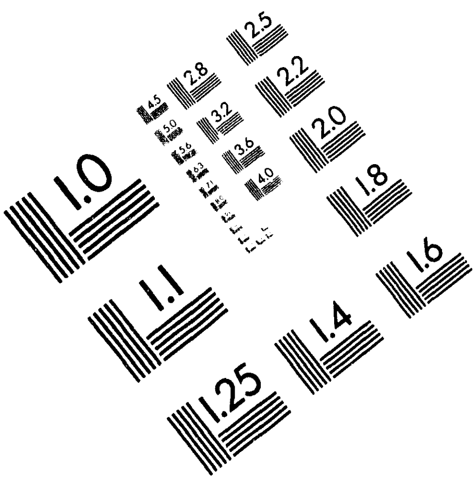

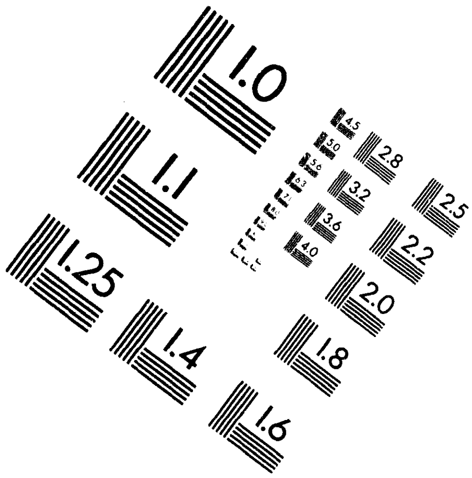

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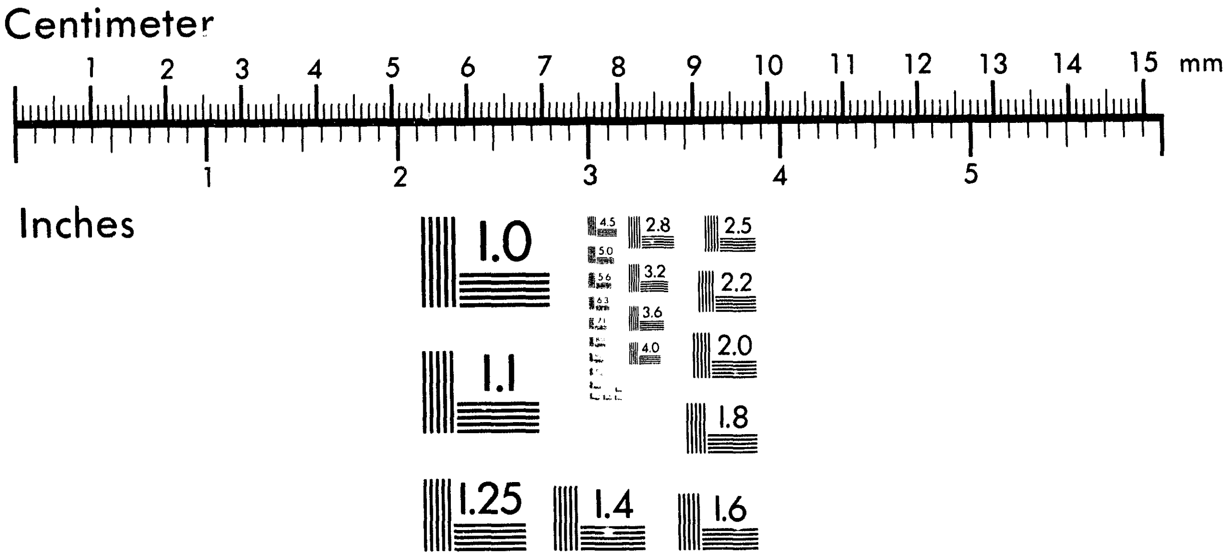

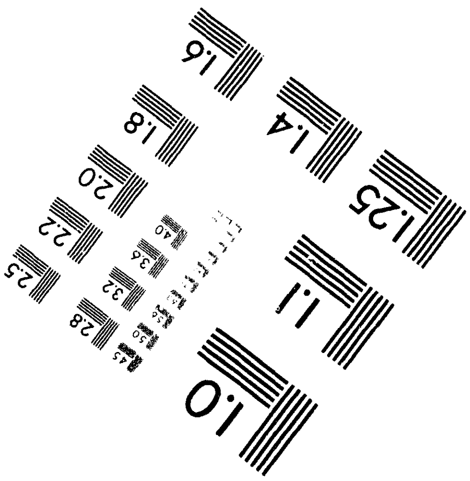

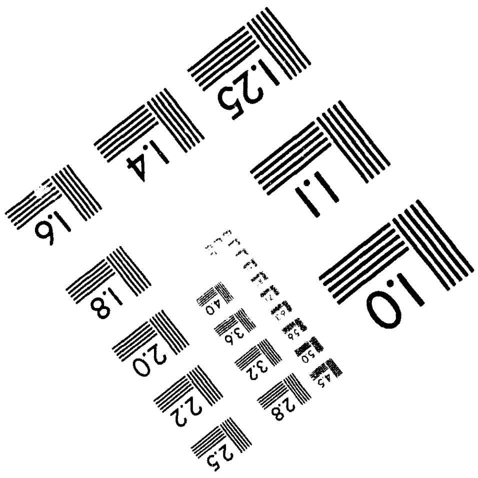

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Mass Transfer and Biodegradation of PAH Compounds from Coal Tar

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ABSTRACT

This study examines the role of physico-chemical mass transfer processes on the rate of biotransformation of polycyclic aromatic hydrocarbon (PAH) compounds released from non-aqueous phase liquid (NAPL) coal tar present at residual saturation within a microporous medium. A simplified coupled dissolution-degradation model is developed that describes the concurrent mass transfer and biokinetic processes occurring in the system. Model results indicate that a dimensionless Damkohler number can be utilized to distinguish between systems that are mass transfer limited, and those that are limited by biological phenomena. The Damkohler number is estimated from independent laboratory experiments that measure the rates of aqueous phase dissolution and biodegradation of naphthalene from coal tar. Experimental data for Stroudsburg coal tar imbibed within 236μm diameter silica particles yield Damkohler numbers smaller than unity, indicating, for the particular system under study, that the overall rate of biotransformation of naphthalene is not limited by the mass transfer of naphthalene from coal tar to the bulk aqueous phase. There is a need for investigation of mass transfer for larger particles and/or other PAH compounds, and study of microbial rate-limiting phenomena including toxicity, inhibition and competitive substrate utilization.

KEYWORDS

Coal tar; non-aqueous phase liquid; NAPL; naphthalene; mass transfer; biodegradation; Damkohler number; manufactured gas plant.

INTRODUCTION

Coal tar is a dense, non-aqueous phase liquid (NAPL) that is often associated with sub-surface contamination at former manufactured gas plant sites. Coal tar is a multicomponent NAPL composed of hundreds of aromatic organic compounds, including polycyclic aromatic hydrocarbon (PAH) compounds such as naphthalene, phenanthrene, etc. (Harkins *et al.*, 1988). Like other NAPLs, coal tar may exist in the subsurface in the form of trapped pools of organic liquid, or as immobilized macroporous ganglia. The presence of several surface active or polar compounds in coal tar may cause it to be the wetting fluid in the subsurface, and hence coal tar may also be found at residual

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MASS TRANSFER AND BIODEGRADATION OF NAPHTHALENE FROM COAL TAR

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INTRODUCTION

Coal tar is a non-aqueous phase liquid (NAPL) found in the subsurface at some former manufactured gas plant (MGP) sites. Coal tar is a mixture of several hundreds of organic compounds including various polycyclic aromatic hydrocarbons (PAHs). In the subsurface, coal tar may partially saturate the macropores of the soil/aquifer matrix or may exist as entrapped pools of dense non-aqueous phase liquid (DNAPL). Also, the presence of some surface active and polar compounds in the coal tar may cause it to be the preferentially wetting fluid and facilitate entry of coal tar into the micropores of the soil/aquifer matrix. The immobilized coal tar may serve as a continuous source of groundwater contamination due to the dissolution of PAH compounds and other solutes.

Various studies on biodegradation of PAHs from contaminated MGP site soils (Nakles et al., 1991; Morgan et al., 1992; Erickson et al., 1993) have hypothesized that mass transfer limitations may cause the PAHs to be unavailable to microorganisms in the aqueous bulk phase, and thereby limit biodegradation of PAHs from MGP-site contaminated soils. This study focuses on quantitatively evaluating the rate limiting processes governing biodegradation of naphthalene released from coal tar entrapped in a microporous matrix. Independent measurements of rates of dissolution and biodegradation have been made to that effect.

EXPERIMENTAL TECHNIQUES

The coal tars used in these experiments were obtained from former manufactured gas plant sites. The sites were located in Stroudsburg, PA and at the Baltimore Gas and Electric (BG&E) site in Spring Gardens, MD. The coal tars were primarily a mixture of polycyclic aromatic hydrocarbons with naphthalene as the most abundant compound (10% w/w for the BG&E coal tar and 2.2% w/w for the Stroudsburg coal tar). Radiolabeled ^{14}C naphthalene was added to the coal tar (1 μCi ^{14}C naphthalene per mL of coal tar) and the fate of the radiolabeled naphthalene was assumed to be representative of the naphthalene present in the coal tar. The radiolabeled coal tar was imbibed into microporous silica beads (mean dia $\simeq 250\mu m$, average pore dia =140 Å) to model coal tar entrapped in microporous media. The coal tar-containing microporous media was used for the mass transfer and biodegradation experiments.

Mass Transfer Experiments: Mass transfer tests were carried out in batch and flow-through systems to verify the use of Raoult's law for equilibrium predictions and to determine lumped mass transfer coefficients that would describe the rate of dissolution of naphthalene from coal tar. These experiments are described in Luthy et al. (1993). In order to assess the effect of 'aging' (Luthy et al., 1993) on mass transfer rates, the flow-through tests were conducted using both 'fresh' and 'aged' systems. 'Fresh' systems were tested soon after contacting the coal tar-containing beads

with water, while in 'aged' systems the the coal tar was in contact with water over periods of 1 week to 6 weeks before commencing the pumping test. Flow through tests were also conducted with beads obtained from the biometers at the conclusion of the mineralization experiments to evaluate the mass transfer rate coefficients.

Biomineralization Experiments: Experiments were carried out under aerobic conditions in 250 mL biometer flasks fitted with a side tube. The side tube and the flask were sealed with neoprene stoppers covered with aluminum foil. Five grams of silica beads were imbibed with 1 mL of coal tar spiked with radiolabeled ^{14}C naphthalene, and added to each biometer along with 50 mL of autoclaved nutrient media. The pH of the slurry was then adjusted to approximately 7.2. Biometers were inoculated with 2 mL of an actively growing bacterial culture of naphthalene degrading organisms (PA101) containing approximately 5×10^7 cfu/mL, as determined by naphthalene plate counts. The PAH degrading organisms used for inoculation were grown in a supersaturated solution of naphthalene in nutrient media, with naphthalene as the sole carbon source. Standard sterile techniques were followed for plate counts and innoculation. Biometers were shaken in a gyratory shaker. Duplicate biometers were set up for each set of conditions to assess variability in results. Sterile controls containing mercuric chloride were used to assess any abiotic mineralization. Radiolabeled CO_2 from biomineralization of naphthalene was trapped in the NaOH contained in the side arms of the biometers. The activity of the $^{14}CO_2$ in the NaOH was measured periodically with a Beckman LS 5000TD scintillation counter with automatic quench compensation.

At the end of both mass transfer and biodegradation experiments, the residual radioactivity of the silica beads and of the supernatant in selected test systems was measured to check for mass balance of the radiolabeled naphthalene. Recovery of ^{14}C from the systems ranged from 85% to 105% with an average of 93%.

RESULTS

Mass Transfer Experiments: Results from batch and flow through tests showed that both the initial equilibrium aqueous-phase naphthalene concentration, as well as changes in equilibrium concentration due to flushing, could be predicted fairly accurately from Raoult's Law. Various flushing tests were conducted to measure the rate of release of naphthalene from both coal tars under different conditions with 'fresh' systems and 'aged' systems. Average values of the lumped mass transfer coefficients, k_{la} , determined from the flow through experiments ranged from 3000/day for 'fresh' systems to about 500/day for 'aged' systems. While the 'aging' phenomenon (Luthy et al., 1993) resulted in a significant reduction in mass transfer rates, the rate of mass transfer remained much higher than estimates of naphthalene biodegradation rate constants which range from 1/day to 25/day (Mihelcic and Luthy, 1991; Guerin and Boyd, 1992). This indicates that mass transfer does not limit biodegradation in the system studied. A lumped mass transfer rate-coefficient of approximately 700/day was also estimated for coal tar-silica bead slurry samples obtained from biometers at the end of the mineralization test, further demonstrating that naphthalene biodegradation was not mass transfer limited by dissolution from the coal-tar DNAPL.

Mineralization Studies: Experiments to assess microbial mineralization of naphthalene were designed to obtain information on mineralization rates and end points. Typical results from mineralization experiments with Stroudsburg and BG&E tars are shown in Figure 1. The mineralization pattern for both tars is characterized by an initial period of rapid mineralization over a few days, followed by gradual decrease in mineralization. An estimate of the first order biomineralization rate constant may be derived from the slope of the mineralization curve over the interval of day 2 to day 5, and knowledge of the initial naphthalene concentration, C_{so}, and the total mass of naphthalene in the system. The initial value of k_{bio} for Stroudsburg tar was approximately 15/day

and for the BG&E tar was about 3/day. The initial first order mineralization rate constants are comparable for both the tars, but significantly less than the measured mass transfer rate coefficients. The total naphthalene in the BG&E tar degraded to only about 15%, whereas for the Stroudsburg tar mineralization ceased after approximately 60% of the naphthalene was depleted.

Bacterial counts taken from supernatant samples of the biometers indicated the presence of a significant bacterial population. Thus the lack of potentially active bacteria was not responsible for the attenuation in mineralization activity. This was further verified by adding fresh inoculum to biometers after naphthalene mineralization had ceased. The addition of fresh inoculum did not recommence mineralization.

The important observation from the mineralization data is that for both the tars mineralization end points were notably less than the total naphthalene present. Naphthalene concentrations in the aqueous bulk phase were measured at the 14th day and 30th day of the biodegradation test. Filtered supernatant of biometers containing BG&E coal tar imbibed in silica beads, were analyzed by GC. The naphthalene concentrations ranged from 9 mg/L to 16 mg/L, and match well with a predicted equilibrium concentration of 15.7 mg/L calculated using Raoult's Law and an estimate of the residual mole fraction of naphthalene in coal tar following biodegradation. This result shows that naphthalene was available to the microorganisms in the biometers at the point where mineralization had ceased.

Further investigations with naphthalene-spiked coal tar revealed that the mass of naphthalene degraded remained fairly constant irrespective of the total naphthalene content of the tar. The biodegradation test systems were evaluated as to whether toxic and inhibitory conditions may have limited naphthalene mineralization. Dilution experiments, where nutrient media was added to the biometers at the time when mineralization had ceased, showed that in many cases dilution resulted in reviving mineralization. Salicylic acid, an easily-degradable compound that is in an intermediate in the degradation pathway of naphthalene, was scarcely degraded when added to the biometers after the appearance of negligible naphthalene mineralization. In some biometers, dilution with nutrient media was followed by rapid mineralization of salicylic acid, suggesting that dilution eliminated an inhibitory condition. All these observations indicate that conditions inhibitory to the microorganisms developed during the course of the experiment.

CONCLUSIONS

Mass transfer and biomineralization studies have revealed for the small size of the microporous media used in these tests that the degradation of naphthalene from coal tar becomes limited by toxic-inhibition and not by mass transfer constraints. Despite the compositional variation of coal tars from different sources, the observation of limited naphthalene mineralization due to inhibitory conditions was consistent between the two coal tars studied.

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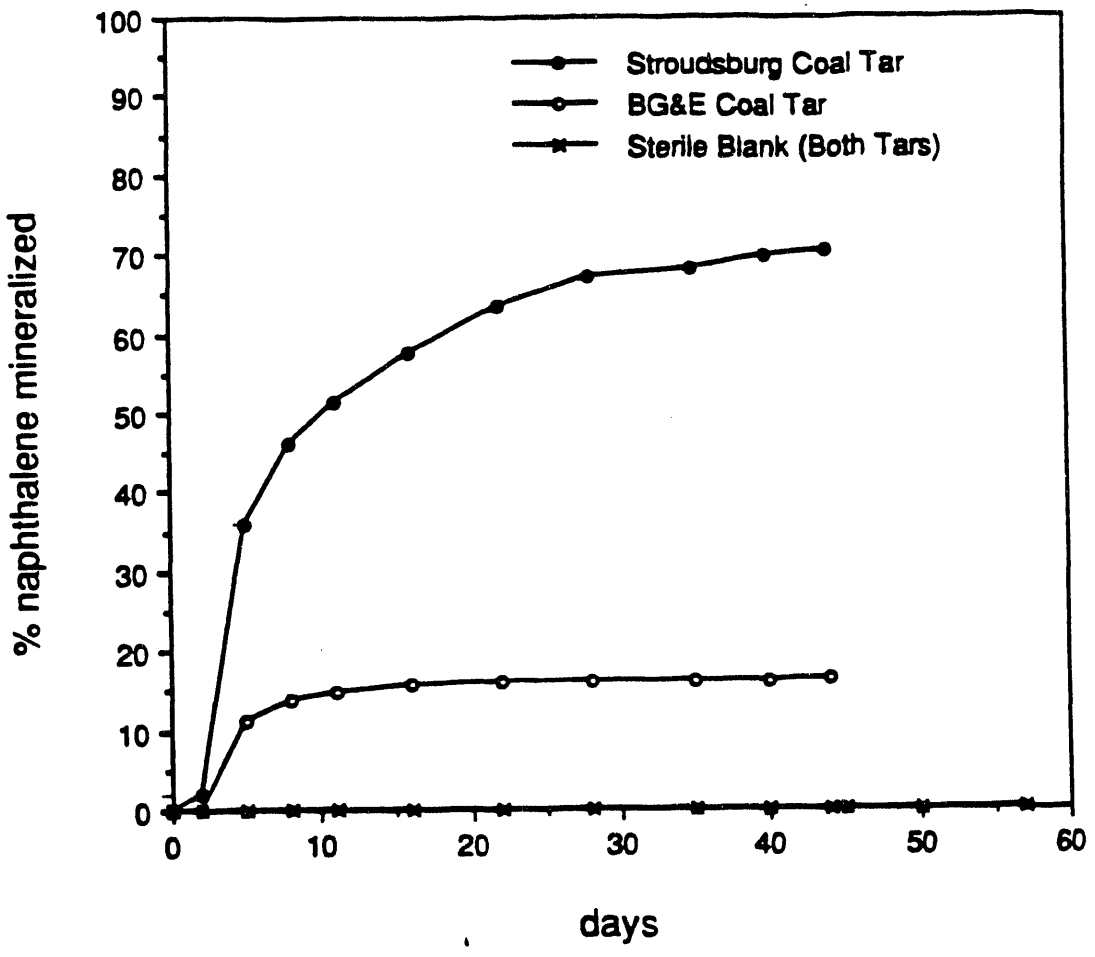

Figure 1. Mineralization patterns of naphthalene from the Stroudsburg and BG&E coal tar imbibed in microporous silica beads. The estimated first order biomineralization rate constants k_{bio} for the Stroudsburg tar is 15/day and for the BG&E tar is 3/day.

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