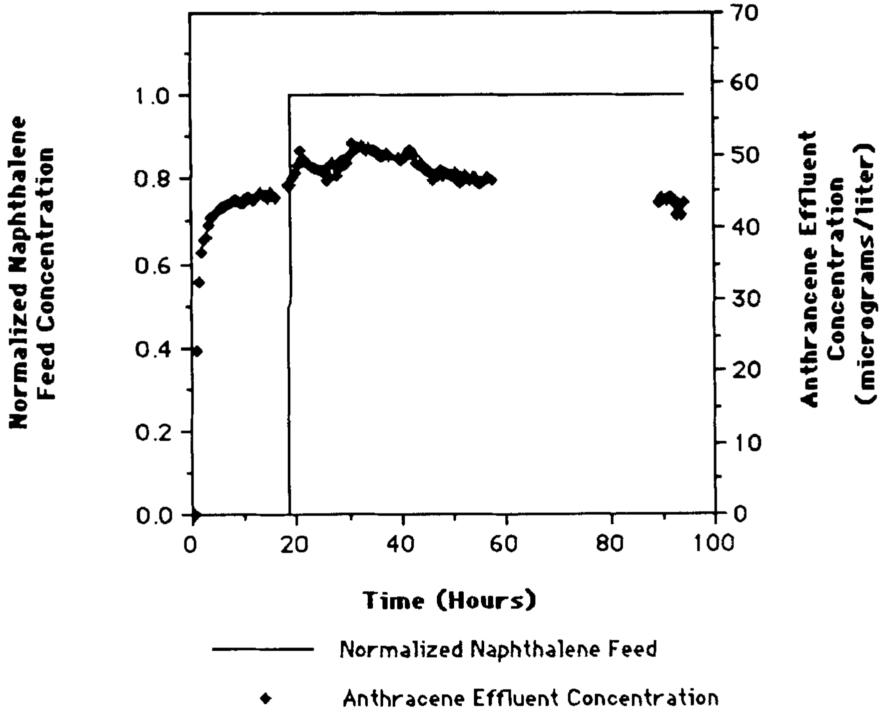

Figure 10. Anthracene response to step perturbation. Anthracene effluent concentrations from an adsorber packed with PAH contaminated soil.

was passed through the bed, the effluent phenanthrene concentration increased by 10 %. The phenanthrene concentration continued the decay although possibly at a reduced slope. The effluent phenanthrene concentration was affected by the addition of naphthalene.

Fig. 10 illustrates the response of anthracene to the step perturbation in naphthalene feed. The left hand axis is the normalized concentration of naphthalene feed with experiment time shown on the horizontal axis. The right axis is the effluent anthracene concentration. Because only naphthalene was present in the feed, the anthracene effluent concentration was the result of leaching and sorption processes occurring in the soil. When distilled water was

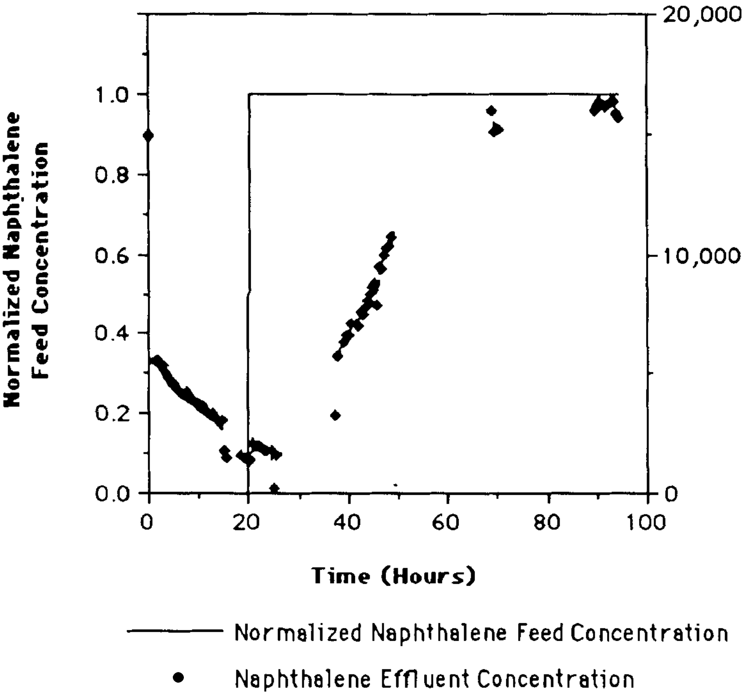

Figure 11. Naphthalene effluent response to a step change in naphthalene feed concentration. The PBR was packed with 45 mL of MGP soil.

passed through the soil bed, anthracene concentration was constant. The effluent concentration increased by approximately 10 % when naphthalene solution was added. The anthracene effluent concentration continued at or above concentrations previous to the step increase in naphthalene feed concentration.

Fig. 11 illustrates the response of naphthalene to the step change in naphthalene feed concentration. The left hand axis is the normalized concentration of the naphthalene feed with the experiment time shown on the horizontal axis. The right axis is the effluent naphthalene concentration. When water was passed through the bed, the naphthalene effluent concentration initially reached a maximum and then began decreasing. When naphthalene solution began flowing through the bed, the effluent naphthalene concentration began increasing (estimated to be within several bed volumes). Gaps appear in the data of Fig. 11 because of required maintenance and equipment problems. Approximately 50 hours (40 bed volumes) after the step change in the feed concentration, the effluent concentration was equal to the feed concentration. The effluent naphthalene concentration was equal to one half the feed concentration approximately 30 hours (24 bed volumes) after the addition of naphthalene solution. The long breakthrough time indicates that the soil had a relatively high adsorption capacity for naphthalene.

Leachate responses to step perturbations were less easily interpreted than responses to sinusoidal perturbations. Figs. 3-8 illustrated the differences between input naphthalene concentration and output leachate concentration fronts from the MGP soil using sinusoidal perturbations. A number of the compounds exhibited sinusoidal responses similar to the input naphthalene feed. Acenaphthene and biphenyl did not appear to exhibit the sinusoidal behavior that many of the other compounds did. Figs. 9 and 10 indicate that anthracene and phenanthrene effluent concentrations were affected by the addition of naphthalene solution. Fig. 11 indicates that the soil had a high capacity for adsorption of naphthalene.

After the experiment was concluded, the sinusoidal feed perturbations were then passed through the stripping column without contacting the packed bed contents. The output signal then tracked the input perturbation (Fig. 1). Adsorption effects were negligible when the naphthalene feed did not contact soil. These results were verified using both the on-line GC and HPLC methods.

Adsorption effects from the soil were important not only in determining the liquid-phase concentration of naphthalene but also of other PAH leaching from the soil.

Because microbial activity was inhibited, the leachate responses are due to adsorption (displacement of solutes from the solid phase by the feed component). Displacement occurs when one component is forced from adsorption sites on the solid by a second component. Displacement commonly occurs for favorable type systems when a previous saturated bed is eluted with a light component feed provided the feed concentration is greater than the watershed concentration (9). The watershed concentration is defined as the intersection of the limiting slope of the light component isotherm at the origin and the heavy component isotherm.

For modeling adsorption in heavily contaminated coal tar soil (MGP soil), the soil particles were assumed to be relatively nonporous. Fluid phase resistance was also assumed to be negligible. The mathematical description of the packed bed consists of n coupled partial differential equations (PDE), one equation for each component:

$$\frac{1}{P_{e_i}}\frac{\partial^2 C_i}{\partial z^2}-\frac{\partial C_i}{\partial z}=\frac{\partial C_i}{\partial t}\left(1+(\frac{1-\varepsilon}{\varepsilon})\frac{dC^*_{S_i}}{dC_i}\right).$$

The appropriate boundary and initial conditions are:

$$C_i\big|_{z=0}=0.5+\frac{\sin(2\pi t\,/\,P_t-\pi\,/\,2)}{2},$$

$$\left.\frac{\partial C_i}{\partial Z}\right|_{z=1}=0,$$

$$C_i=f(Z)\qquad (t<0).$$

Fig. 12 depicts the simulated response of a high-capacity packed bed to a low concentration sinusoidal feed (single component). The simulation was conducted using PDECOL (14). Fig. 12 depicts liquid-phase concentration in the packed column as a function of position and time. The vertical axis indicates concentration. The axis projecting out of the plane of the paper indicates time in cycles of the feed wave. The horizontal axis in the plane of the paper indicates position in the bed. The feed sine wave is damped as it moves through the bed. The response of the bed is a function of the period and amplitude of the feed wave, adsorption, mass transfer, and dispersion. For a high-capacity bed, dampening of the sine wave may depend mostly on adsorption.

Sinusoidal perturbation methods provided a more robust approach for dynamic analysis of the soil system. Sinusoidally perturbing the system forces the system into a continual response pattern which can then be studied in detail. Step and pulse perturbations produce only transient responses which may be

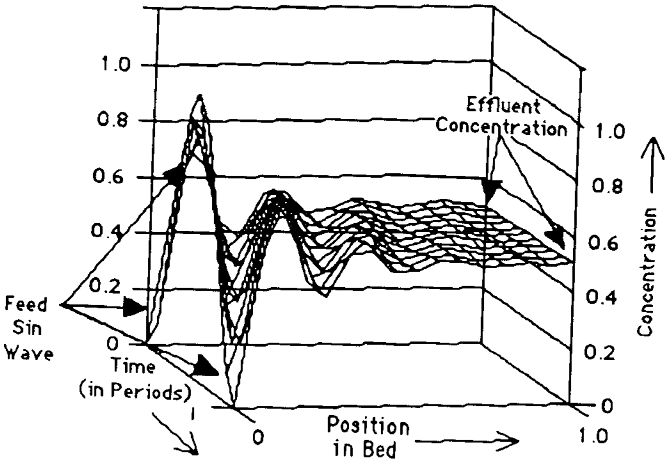

Figure 12. Dampening of a sinusoidal feed wave. The sinusoidal feed wave was significantly damped by adsorption. The numerical solution included effects of favorable single component adsorption and dispersion.

more difficult to interpret. Two parameters, period and amplitude, were also available when using sinusoidal perturbation methods while only one parameter, magnitude of the step function, was available for dynamic studies using traditional step perturbation methods.

CONCLUSIONS

Sinusoidal perturbation methods proved to be more robust than step perturbation methods. System response to the sine wave input was continuous and was more easily interpreted than the step change response. Two parameters, period and amplitude, were also available when using sinusoidal perturbation methods while only one parameter, magnitude of the step function, was available for dynamic studies using traditional step perturbation methods.

Residence time distribution analysis indicated that dispersion approached minimal values and that the feed was evenly distributed to the soil wafer.

Adsorber metal parts and adsorber inorganic filters provided few sites for PAH adsorption. The adsorber design allowed physical perturbation analysis and rapid evaluation of system response.

Several analytical methods were used for off-line and automated on-line measurement of PAH. The on-line GC technique effectively resolved complex mixtures of volatile PAH. HPLC with fluorescent detection proved to be a selective and highly sensitive method for analysis of PAH mixtures (detection limit for naphthalene <100 ng/L). Use of polymeric C_{18} columns provided good separation of PAH and could be used to separate the priority pollutants in SRM 1647. Use of GC and HPLC methods allowed qualitative and quantitative monitoring of complex PAH mixtures leaching from soils in real time.

The continuous flow-packed bed system with on-line GC (FID detection)/HPLC (Fluorescence detection) is well suited for study of adsorption of volatile and non-volatile PAH compounds in soil systems.

The adsorber was used to characterize PAH and PAH-related compounds leaching from contaminated MGP soil. Total concentration of PAH in soils may not correlate well with availability. The adsorber has a small residence time and allows rapid evaluation of kinetics. Because the adsorber could be easily modified for various types of perturbation analysis, the adsorber may be used to address the question of component availability in soil systems.

TABLE OF SYMBOLS

C_i_Concentration of component i in liquid phase (mol/dm^3)

C_{S_i}_Adsorbed solid phase concentration (mol/dm^3)

Pe_Peclet number with bed length as the characteristic length (Dimensionless)

P_t_Period of sine wave

t_Time

Z_Dimensionless position in column

ε_Bed void volume (Dimensionless)

ACKNOWLEDGMENTS

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