



BIODEGRADATION OF DE-ICING COMPOUNDS IN COLUMNS SIMULATING A RANGE OF NATURAL CONDITIONS

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ABSTRACT

The determination of the fate of aircraft de-icing fluids in near runway soils is important in evaluating environmental impacts and in the design of treatment system. The effect of biodegradation of the primary component of de-icing fluids, propylene glycol (PG), was tested in waters-saturated sand columns. Biogrowth significantly reduced the hydraulic conductivity of the sand. This change in hydraulic conductivity affects both the flow of water and the rate of migration of dissolved chemicals in the flowing water. With intermittent loading averaging 43 mg PG/d, hydraulic shear and endogenous biomass decay balanced bacterial growth. A lower final conductivity occurred at a lower flow rate, but increased loading (by two to four times) did not lower the final conductivity. After significant sand plugging by the bacteria grown on PG, periods of five to eight days when PG was not present resulted in significant partial recovery of the original conductivity. A trend of decreasing hydraulic conductivity with increasing biomass was observed. The results are important to consider when determining the fate of de-icing compounds in near runway soils and in the design of biofilters for treatment.

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

INTRODUCTION

Concern is building about releases into the environment of the de-icing chemicals applied to airplanes near both civilian and military airports. The mixture commonly used to de-ice aircraft is a combination of approximately 88% glycol, 2.5% surfactants and corrosion inhibitors, and water. Glycol is therefore released into the environment at very high concentrations (on the order of 1,000 to 100,000 mg/L). Glycol is readily degradable by common soil bacteria, but if this glycol enters streams, the dissolved oxygen could be completely removed, thereby impacting aquatic life. Another problem associated with the de-icing compounds is the toxicity of the surfactants and corrosion inhibitors to fish, water flea, and microorganisms (Cornell et al., 1998).

Studies are ongoing to determine the fate of de-icing compounds in "near runway" soil. As the glycol permeates through the soil and enters the groundwater, significant bacterial growth may occur which in turn may decrease in the hydraulic conductivity of the aquifer. This "plugging" of the soil could be significant in field applications since with the lower conductivity there could be increased spreading of the contamination due to barrier effects and by-passing or a reduction of the biodegradation capacity due to oxygen or nitrogen limitation, which could lead to PG contamination of the groundwater. 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

Experiments were conducted by feeding aqueous solutions of propylene glycol (PG) into columns (7 cm dia. X 15 cm tall) containing saturated sand. The uniform #50 sand with an aver-

age 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 soil samples collected at Denver International Airport 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 PG and trace nutrients was continuously circulated in the upflow direction 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.

Changes in the hydraulic conductivity (K) of the sand were measured over time using constant head tests. The head drop across the sand was measured using piezometer tubes attached to the sides of the column; the piezometers were attached at the level of gravel pack before and after the sand (and negligible head loss in the gravel was assumed). In some experiments, a piezometer tube was located at the mid-depth of the sand. Using Darcy's Law, the measured flow rate and the head loss were used to calculate K. Effluent PG, ammonia, and biomass concentrations were measured. PG was measured using a wet chemistry/colorimetric glycol method (New York State, 1991). Ammonia was measured by the Nessler method using Hach reagents. 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. Nitrogen available for biogrowth was limited relative to the carbon available from the PG; nutrient limitation would be common in natural soils due to the high carbon loading from the PG. The water velocity through the columns was varied to test for the effect of shear on the biofilm growth. Influent PG concentrations were varied, representing a range of environmental dilution prior to the PG entering the saturated zone. The frequency of PG exposure was varied to simulate periods of high loading and absence of loading (since aircraft de-icing operations are intermittent).

Initial studies were conducted with intermittent PG feeding (spike load of 100 mg PG into nutrient solution that was recirculated for two days and then refreshed; C:N ratio 7:1). Other tests were conducted with continuous feeding of PG without recirculation of the column effluent at a C:N ratio of 2:1. In addition, controlled periods of water flow without PG were used to determine the rate at which the biofilm shears away and decays.

RESULTS

In the analysis of the experimental data, of most interest was the significant decrease in the conductivity of the sand that occurred due to the growth of the bacteria on PG. The K of clean #50

sand was 0.035 cm/sec. In the intermittent PG loading experiments, up to three orders-of-magnitude decrease in K occurred over a period of three months. After 60 to 70 days, the hydraulic conductivity appeared to have reached a steady-state minimum value. This is likely the point at which shear of biomass out of column and endogenous decay balanced biomass growth. The rate at which hydraulic conductivity decreased depended on the flowrate of water being recirculated through the columns. The log K decreased linearly over time until reaching a steady state value. Results are summarized in Table 1.

At an average loading of 43 mg PG/d, the conductivity change and final steady state K were similar for the 8 and 12 mL/min flow rates. In addition, the rate of conductivity change at the higher flow rates was significantly slower than the lower flow rates of 1.5 and 3.5 mL/min. The final steady state K at the slower flow rate of 3.5 mL/min was also lower than the final K in the sand subjected to a higher flow rate. These results are logical since the biofilm would accumulate more slowly under the conditions of higher shear imposed at the higher flow rate. Similar results of faster conductivity decline and lower final steady state conductivity at lower flow rates were obtained for continuous PG feeding at 0.35 mL/min versus 1.14 mL/min at 100 mg PG/d loading.

The effect of PG loading on hydraulic conductivity changes is also shown in Table 1. Comparing the columns operated at 8 mL/min flow rate with a loading of 43 mg/d and 96 mg/d, the rate of conductivity decrease is similar, although slightly faster with the higher loading. Comparing the tests at 3.5 mL/min flow rate, an unexpected result was obtained. The higher loading of 173 mg/d resulted in a slower conductivity decrease over time and a significantly higher final steady state conductivity compared to the 43 mg/d loading. In these tests the initial PG concentration immediately after the spike load was 400 mg/L versus 1600 mg/L; the temporarily higher concentration caused the effluent from the higher loaded column to smell significantly anaerobic. The biomass in this column may have had a higher baseline metabolism due to temporarily high activity induced by the high PG load which caused a faster decay rate of the biomass. However, this result cannot be fully explained at this time and is under further investigation.

The effects of periods of time without a supply of PG on changes in the hydraulic conductivity of the saturated sand containing biomass were investigated. After intermittent feeding of 43 mg PG/d and 173 mg PG/d for 46 days at 3/5 mL/min, the K of the #50 sand had dropped to 7.6×10^{-5} cm/s and 1.9×10^{-4} cm/sec, respectively. Then after a five-day period with groundwater flow but without PG addition, K increased to 1.3×10^{-3} cm/s in both columns. During the endogenous period, the effluent biomass from the columns was significantly higher than pre-endogenous conditions in both columns. Therefore, the conductivity increase observed is likely due to a combination of increased biomass detachment, and washout and endogenous decay. By increasing the PG loading four times by feeding PG every 12 hours over the next two days, the conductivity returned to near pre-endogenous levels (6.7×10^{-5} cm/sec and 3.9×10^{-4} cm/s, respectively). This indicates that

loading amount and frequency will be important in the clogging of the soil.

Another test for the effect of endogenous time was conducted with continuously fed columns. Three columns were fed 100 mg PG/d at an average flow rate of 0.8 mL/min. After 16 days the K of all three columns dropped to 3.3×10^{-4} cm/s. Then PG loading to two columns was stopped, and by day 24, K increased to 1.04×10^{-3} cm/s in the unfed columns; K in the column that continued to be fed PG was 3.0×10^{-4} cm/s. PG feeding was resumed on day 24 and by day 32 K had returned to the pre-endogenous level of 3.3×10^{-4} cm/s. The effluent biomass from the endogenous columns was about half the effluent biomass from the fed columns, indicating that the primary mechanism of biomass loss in the unfed columns was endogenous decay.

In the columns with the most significant drop in conductivity, the biomass was not evenly distributed in the column. Most of the biomass was present in the bottom 2 cm of the sand, closest to the inlet of PG. For example, in the column fed 43 mg PG/d at 3.5 mL/min, the biomass concentration in the bottom 2 cm was 3.1 ± 1.4 mg VS/g sand versus an average biomass in the top 8 cm of 0.6 ± 0.1 mg VS/g sand. In contrast, the biomass in the column fed 43 mg PG/d at 8 mL/min had biomass evenly distributed with at 1.6 ± 0.2 mg VS/g sand. Looking at all the data of biomass versus K, including cases where the columns were sacrificed prior to reaching a final steady state value, the biomass in the bottom of the column seems to control the observed overall conductivity, with a trend to decreasing K with increasing biomass. When mid-depth piezometers were used, it was observed that more than 90% of the head loss was in the bottom half of the columns within the first 7 to 15 days of growth, and more than 98% head loss in the bottom half of the columns after 15 to 24 days of growth. This illustrates that the conductivity of the sand throughout the column depth was not uniform, and this can be attributed to the high biomass at the bottom.

In all cases the measured effluent PG concentrations from the columns were very low (<2 mg/L), despite the fact that oxygen was likely limited in the columns. Since there was no nitrogen or ferric iron in the groundwater and only a small amount of sulfate, most of the propylene glycol biodegradation apparently occurred under methanogenic or fermentative redox conditions.

DISCUSSION

These experimental results from packed-sand columns indicate that biological growth on the primary component of de-icing fluids, propylene glycol, can have significant impacts on the hydraulic conductivity of the saturated sand. Previous tests with naphthalene found that dispersivity of saturated sand was also significantly impacted by biogrowth. Similar results have also been reported in research with glucose and methanol (Cunningham et al., 1991; Taylor and Jaffe, 1990; Vandevivere and Baveye, 1992). Further experiments in larger two-dimensional tanks have demonstrated that this plugging of the aquifer with biogrowth significantly changes groundwater flow due to slower groundwater movement through the area containing biogrowth and groundwater flow around the area plugged by the biomass.

CONCLUSIONS

Biological growth on propylene glycol can significantly reduce the hydraulic conductivity of saturated sand in one-dimensional columns. This biological growth occurs under either aerobic or anaerobic conditions and with nitrogen limitation. At slower groundwater flow rates, the hydraulic conductivity of the sand decreases faster and to a lower final steady state level than at higher groundwater flow rates. Ongoing efforts to model these systems will allow the results of laboratory studies to be applied at a field scale. Understanding how biogrowth affects the properties of porous media will aid in predicting the fate of de-icing compounds in the environment and engineering processes to reduce their environmental impact.

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REFERENCES

- APHA, AWWA, and WPCF, 1992. Standard Methods for the Examination of Water and Wastewater, 18th ed. Washington, D.C.
- Cornell, J., D. Pillard, and M. Hernandez, 1998. Chemical Components of Aircraft De-icer Fluid: How They Affect Propylene Glycol Degradation Rates and De-icing Waste Stream Toxicity. Proceedings of Water Env. Fed 71st Conference, Vol 1, pp. 183-194.
- Cunningham, A.B., W. Characklis, F. Abedeen, and D. Crawford, 1991. Influence of Biofilm Accumulation on Porous Media Hydrodynamics, Environ. Sci. Technol., 25, pp. 1305-10.
- New York State Department of Health, 1991. Tentative Method for the Detection of Glycols in Water, APC-44, Wadsworth Center for Laboratories and Research, Division of Environmental Sciences, Albany.
- Taylor, S.W., and P.R. Jaffe, 1990. Biofilm Growth and the Related Changes in the Physical Properties of a Porous Medium: Experimental Investigation, Water Res. Res, 26, pp. 2153-59.
- Vandevivere, P., and P. Baveye, 1992. Saturated Hydraulic Conductivity Reduction Caused by Aerobic Bacteria in Sand Columns, Soil Sci Soc Am J, 56 pp. 1-13.

Table 1. Effect of intermittent PG loading on changes in the hydraulic conductivity of #50 sand.

Avg. loading (mg PG/d)	Flow rate (mL/min)	Rate of K decrease ([log cm/s]/d)	Days of constant K decrease	Final steady state K \pm stdev (cm/s)	Days steady state K	Avg steady state biomass \pm stdev (mg VS/g sand)
43	1.5	0.069	0-24	not reached	NA	NA
43	3.5	0.076	0-28	$2.2 \times 10^{-5} \pm 0.3 \times 10^{-5}$	60-72	3.1 ± 1.4^b 0.6 ± 0.1^t
43	8	0.036	0-60	$7.7 \times 10^{-5} \pm 1.2 \times 10^{-5}$	71-80	1.6 ± 0.2
43	12	0.042	0-60	$7.5 \times 10^{-5} \pm 3.3 \times 10^{-5}$	66-80	1.4 ± 0.3^b 0.6 ± 0.1^t
96	8	0.041	0-23	not reached	NA	NA
173	3.5	0.056	0-23	$5.9 \times 10^{-5} \pm 0.5 \times 10^{-5}$	60-72	9.9 ± 1.9^b 0.9 ± 0.2^t

NA = not applicable; ^b = bottom 2-cm of sand from column; ^t = top sand from column