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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 $236\mu\text{m}$ 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

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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

saturation, imbibed within the micropores of the soil/aquifer matrix. Due to the slow release of organic solutes from the immobilized organic phase, coal tar can function as a long-term source of contamination in the sub-surface environment.

The focus of the present study is on the biotransformation of PAH compounds from coal tar present at residual saturation within a microporous medium. Several factors may influence the overall biotransformation rate of aromatic compounds released from multi-component NAPLs such as coal tar. These factors include:

- Physico-chemical phenomena related to dissolution and mass transfer of PAH compounds from the organic phase to the bulk aqueous phase, and,
- Biokinetic phenomena pertaining to the intrinsic biodegradation rates of the microbes, the competitive utilization of tar-derived substrates, and toxic/inhibitory effects of coal tar solutes and/or their degradation products.

Physico-chemical phenomena such as sorption and pore diffusion have been found to limit the rate of biotransformation of dissolved hydrophobic organic compounds in soil or porous media-water systems (Rijnaarts *et al.*, 1990; Mihelcic and Luthy, 1991; Alvarez-Cohen, 1991; Scow and Alexander, 1992). When NAPLs such as coal tar are also present, the 'bioavailability' and hence the biotransformation of coal tar constituents may be limited by equilibrium partitioning and/or the rate-limited mass transfer of the organic compound between the NAPL and the aqueous phase. The aqueous phase concentration of an aromatic compound in equilibrium with a NAPL is related by Raoult's law to the solubility of the pure liquid (or hypothetical sub-cooled liquid) compound in water, and to the mole fraction of the aromatic compound in the multi-component organic phase (Schwarzenbach, Gschwend and Imboden, 1993). For complex multi-component NAPLs such as gasoline or coal tar, mass or volume fractions of the organic compound in the NAPL have been used in place of mole fraction to provide fairly accurate estimates of equilibrium aqueous concentrations using Raoult's law (Mackay *et al.*, 1991; Lee *et al.*, 1992).

Mass transfer from coal tar under non-equilibrium conditions, may be limited by several factors such as inter-phase transfer, sorption and pore diffusion. In addition, interfacial films have been observed to form at coal tar interfaces that have aged in water over a period of several days (Luthy *et al.*, 1993). The influence of interfacial 'aging' on mass transfer, and the impact of such on the 'bioavailability' of tar-derived solutes has not yet been investigated.

Biotreatment studies with soils recovered from former manufactured gas plant sites having PAH-containing coal tar indicate that PAH compound dissolution may be a limiting factor in achieving bioremediation of such sites (e.g., Smith *et al.*, 1989; Gauger *et al.*, 1989; Morgan *et al.*, 1992; Erickson *et al.*, 1993). However, the investigations of rate-limiting factors in the above studies were performed qualitatively and on a case-by-case basis, i.e., no generalized criterion was used to distinguish between systems that were mass transfer limited and those that were limited by biokinetics. The objective of this study is to develop an investigative framework that assesses the effect of physico-chemical mass transfer processes on the overall rate of biotransformation of coal tar NAPL-derived organic solutes. Mass transfer and biodegradation experiments are conducted independently, and a coupled dissolution-degradation model is developed to interpret the experimental data and evaluate rate-controlling factors. Modeling efforts and laboratory experiments are designed to develop quantitative criteria to determine whether mass transfer or biokinetic limitations control the rate of biotransformation of PAH compounds present as non-aqueous liquids in microporous solid-water systems.

EXPERIMENTAL METHODS

Laboratory experiments measure the rates of mineralization and aqueous phase dissolution of naphthalene that is released from non-aqueous phase liquid coal tar present at residual saturation within microporous silica beads. The microporous silica beads are of a uniform size distribution ($D_v = 236\mu m$, $d_{v10}/d_{v90} = 2.7$), and are used as a representative porous medium. Coal tar used in the experiments was acquired from a former gas plant site in Stroudsburg, PA (Villaume, 1985). Naphthalene, which is one of the dominant components in this coal tar (2.2% by weight), is tracked by adding to the coal tar a small amount of ^{14}C -radiolabeled naphthalene. The behavior of the ^{14}C naphthalene is assumed to be representative of the naphthalene presented in coal tar. The rates of dissolution and biomineralization of naphthalene are determined by measuring ^{14}C activity using a Beckman LS5000TD liquid scintillation counter with automatic quench compensation.

Preparation of Microporous Medium: The silica beads are conditioned to be slightly hydrophobic by heating to $800^\circ C$ and converting surface silica hydroxide groups to silica oxide. The beads are then imbibed with the radiolabeled coal tar and mixed for 24 hours in a centrifugal tube rotator. The centrifuge tubes containing the beads are then allowed to stand for 7 days before use to ensure maximum penetration of coal tar into the microporous medium.

Biomineralization Experiments: The aerobic biodegradation tests are carried out in biometer flasks fitted with a side tube. The flask and the side tube are capped with neoprene stoppers covered with aluminum foil to minimize sorptive losses. Each biometer flask contains 5 g of silica beads imbibed with 1 mL of radiolabeled coal tar. At the start of the experiment, the silica beads are suspended in 50 mL of nitrogen and phosphorus-amended BOD water and inoculated with 2 mL of a bacterial culture consisting of a mixed population of PAH degraders (RET-PA-101). The PAH degrading bacteria were isolated from PAH contaminated soils and waste streams, and were grown on autoclaved BOD dilution water and crystalline naphthalene (Laha and Luthy, 1991). The inoculum size corresponds to about 5×10^7 bacteria per mL, as determined by plate counts with naphthalene. The pH of the silica beads-BOD water slurry is maintained between 6.5 and 7.2 by the phosphate buffer to provide viable conditions for biodegradation. The headspace in the flask is replenished periodically to ensure that the system is not oxygen limited. The $^{14}CO_2$ produced during the course of biodegradation is trapped in the side arm of the biometer flask, which contains 5 mL of 2N sodium hydroxide solution. Triplicate samples of 0.5 mL NaOH are pipetted from the side arm of the biometer flasks, the activity of the evolved $^{14}CO_2$ measured, and thus the rate of biomineralization of naphthalene is determined at different times during the test period. Control blanks, where microbial activity is inhibited by the addition of 200 mg/L mercuric chloride, are also maintained throughout the test period.

Mass Transfer Experiments: Mass transfer tests are carried out in batch and flow-through systems. In batch tests, 5 g of silica beads imbibed with 1 mL of radiolabeled coal tar are contacted with 50 mL of water and the aqueous phase naphthalene concentration is measured at equilibrium. The measured equilibrium aqueous phase naphthalene concentration is compared with that predicted from Raoult's law,

$$C_{so} = x_{PAH} * C_{pure liquid}^{PAH} \quad (1)$$

according to which the equilibrium concentration of naphthalene in water, C_{so} , is proportional to the mole or mass fraction of the naphthalene in coal tar, x_{PAH} , and the solubility of pure sub-cooled liquid naphthalene in water, $C_{pure liquid}^{PAH}$.

In order to assess the effect of 'aging' on equilibrium partitioning and mass transfer rates, the dissolution of naphthalene from coal tar is studied in continuously stirred flow-through reactors. In the flow-through tests, the beads containing radiolabeled coal tar are stirred with a fixed volume

of water, V , in an air-tight reactor vessel, and water is flushed through the system at different volumetric flow rates, q . The outflow of water creates a driving force for further dissolution, and by varying the flow-rate, experiments may be conducted at different residence times, θ . The aqueous phase concentration of naphthalene in the reactor is monitored periodically by measuring the ^{14}C activity of the effluent. The change in aqueous phase naphthalene concentration, $C_{(t)}$, with pumping time, t , may be described by writing a naphthalene mass balance equation for the water in the reactor vessel:

$$\frac{\partial C_{(t)}}{\partial t} = k_{la(t)} [C_{eq(t)} - C_{(t)}] - \frac{q C_{(t)}}{V} \quad (2)$$

The second term on the right hand side of Equation 2 represents the rate of outflow of naphthalene from the stirred reactor due to flushing at a volumetric rate of q , while the first term represents the rate of input of naphthalene to the aqueous phase due to dissolution from coal tar. The dissolution rate is described using a lumped mass transfer rate coefficient, $k_{la(t)}$, and a linear driving force term that represents the departure of the measured aqueous concentration, $C_{(t)}$, from equilibrium, $C_{eq(t)}$. Since most of the coal tar constituents are insoluble in water, the naphthalene mole fraction in coal tar, and hence the equilibrium aqueous phase naphthalene concentration (as predicted from Raoult's law), should decrease continuously with pumping time as more naphthalene is flushed out of the reactor. Using Raoult's law, the change in equilibrium aqueous phase naphthalene concentration, $C_{eq(t)}$, is given by:

$$C_{eq(t)} = F_{PAH(t)} * C_{s0} \quad (3)$$

where C_{s0} is the initial solubility of naphthalene in water, and $F_{PAH(t)}$ is the fraction of naphthalene remaining in coal tar at time, t . Thus, knowing the initial aqueous solubility of naphthalene, C_{s0} , from batch solubilization tests, and by keeping track of the fraction of naphthalene remaining in coal tar at any time, $F_{PAH(t)}$, the time-varying equilibrium aqueous phase naphthalene concentration, $C_{eq(t)}$, may be estimated from Equation 3. Equation 2 is then used to evaluate the lumped mass transfer rate coefficient, $k_{la(t)}$. The mass transfer rate coefficient is observed to decrease with time, and this is believed to be a result of the interfacial 'aging' phenomenon that has recently been observed in coal tar-water systems (Luthy *et al.*, 1993). In order to measure the mass transfer rates under different 'aging' conditions, flow-through tests are conducted in 'fresh' systems and in 'aged' systems in which the beads carrying coal tar have been in contact with water over periods of 1 week to 1 month before commencing pumping.

DISSOLUTION-DEGRADATION MODEL

A simple dissolution-degradation model is developed that describes changes in PAH concentration and biokinetics in the well-mixed biometer batch-reactor system. The biometer batch reactor contains microporous silica beads imbibed with PAH containing coal tar, suspended in a nutrient rich aqueous buffer along with PAH-degrading microbes. The system comprising microporous beads, coal tar, water and bacteria is represented schematically in Figure 1. The PAH compound is present in the coal tar held within the micropores of the particle. The bacteria are assumed to be size-excluded from the small micropores (pore dia $\approx 170\text{\AA}$). This condition is satisfied in the experiments, thus essentially only solubilized aqueous phase PAH present in the external buffer solution is available for degradation.

As shown in Figure 1, the release of naphthalene from the coal tar present in the micropores occurs through a sequence of several mass transfer steps, namely, dissolution at the intrapore tar-water interface, pore sorption-diffusion, and particle surface to bulk water transport. For $236\text{ }\mu\text{m}$ diameter silica beads with small pore diffusion path lengths, a simple dissolution-degradation model

Figure 1: Schematic representation of the processes through which dissolution, mass transfer and biodegradation may occur for PAH compounds released from coal tar imbedded in microporous silica media (not to scale).

is developed in which all the above microscale processes are lumped together, and the mass transfer rate coefficient, $k_{la(t)}$, defined in Equation 2, is used to describe the rate of release of naphthalene from coal tar to the bulk aqueous phase. The rate of bacterial degradation of the aqueous phase naphthalene in the buffer solution is assumed to be first order with respect to PAH concentration, and k_{bio} represents the pseudo-first-order biomineralization rate constant assuming zero growth of the acclimated cultures. The change in aqueous phase naphthalene concentration in the biometer is thus given by:

$$\frac{\partial C(t)}{\partial t} = k_{la(t)} [C_{eq(t)} - C(t)] - k_{bio} C(t) \quad (4)$$

Here, as in Equation 2, the first term on the right hand side represents the rate of dissolution of naphthalene from the coal tar to the bulk aqueous phase. The dissolution rate is represented by a lumped mass transfer rate coefficient, $k_{la(t)}$, which is determined from the mass transfer experiments. The second term in Equation 4 represents the rate of removal of bulk aqueous phase naphthalene due to biodegradation. The first order biokinetic coefficient is estimated from the biomineralization experiments. The change in equilibrium aqueous phase naphthalene concentration due to microbial degradation is estimated from Raoult's law using Equation 3.

Equation 4 is a differential equation that couples the dissolution and degradation processes taking

place in the biometer. The overall rate of biotransformation is controlled by the slowest of the two processes. Computer simulations and analytical solution of Equation 4 show that when $k_{la(t)} \gg k_{bio}$, i.e., mass transfer occurs much faster than biodegradation, and the aqueous phase naphthalene concentration in the reactor, $C(t)$, is very close to equilibrium, $C_{eq(t)}$. The first term on the right hand side of Equation 3 can be neglected, and Equation 4 reduces to:

$$\frac{\partial C(t)}{\partial t} = k_{bio} C_{eq(t)} \quad (5)$$

Equation 5 represents a system where the overall biotransformation rate is completely controlled by biokinetic phenomena.

Conversely, when $k_{la(t)} \ll k_{bio}$, i.e., mass transfer occurs much slower than biodegradation, the aqueous phase naphthalene concentration in the reactor is very small compared to the equilibrium concentration. The second term in the right hand side of Equation 4 can be neglected under such conditions, and Equation 4 now reduces to:

$$\frac{\partial C(t)}{\partial t} = k_{la(t)} [C_{eq(t)} - C(t)] \quad (6)$$

Equation 6 represents a system in which the overall biotransformation rate is controlled completely by mass transfer processes. Thus, the ratio of the mass transfer rate coefficient to the biokinetic coefficient is a quantitative criterion that can be used to identify if mass transfer phenomena or biological processes pose a limiting constraint on biotransformation rates. The ratio of the maximum rate of mass transfer to the maximum rate of biodegradation can be represented as a type of Damkohler number for the coal tar-water system. The Damkohler number, Da , computed as

$$Da = k_{bio}/k_{la(t)} \quad (7)$$

indicates mass transfer control for values much greater than unity and biokinetic control for values much less than unity. Da may be computed from independent mass transfer and biodegradation experiments, similar to those described in the earlier section.

RESULTS

Biom mineralization Experiments: Typical results from the biom mineralization experiments are shown in Figure 2. The mineralization of naphthalene from coal tar proceeds at a more rapid rate during the first 10 days and then diminishes, resulting in about 55%-60% conversion over a 30 day period. Batch solubilization tests indicate that at the start of the experiments, equilibrium is attained within a span of 30 minutes. Naphthalene degradation generally occurs at a much slower rate, with changes occurring over periods of days. Thus, in the initial stages, mass transfer occurs much faster than biodegradation, and the rate of mineralization, i.e., the incremental mass of naphthalene degraded per unit time, may be described by Equation 5. The biom mineralization rate at the start of the experiment is determined from the initial slope of the biom mineralization curve (Figure 2), and Equation 5 is then used to estimate a first order biokinetic coefficient of $\simeq 5/\text{day}$. This number lies in the range of naphthalene biokinetic coefficients estimated from other laboratory studies (e.g., Mihelcic and Luthy, 1991). Thus, for modeling purposes, the intrinsic biokinetic coefficient k_{bio} is set to $\simeq 5/\text{day}$; however, after about 10 days, the observed biom mineralization rate decreases in an anomalous manner not consistent with the estimated biokinetic coefficient. Flow-through mass transfer tests are conducted to examine if mass transfer phenomena limit biotransformation rates when the system has 'aged' in water over long periods of time.

Figure 2: Biomineralization of naphthalene from Stroudsburg coal tar imbibed within microporous silica beads. The biomineralization rate is rapid initially, and then decreases.

Mass Transfer Experiments: Results from the flow-through mass transfer experiments are shown in Figure 3. In Figure 3a, the flow-through reactor was operated at a residence time of 30 minutes, using a freshly prepared slurry of coal tar containing beads in water. The measured naphthalene concentration in the reactor was found to be very close to the equilibrium concentration predicted from Raoult's law. In order to verify the accuracy of Raoult's law, the pump was turned off at points *a*, *b*, *c* and *d*, and the contents of the reactor were allowed to re-equilibrate. No change in aqueous phase naphthalene concentration was observed, indicating that at residence times of 30 minutes, equilibrium is attained in 'fresh' coal tar-water systems. The change in aqueous phase equilibrium concentration could be predicted fairly accurately from Raoult's law [Equation 3].

Shown in Figure 3b are results from a reactor containing a 'fresh' bead-water slurry that was operated at a residence time of 1 minute. The measured aqueous phase naphthalene concentrations showed departure from equilibrium at this smaller residence time. The change in the equilibrium aqueous phase naphthalene concentration with pumping time was estimated from Equation 3, and confirmed by letting the contents of the reactor re-equilibrate after pumping was terminated at the end of the experiment. Mass transfer coefficients were then calculated using Equation 2. Similar experiments were conducted with systems in which the beads imbibed with coal tar had aged in water over periods of time ranging from 1 week to 1 month, and with biotreated-slurry samples obtained from the biomineralization tests. The lumped mass transfer rate coefficient, $k_{la(t)}$ determined from the flow-through experiments ranges from 3000/day for 'fresh' systems at the start of pumping, to about 200/day for 'aged' systems at the end of the pumping test.

Modeling Insights: Based on the results presented above, it can be seen that, for the experimental conditions and small media-size employed in these tests, the mass transfer rate is much faster than the intrinsic biokinetic rate. While the interfacial aging phenomenon may account for a reduction

Figure 3: Aqueous phase naphthalene concentration in flow-through stirred tank reactors containing coal tar imbibed in microporous silica beads. **A.** System operated at a residence time of 30 minutes appears to have attained equilibrium. Equilibrium concentrations could be predicted fairly accurately from Raoult's law. **B.** System operated at a residence time of 1 minute shows departure from equilibrium.

of the mass transfer coefficient to about 200/day at the end of a 30 day 'aging' period in water, the Damkohler number remains much less than unity ($Da \simeq 0.025$), indicating that mass transfer does not control the biotransformation of naphthalene from coal tar present at residual saturation in the small diameter microporous silica beads.

SUMMARY AND FUTURE WORK

An investigative framework is developed to assess the role of physico-chemical mass transfer processes on the biotransformation of organic compounds that are released from coaltar-NAPL present at residual saturation within a microporous medium. The investigative protocol consists of developing a simple dissolution-degradation model that couples the concurrent mass transfer and biokinetic processes occurring in the system. The relative importance of mass transfer to biotransformation is quantified by developing a dimensionless Damkohler number. The Damkohler number for the NAPL-water system is estimated from independent mass transfer and biodegradation experiments.

Biom mineralization experiments conducted with Stroudsburg coal tar indicate an initial rapid rate of naphthalene degradation, corresponding to an intrinsic first order biokinetic constant of $\simeq 5/\text{day}$. However, after a period of about 10 days, the biom mineralization rate decreases anomalously. Mass transfer experiments were conducted to evaluate the role of physico-chemical phenomena on the biotransformation rate. The results from the mass transfer tests indicate that:

- A Raoult's law type relationship can be used to predict the aqueous phase concentration of naphthalene in equilibrium with coal tar under dynamic conditions. The equilibrium concentration represents the maximum amount of naphthalene that is 'bioavailable' in the aqueous phase at any time.
- A lumped mass transfer rate coefficient can be used to describe mass transfer from coal tar to bulk water under conditions of disequilibrium. The mass transfer rate coefficient, $k_{la}(t)$, decreases with 'aging' of the coal tar-water system to a minimum of $\simeq 200/\text{day}$ after a 30 day 'aging' period.

Comparison of the mass transfer and biokinetic coefficients yields a Damkohler number of $\simeq 0.025$, indicating that mass transfer occurs much faster than biodegradation, resulting in equilibrium conditions in the biometer systems throughout the duration of the experiment. Thus, while equilibrium partitioning between coal tar and water controls the mass of naphthalene that is 'bioavailable' in the aqueous phase, the rate of biotransformation of aqueous phase naphthalene is not constrained by mass transfer limitations. Ongoing experiments will attempt to identify alternative rate-controlling processes related to biological phenomena such as toxicity, inhibition and competitive substrate utilization. Future experiments, conducted with larger particle sizes and/or other PAH compounds, will be used to verify the utility of the dissolution-degradation model and the Damkohler number in evaluating the role of physico-chemical mass transfer processes on the biotransformation of coal tar-derived organic solutes.

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