Calcium Magnesium Acetate Degradation in Roadside Soil: Acetate Microcosms

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Aseptic soil samples from the loam cover of a state highway shoulder in southeastern Massachusetts were placed in sterile serum bottles, forming a series of aerobic soil microcosms. The samples were dosed with reagent grade acetate solutions without acclimation, then sacrificed at various time intervals and analyzed by gas chromatography in a laboratory determination of the aerobic microbial degradation kinetics. The acetate degraded rapidly in the loam layer, demonstrating that the shoulder has the potential to reduce oxygen demand by acetate on groundwater under the highway.

The aerobic degradation of acetate in roadside soils was measured in soil microcosms in this study. The work provides data on the fate and transport of the deicing agent calcium magnesium acetate (CMA) in the subsurface environment as it migrates from plowed snow on the highway shoulders through the unsaturated zone to the water table. In this regard, the aerobic decomposition of the acetate consumes oxygen in the subsurface environment, so that there is concern for potential oxygen depletion if an appreciable amount of acetate reaches the underlying unconfined aquifer (*1*).

FHWA, in an effort to weigh this possibly adverse impact against the many benefits associated with CMA use, has funded a series of research projects (*2*), including a thorough environmental study of a pilot scale test runoff plot in Washington State (*3*). The FHWA initiative, administered by the New England Transportation Consortium (NETC), extends the effort to the field by studying a highway in southeastern Massachusetts that has been deiced with CMA since it opened to traffic in August 1987. The laboratory work reported here is the first phase of the NETC project, which will feature additional microcosms, field measurements of acetate profiles, and comparative analyses of the Washington pilot scale and Massachusetts field scale data.

FIELD SITE AND SAMPLING METHODS

The research site is in southeastern Massachusetts along State Route 25. The test area is on the north-sloping highway shoulder that was constructed with native sandy fill covered with a nominal 0.20-m layer of loam. The road was opened in August 1987 under environmental constraints requiring the use of nonchloride deicing chemicals in the survey area, which receives plowed snow, airborne drift, and breakdown lane runoff (but no travel lane runoff) from the three 3.66-m-wide westbound lanes of this divided highway. About 25,000 vehicles travel on State Route 25 each day, and CMA has been applied at an annual rate of about 0.71 kg/m^2 pavement in response to 0.94 m of annual snowfall, on the basis of 1987–1988 data. This loading implies a representative surface CMA concentration of 700 mg/L, on the basis of 50 percent of the applied agent distributed over 20 m of the northern highway shoulder as drift, breakdown lane runoff, and plowed snow.

Environmental Engineering Program personnel sampled the northern slope on June 27, 1991, from the pared wall of a soil pit 0.80 m deep located 2.44 m from the edge of the breakdown lane. Soil samples of about 0.01 kg were taken from the two depths cited in Table 1 with the deepest location sampled first, using autoclaved 10-mL Becton Dickinson disposable syringe barrels and acid-washed, milliQ-rinsed, autoclaved 20-mL serum bottles with aerated headspace, Teflon closures, and plastic screw caps. The serum bottles were iced and sent back to the laboratory for storage and testing in a Fisher Scientific Mini Lo-Temp incubator at 5°C. Soil moisture, pH, and grain size distributions were also measured at the two depths using conventional methodology; the results are given in Table 1.

MICROCOSMS AND CHROMATOGRAPHY

The serum bottles served as aerobic soil microcosms; they were dosed without prior exposure to acetate (no acclimation). The spiking liquid was a nominal 1000 mg/L solution of reagent grade glacial acetic acid, buffered to its nonvolatile (ionic) acetate state with sodium bicarbonate to a pH of 6. The spiking solution was added while the bottles were held sideways using a Becton Dickinson 3-mL disposable sterile syringe with a bevel-tipped 20-gauge needle 0.064 m long in five separate injections spaced uniformly over the exposed surface of the soil. The soil was gently shaken to mix the spiking solution into the matrix with sufficient liquid added to bring the soil to about half saturation, facilitating sample extraction and analysis without unduly displacing oxygen from the porespace. Autoclaved microcosms were similarly spiked

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TABLE 1 Soil Characteristics and Calibrated Kinetics

Depth	Mean Grain	Fine	Moisture Content	pH	V	K
m	Size, mm[a]	Fraction[b]	kg water / kg wet soil		mg/l-hr	mg/l
0.025	0.80	0.152	0.0258	6.5	16.4	148
0.153	0.82	0.126	0.0496	5.5	5.29	68

[a]As fit with a Van Genuchten (4) distribution.

[b]Less than 0.15 mm.

to check for abiotic losses, and ample headspace existed in the microcosms to provide abundant oxygen.

Replicate bottles and abiotic controls were sacrificed at varying time intervals by the addition of 6 mL of distilled water to dissolve the microcosm fluid, followed by extraction (agitation, centrifugation, and filtration). The filtrate (0.9 μL) was then injected with a 0.1-μL plug of oxalic acid through a flash vaporization injector at 200°C into a Perkin Elmer Sigma 1 gas chromatograph (GC) using a 2-μL Hamilton 7000 series syringe with a Chaney adaptor. The oxalic acid plug lowered the pH to below 2, converting essentially all the acetate into its volatile acetic acid form for GC analysis in a 1.83-m-long, 2 mm ID packed glass column in a constant oven temperature of 165°C. A 25-mL/min zero-grade nitrogen gas flow carried the separated sample to a flame ionization detector set at 250°C, and daily calibration curves related instrument response to acetate concentration. Blanks and replicate injections were run routinely to verify quality control and instrument performance. Instrument sensitivity was about 1 mg/L, some three orders of magnitude below the maximum extract concentrations observed in the experiments.

DATA AND REACTION KINETICS

Figure 1 summarizes the degradation data observed at the two depths, along with calibrated Michaelis-Menton kinetic curves fit to the observations. Ambient concentrations were less than 1 mg/L at the site. The recovery efficiency from the abiotic controls varied between 91 and 118 percent and was used to adjust the biotic data as part of the calibration. In the assumed abundance of oxygen and nutrients, the substrate limited reaction is governed by a half-saturation constant K and a maximum reaction rate V in accordance with Alexander and Skow (5).

$$\frac{dc}{dt} = \frac{Vc}{c + K} \tag{1}$$

$$c = \frac{\text{mass acetate}}{\text{volume soil water}} \tag{2}$$

with concentration c and time t since spiking began. Oxygen limitations would impose an additional multiplying factor on the Michaelis-Menton term with its own half-saturation constant (6). In this absence of this effect, the theoretical degradation rate yields a temporal decay of observed concentration when Equation 1 is integrated from its initial concentration c_0 to any subsequent condition (7)

$$t = \frac{K}{V}\ln\left(\frac{c_0}{c}\right) + \frac{c_0 - c}{V} \tag{3}$$

The half-saturation constant and maximum reaction rate values cited in Table 1 were used to zero the error mean and

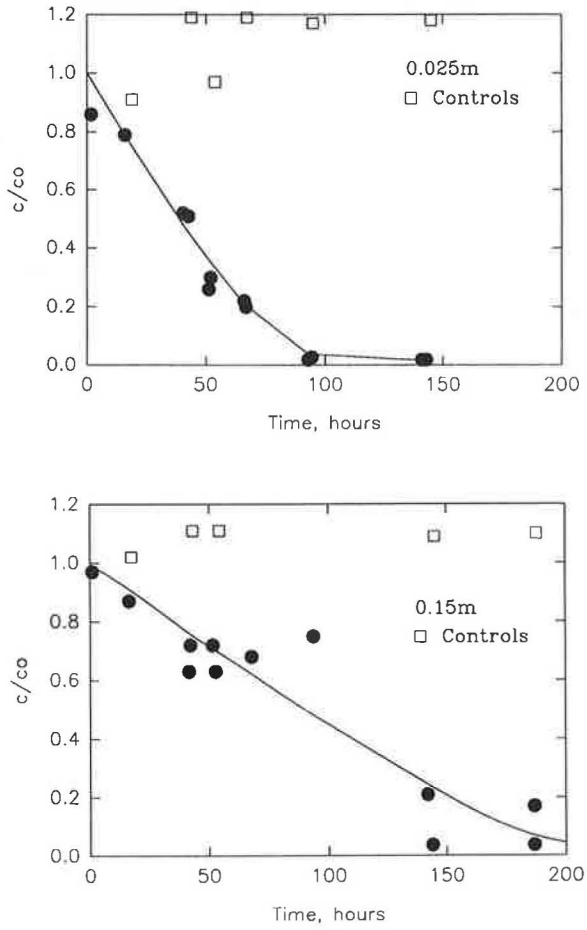

FIGURE 1 Observed (circles) and predicted (curves) acetate concentration in soil microcosms as function of time for loam cover of road shoulder 0.025 m deep (*top*) and 0.15 m deep (*bottom*), adjusted for abiotic losses (squares); predictions reflect *V*- and *K*-values of Table 1.

standard deviation through a nested Fibonacci curve-fitting subroutine (*8*). The half-saturation constant varied from 70 to 150 mg/L, and the maximum reaction rate decreased from a high near surface loam value of 16.4 mg/L-hr to a lower value of 5.3 mg/L-hr near the sand interface. The respective one- and two-day half-lives implied by Figure 1 represent relatively rapid aerobic degradation in a natural setting.

DISCUSSION OF RESULTS

The experiments were run without acclimation to prior doses of acetate substrate and as such represent the initial response the roadside soil to CMA applications early in the salting season. Typically, the microbial population would grow in response to repeated exposures to the substrate (*5*), thereby increasing the speed of reaction so long as nutrients and oxygen are present in abundance. In the latter regard however, the high solubility of acetate and relative insolubility of oxygen (roughly 10 mg/L) suggest that oxygen may control the speed of the reaction in water saturated soil of low permeability. Thus the loam cover, which is likely to be saturated near the surface with deiced runoff due to its low permeability, may not perform at the rapid rates of Table 1 under field conditions. The sandy fill is much more permeable than the loam and is considerably drier (samples collected in February 1991 contained a moisture content of 0.035 kg water/kg wet soil in the sand compared with 0.17 in the loam). Oxygen should not limit the degradation rate in the sand as a consequence; a comparable set of microcosms is currently being run on the sandy fill to quantify its kinetics.

Approximate calculations suggest that there is enough oxygen in the unsaturated zone to satisfy the estimated 30 000 kg of acetate that annually infiltrates the shoulders and median of the highway in the survey area, which is 1930 m long and 100 m wide. The stoichiometry for complete aerobic mineralization of acetate is given by

$$2C_2H_3O_2^- + 3.5O_2 \rightarrow 3H_2O + 4CO_2 \quad (4)$$

Thus 0.95 kg of oxygen are required to consume 1 kg of acetate, corresponding to an annual demand of about 28 000 kg oxygen imposed by CMA application in the study area. Allowing for a 30 percent reduction of oxygen through the root zone due to ambient plant and soil activity (*9*), the 5-m-deep, 0.20–air porosity unsaturated zone would contain 37 000 kg of O_2 in the absence of CMA loading. Thus aerobic conditions are expected to prevail in the unsaturated zone.

If the microbes are rapid enough (and the infiltration rate is slow), the acetate will degrade before the percolation reaches the water table and the deficit of oxygen will not extend to the underlying unconfined aquifer. One would then expect a winter deficit of oxygen in the unsaturated zone due to CMA degradation, followed by diffusive reaeration in drier summer and fall months. Rapid infiltration and slow reactions, on the other hand, will permit acetate penetration to the water table with a resulting oxygen demand on the groundwater. The interaction of reaction and infiltration is currently being modeled mathematically in order to quantify the transport processes and potential oxygen demand at the research site.

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REFERENCES

1. I. L. Stevenson and G. H. Katznelson. The Oxidation of Ethanol and Acetate in Soils. *Canadian Journal of Microbiology*, Vol. 4, 1958, pp. 73–79.
2. B. H. Chollar. Federal Highway Administration Research on Calcium Magnesium Acetate—An Alternative Deicer. *Public Roads*, Vol. 47, 1984, pp. 113–118.
3. R. R. Horner. *NCHRP Report 305: Environmental Monitoring and Evaluation of CMA*. TRB, National Research Council, Washington, D.C., 1988.
4. M. T. Van Genuchten. A Closed Form Solution for Predicting the Hydraulic Conductivity of Unsaturated Soils. *Soil Science Society of America Journal*, Vol. 44, 1980, pp. 892–898.
5. M. Alexander and K. M. Skow. Kinetics of Biodegradation in Soil. *Reactions and Movement of Organic Chemicals in Soils*. SSSA, Madison, Wis; 1989, p. 243–269.
6. F. J. Molz, M. A. Widdowson, and L. D. Benefield. Simulation of Microbial Growth Dynamics Coupled to Nutrient and Oxygen Transport in Porous Media. *Water Resources Research*, Vol. 22, 1986, pp. 1207–1216.
7. D. W. Ostendorf and D. H. Kampbell. Bioremediated Soil Venting of Light Hydrocarbons. *Hazardous Waste and Hazardous Materials*, Vol. 7, 1990, pp. 319–334.
8. G. S. G. Beveridge and R. S. Schechter. *Optimization: Theory and Practice*. McGraw-Hill, New York, N.Y., 1970.
9. D. W. Ostendorf and D. H. Kampbell. Biodegradation of Hydrocarbon Vapors in the Unsaturated Zone. *Water Resources Research*, Vol. 27, 1991, pp. 453–462.

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