THE IMPACT OF BIODEGRADATION OF DE-ICING CHEMICALS ON THE CONDUCTIVITY AND DISPERSIVITY OF POROUS MEDIA

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ABSTRACT

Environmental contamination with aircraft de-icing fluids (ADF) is becoming a concern. Propylene glycol (PG) composes the largest fraction of the ADF most commonly in use in the U.S. The biodegradation of PG and ADF in saturated and unsaturated sand columns was evaluated, in addition to the impact of biodegradation on the hydrodynamic characteristics of the porous media. In studies with unsaturated sand, the amount of PG removed increased with spilled concentration (from 1000 to 300,000 mg/L), but decreased as multiple pore volumes were spilled. Tests in saturated columns were conducted at average loadings of ADF or PG of 43 to 32,000 mg/d. The hydraulic conductivity of the sand was reduced due to biogrowth, but to a lesser extent with increasing PG or ADF loadings above 110 mg/d. At higher groundwater flow rates, there was less biomass accumulation in the sand and therefore less decrease in hydraulic conductivity. Dispersivity increased over time as bacteria grew in the sand. Understanding the effects of bacterial growth in sand on the hydrodynamic properties of the media and the net biokinetics of the system will aid in predicting the fate of de-icing compounds in the natural environment and engineered treatment biofilters.

Key words: *biofilms, porous media, de-icing fluid*

INTRODUCTION

To maintain safe operation of airplanes during adverse winter weather conditions, specially formulated de-icing fluids are applied to aircraft. Large quantities of this material are used every year in the U.S., estimated at 11.5 million gallons of glycol in 1992, of which a significant fraction of around 50% is released into the environment (Noble, 1997). Concern is building about potential harmful effects to the environment resulting from these releases of aircraft de-icing fluid (ADF). The mixture commonly used to de-ice aircraft is a combination of approximately 88% propylene glycol (PG), 2.5% surfactants and corrosion inhibitors, and water. (Older ADF used ethylene glycol instead of PG, but newer formulations use PG due to its lower perceived toxicity.) PG may therefore be released into the environment at very high concentrations (on the order of 1,000 to 500,000 mg/L). Although PG is readily degradable by many bacteria that are commonly present in soil, the high loading may overwhelm the ability of the natural bacteria to fully degrade the PG before it reaches the groundwater (where it has been detected as reported by Cancilla et al., 1998) or other surface water bodies. If PG enters streams at even fairly low concentrations (10 to 100 mg/L), the dissolved oxygen could be completely consumed by aquatic microorganisms, which would negatively impact fish and other aquatic life. Another problem associated with ADF is the toxicity of the surfactants and corrosion inhibitors to fish, water fleas, and microorganisms (Cornell and Hernandez, 1998 WEF). Therefore, it is

important to consider the impact of the entire ADF mixture on environmental systems in addition to the effects of PG.

Studies are ongoing to determine the fate of ADF in the "near runway" environment. The work is relevant to both natural soil where the de-icers may be released and engineered biofilters used to treat the releases, such as those used at Norway's new international airport (Danielsberg et al., 1998). As the ADF permeates through the soil and enters the groundwater, significant bacterial growth may occur which in turn may decrease the hydraulic conductivity of the aquifer. This "plugging" of the soil could have significant impacts, since with the lower conductivity there could be increased spreading of the contamination or a reduction of the biodegradation capacity due to the limitation of oxygen or other electron acceptors. Understanding how biological growth affects subsurface hydrodynamics and predicting the effect of this bioactivity on contaminant fate and transport will help improve bioremediation design and risk management strategies.

PROCEDURES

Preliminary experiments in unsaturated columns packed with sand were conducted to determine an approximate amount of ADF or PG that could reach the saturated zone, while the majority of experiments were conducted in saturated sand columns.

Unsaturated column experiments were conducted in both large (80 cm tall x 9 cm diameter) and small (15 cm tall x 7 cm diameter) Plexiglas columns. First, #50 sand was mixed with a suspension of bacteria grown on PG. The large column was packed under water-saturated conditions and then the water was allowed to free-drain out of the column. The volume of water drained was measured in order to compute the residual saturation in the column. A volume of water equal to the free-drained water containing 1,000 to 10,000 mg/L PG was spilled into the column, and samples taken with depth at 10 cm intervals and analyzed for PG content. At the end of the experiment, the column was sectioned into vertical slices and measured for moisture content (by weight difference after drying at 105°C) and biomass concentration (by volatile solids analysis). Small column experiments were conducted in the same way, except that sampling ports were located at a depth of 3 cm, 7.5 cm, and 12 cm.

Saturated column experiments were conducted in the small Plexiglas columns (15 cm tall x 7 cm diameter). The uniform #50 sand with an average particle diameter of 0.32 mm was passed through a No. 200 sieve to remove fines and burned at 550°C to remove organic matter prior to use. The sand was pre-seeded with natural bacteria that were enriched from Denver International Airport soil by growth on PG in a mixed, aerobic batch flask. This resulted in an initially even distribution of biomass throughout the sand that was packed in the columns (approximate sand depth 8 to 10 cm, with gravel pack at each end). Simulated groundwater containing trace nutrients and ADF or PG was continuously upflow circulated

through the columns at a constant rate via a peristaltic pump. The feed solution was incubated on a rotary shaker table (160 rpm) to provide aeration prior to entering the columns. The groundwater was recirculated through the columns for a period of two days, and then replaced with fresh solution.

Changes in the hydraulic conductivity (K) of the saturated sand over time were determined by measuring the head drop across the sand using piezometer tubes attached to the sides of the column. Using Darcy's Law, the measured flowrate and headloss were used to calculate K. Hydrodynamic dispersivity in the columns was periodically measured by injecting a slug of bromide and analyzing the column effluent to determine the breakthrough curve. Effluent PG, ammonia, and biomass concentrations were measured. PG was measured using the colorimetric glycol method (New York, 1991). Ammonia was measured by the Nessler method using Hach reagents (APHA, 1992). Biomass was measured as dry weight by volatile suspended solids (APHA, 1992). At the end of a given growth period, the columns were sacrificed to determine the total mass of biogrowth on the sand as mg volatile solids (VS) per dry weight sand. The biomass distribution with depth in the column was determined by sectioning the column sand into 1 to 2 cm depth slices.

Experimental conditions were varied to simulate a range of environmental conditions. Influent ADF and PG concentrations were varied, representing a range of environmental dilution and degradation prior to entering the saturated zone. The flow rate of water through the columns was varied to test for the effect of shear on the biofilm growth.

RESULTS AND DISCUSSION

The unsaturated column experiments were conducted by spilling PG-contaminated solutions into sand at a free-drained saturation on the order of 40 to 56%. In the large column, the overall removal efficiency of PG from one pore volume of water over the 67 cm of sand was 81%, 91%, and 92% when 10, 5, and 1 g/L PG were spilled, respectively. The biomass concentration at the end of the three spills averaged 1.26 mg VS/g sand, with higher biomass concentrations in the top 15 cm and a constant concentration in the bottom 52 cm of sand. Subsequent unsaturated experiments were conducted in the smaller columns. When one pore volume of 1000, 2000, and 20,000 mg/L of PG was spilled, the average removal efficiency over the length of the column averaged 85%, 68%, and 64%, respectively. This is logical due to the rate limitation for PG degradation as the water migrated past. A final set of experiments was conducted with one pore volume of water spilled three to four times in succession. The removal efficiency of 2,000 to 300,000 mg/L of PG decreased from 51 to 80% in the first spill to 0 to 3% by the third spill for all of the different concentrations tested. The final biomass concentration on the sand averaged 0.47 to 0.71 mg VS/g sand. The results indicated that a small spill could be significantly attenuated, but that larger volumes (represented by the multiple-pore volume

experiment) could have very little attenuation in the vadose zone.

The results of the unsaturated zone experiments indicated that a wide range of ADF and PG concentrations should be tested in the saturated zone experiments. Example results from the saturated experiments are presented in Table 1. In general, the hydraulic conductivity decreased and the dispersion increased over time as the biomass grew on the PG or ADF. This continued until steady values of conductivity and dispersion were achieved (after 10 to 40 days), which indicates the point where biomass growth due to degradation of the contaminant was balanced by the shear of the biomass out of the column via the groundwater and endogenous biomass decay. This general result of the hydrodynamic effects of biomass growth in porous media has been shown by other researchers working with different bacterial growth substrates (Cunningham et al., 1991; Taylor and Jaffe, 1990; Vandevivere and Baveye, 1992). As shown in Table 1, the highest PG and ADF loading caused little change in hydraulic conductivity, less than one order of magnitude, while the lower inlet concentrations caused two to three orders of magnitude decrease in hydraulic conductivity. The dispersivity increased as conductivity decreased, reaching about three times the value of the clean sand.

The best PG removal was achieved for the lower loadings, with greater than 99% for inlet concentrations below 1000 mg/L. As the inlet concentrations increased, PG removal efficiency decreased. Differences in the PG removal when PG was the sole contaminant versus in the ADF mixture were not significant. The final biomass in the columns indicates, however, that significant biomass was present in the columns which had the very high PG and ADF loading. Therefore, although some inhibition is apparent at the

Table 1. PG and ADF removal in saturated columns and effects on hydrodynamic properties of the #50 sand.

Contaminant	Initial inlet conc (mg/L)	Average loading (mg/d)	Flow rate (mL/min)	PG removal (%)	Final steady state K (cm/s)	Final dispersivity (cm)	Final total biomass in column (mg VS)
none	0	0	0.5	-	3×10^{-2}	0.6	0
PG	300,000	32,000	0.7	3	9×10^{-3}	NM	940
ADF	300,000	32,000	0.9	3	9×10^{-3}	NM	730
PG	10,000	1070	0.5	20	3×10^{-3}	NM	370
ADF	10,000	1070	0.8	30	2×10^{-3}	NM	280
PG	1,000	110	0.5	99.9	5×10^{-4}	1.3	415
ADF	1,000	110	0.8	99.9	4×10^{-4}	1.8	733
ADF	1,000	110	0.2	99.9	3×10^{-5}	NM	1145

higher loadings, complete toxicity is not indicated. Using the measured biomass in the columns, an estimated specific first-order biodegradation rate of PG was calculated. This rate decreased at increasing inlet concentrations of PG or ADF; however, it is unlikely that a first-order rate expression would be valid over the very high concentrations tested. If a zero-order rate is assumed instead (which is the simplification of the Monod kinetics when the substrate concentration is significantly higher than the half-saturation concentration), then there is actually a weak trend of an increasing maximum specific degradation rate (ranging from 0.1 to 1.2 g PG/g VS-d) with increasing inlet concentration. Therefore, it is not obvious that toxicity is occurring, rather a limitation of electron acceptor or nutrients appears to be indicated. Alternatively, the shear forces in the column may simply limit the maximum amount of biomass that can accumulate.

CONCLUSIONS

Biomass growing on aircraft de-icing fluid and the main component of ADF, propylene glycol, accumulates to a significant extent in saturated sand columns, which causes a significant decrease in hydraulic conductivity and increase in hydrodynamic dispersivity. While significant quantities of ADF and PG can be biodegraded, this capacity can be overwhelmed at very high loadings. Further research is needed to determine ways to increase the biodegradation capacity. At present, the non-PG "additives" in ADF (including surfactants and corrosion inhibitors) do not appear to have a significant inhibitory effect on bacterial degradation of PG. Understanding the effects of bacterial growth in sand on the hydrodynamic properties of the media and the net biokinetics of the system will aid in predicting the fate of de-icing compounds in the natural environment and engineered treatment biofilters.

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