"INVESTIGATION OF FATE AND TRANSPORT OF ORGANIC CONTAMINANTS IN SOIL COLUMNS PACKED WITH DIFFERENT SOIL TEXTURES: DETERMINATION OF RETARDATION COEFFICIENTS UNDER VARIOUS DYNAMIC CONDITIONS"

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INTRODUCTION

Although great strides have been made in underground storage tank (UST) design and release prevention technology, the huge number of retail petroleum businesses opening daily provides an immense pool of potential accidents. Leaking USTs and accidental spills have contaminated our subsurface soil matrices. Understanding interactions between hydrocarbons and Alabama soil is critical to selecting remediation methods needed to protect the state's water resources from petroleum releases. This project addresses fate and transport of contaminants for groundwater and improved methods for groundwater remediation and hydrologic and hydraulic modeling processes. This project seeks to: (i) conduct adsorption isotherm experiments to characterize the adsorption of various contaminants (e.g., petroleum hydrocarbons, chlorinated organics, and heavy metals) onto various types/textures of soil, (ii) conduct continuous flow experiments through packed soil columns to determine the breakthrough characteristics and retardation coefficients; (iii) model the results from the batch experiments using various isotherm models (e.g., Langmuir and Freundlich isotherms), and (iv) model the results from the continuous-flow packed bed experiments using the bed depth-service time model and the 1-D and 2-D advective dispersion models describing flow-through columns.

The project objectives are to: (1) quantify the adsorption characteristics obtained for the Langmuir and Freundlich isotherm models as a function of the soil texture/soil type; (2) compare and contrast the adsorption characteristics for adsorption of selected common contaminants (e.g., petroleum hydrocarbons, benzene, toluene, ethylbenzene, xylenes, chlorinated organics, and heavy metals) to observe the effect of contaminant molecular structure (e.g., chain length, aliphatic vs. aromatic compounds, saturated vs. unsaturated organic structures, etc.) on the adsorption characteristics of these compounds on various types of soils; (3) determine the retardation coefficients of the various contaminants in continuous-flow experiments in soil columns packed with soils of different texture; (4) determine whether the hydraulic conductivity/permeability changes over time for different contaminants and treatment conditions; (5) determine whether the soil columns can be effectively treated by injecting microorganisms or by introducing *in-situ* oxidation chemical agents in the injection fluids; and (6) model the performance of the flow through the packed bed/soil columns using the bed depth-service time relationship and the 1-D and 2-D advective dispersion transport models.

The general approach for the packed column experiments involves performing both batch and continuous flow operation in order to generate sufficient data to pursue follow-on funding to perform the research in pilot-scale demonstrations. Seven primary tasks are being performed in this project: (1) Collection of appropriate contaminated soils for use in the continuous flow soil column experiments; (2) Perform bench-scale batch adsorption/desorption tests of various concentrations of contaminants in contact with various soil matrices to determine the uptake of contaminant; (3) Model the adsorption uptake using Langmuir and Freundlich isotherm models; (4) Perform continuous-flow processing of contaminant solutions (single contaminant systems) through packed bed reactors containing different soil types; (5) Perform continuous-flow processing with injection of microorganisms through packed soil columns containing different soil types contaminated with various organic contaminants; (6) Perform continuous-flow processing with injection of advanced oxidants through packed soil columns containing different soil types contaminated with various organic contaminants; and (7) Modeling the desorption/treatment performance of the continuous flow experiments using the bed depth-service time and advective dispersion model.

The cost of cleanup of sites contaminated with petroleum hydrocarbons is of great importance, especially to small businesses in Alabama. Natural attenuation (the bioremediation of pollutants by microorganisms already present in the soil) offers the most economical method of dealing with this pollution problem. It is therefore of great importance to determine the rate and extent of degradation of petroleum hydrocarbons in various types of Alabama soil, with and without addition of supplemental nutrients.

RESEARCH GOAL

The primary goal of this research is to better understand contaminant interaction in soil representative of the state. This research quantifies the separate contributions to contaminant attenuation by soil and microbes. This information could be used to quantify minimum natural attenuation effects. This research can provide the foundation for a database of Alabama soil/contaminant interaction, which could greatly assist consultants and state regulators in remediation programs for contaminated soil. In actual operation in the field, the research would tie in with preliminary efforts of site remediation activities. The desorption capability of the organic contaminants from the soil strata would be examined using mild acid conditions. If successful, such an approach could be field-tested.

RESEARCH SCOPE AND EXPERIMENTAL PROCEDURES

The scope of the research is four-fold: (i) to conduct adsorption isotherm experiments to characterize the adsorption of various contaminants (e.g., petroleum hydrocarbons, chlorinated organics, and heavy metals) onto various types/textures of soil, (ii) to conduct continuous-flow experiments through packed soil columns to determine the breakthrough characteristics and retardation coefficients; (iii) to model the results from the batch experiments using various isotherm models (e.g., Langmuir and Freundlich isotherms), and (iv) to model the results from the continuous-flow packed bed experiments using the bed depth-service time model and the 1-D and 2-D advective dispersion models describing flow through columns.

Glass soil columns and other sample columns (made of PVC pipe) to conduct the continuous-flow experiments through the packed bed columns are used in this study. The general approach for the packed column experiments involves performing both batch and continuous-flow operation in order to perform the research in pilot-scale demonstrations. Heavy metals are spiked into water samples. Organic analyses, and cation/anion chemical analyses are performed to characterize the untreated and treated water sources.

For the batch isotherm experiments, various concentrations of the contaminants (e.g., petroleum hydrocarbons, chlorinated organics, heavy metals, etc.) are contacted with different soil textures to obtain adsorption-type isotherms for uptake of the contaminants by the particular soil matrix. The uptake is modeled using Langmuir and Freundlich isotherms. The adsorption isotherm plots are determined.

For the continuous-flow experiments, small-scale columns are packed with samples of different soil types. The columns use both spiked contaminants (simulating fresh spills) and aged samples (simulating spills that occurred many years ago). At both ends of the column, the column has a fine-mesh screen placed over the inlet and exit lines from the column to minimize the potential for plugging of the column. In the first set of experiments, a solution of known contaminant concentration is applied to the column. Initially, the soil column is contacted with water (in an upflow arrangement); the volume of water contacting the soil (knowing the time required for a particular flow rate to first exit the column) provides an estimate of the soil porosity within the soil column. Afterwards, the contaminant solution is applied to the column. Packed columns are operated in both an upflow and downflow mode, to compare the movement (dispersion) of the contaminant in the soil columns. The soil columns have several sample ports located within the column, so the movement is monitored along the length of the column as a function of time (to use in the bed depth-service time model).

In the second set of experiments involving the continuous-flow operation, a solution is contacted with the particular soil matrix for a 6-hour period; the filtrate from the soil is collected and analyzed using gas chromatography (GC) techniques (for the organic contaminants) and atomic absorption spectroscopy (AAS) [for the heavy metals]. After drying, the soil matrix is packed in the soil column. Initially, the soil column is contacted with water (in an upflow mode); the volume of water contacting the soil (knowing the time required for a particular flow rate to first exit the column) provides an estimate of the soil porosity within the soil column. Using a constant head apparatus, water is applied to the column. The contaminant desorption from the freshly spiked soil (simulating a fresh spill) is monitored along the length of the column as a function of time (to use in the bed depth-service time model). Additionally, the flow rate from the column is monitored to determine any changes in hydraulic conductivity/permeability resulting from the treatment.

In the third set of experiments, water-containing microorganisms are contacted to the soil column (containing organic contaminants), to investigate the microbial degradation achieved for a fresh spill. The operation for this set of experiments is similar to that described above for the second set of experiments.

In the fourth set of experiments, the soil columns containing organic contaminants are treated using *in-situ* chemical oxidation techniques (such as Fenton's reagent, hydrogen peroxide plus ozone, etc.). The procedure for conducting this set of experiments is similar to that described for the second set of experiments. These experiments employ multiple sacrificial columns operated simultaneously, so that a column can be removed from service after various periods of time; the soil is then analyzed for the contaminant remaining on the soil to perform mass balances on the soil column. The column flow rate is monitored to determine any changes in hydraulic conductivity/permeability resulting from the treatment. The concentration of the contaminant remaining in the soil matrix is checked to determine if the concentration can be tolerated by the microorganisms enough to enable biodegradation.

In the last set of experiments, soil columns containing aged contaminants (obtained from various sites in the State of Alabama and elsewhere) are tested using procedures similar to those for the second through fourth set of experiments, described above. The soil columns are operated in a sacrificial manner, similar to the operation described for the fourth set of experiments. The flow rate from the column is monitored to determine any changes in hydraulic conductivity/permeability resulting from the treatment. The concentration of the contaminant remaining in the soil matrix is checked to determine if the concentration can be tolerated by the microorganisms enough to enable biodegradation.

For all these experiment sets, samples are collected periodically throughout the run, to obtain the concentration vs. throughout (void bed volume) profile. This information allows us to determine the bed-depth service-time relationship, and is used to determine column breakthrough. This information is used to identify preliminary conditions for potential remediation of these sites.

ANALYTICAL INSTRUMENTATION

A gas chromatography (GC) system (Model 6890N, Serial No. US10207024) obtained from Agilent Technologies, Inc. (formerly Hewlett-Packard, Inc.) is used to analyze the composition of hydrocarbons and aromatics before and after treatment in the soil column. Operation of the GC was controlled using Chem Station software (Hewlett Packard Inc., model VECTRA VL400SF, Serial No. US14320619). To run the GC, gas cylinders (BOC Group, Inc.) are used. Compressed air gas cylinders (UN1002) of grade 0.1 are used to pass through the column for separation. Compressed hydrogen gas (UN1049) of grade 5.5 is used for the Flame Ionization Detector (FID). Compressed helium gas cylinders (UN 1046) of grade 5.5 are used as make up gas. Additionally, Chicago Chem Consultants Corporation recently donated a mobile analytical trailer to UAB for use on research projects.

The heavy metal concentrations are measured using atomic absorption spectroscopy (AAS) methods. The analyses are performed on a Perkin Elmer AAnalyst™ 800 atomic absorption spectroscopy (AAS) system (at 20% percent capacity) located in the Department of Biomedical Engineering (BME) at UAB. BME is physically located in the same building as the Department of Civil and Environmental Engineering, with the AAS system located down the hall on the same floor as the PI's research laboratory. The Department of Biomedical Engineering at UAB is providing access to this equipment for use on the project.

The Perkin Elmer AAnalyst™ 800 high-performance atomic absorption spectrometer with the new WinLab 32 software has an automated motorized atomizer exchange that allows switching between flame and graphite furnace AA by a simple software command. It is equipped with a high performance burner system and TotalFlow™ gas controls for flame AA. The AAnalyst 800 is equipped with a Transversely Heated Graphite Furnace (THGA) with longitudinal Zeeman-effect background corrector. Both graphite furnace systems include True Temperature Control (TTC) and integrated platform tubes, and both offer full Stabilized Temperature Platform Furnace (STPF) conditions for almost interference-free trace metal analysis. The built-in, high-capacity AS-800 autosampler and the automatic slurry sampler facilitates easy sample handling. The system has been used to analyze ionic and trace metal content (at a ppb level) in the Biocorrosion and Degradation Laboratory. BME has over 18 AAS lamps that can be used for detecting various metals of interest. BME provides access to these AAS lamps for detecting the various heavy metals of interest in this project.

Preliminary results on the soil characterization/soil texture of the various Alabama soils and microbial enumerations are presented in the technical presentation.

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