Environmental Effects of Alternative Deicers: Review and Assessment Method for Calcium Magnesium Acetate Biochemical Oxygen Demand Applied to Illinois Example Case

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A modeling-based method for assessing the potential impact of calcium magnesium acetate (CMA) on the dissolved oxygen in streams through biodegradation is presented. The method was applied to two example Illinois streams—the Kaskaskia River and the Boneyard-Saline Branch-Salt Fork-Vermilion river system, both of which receive urban and rural runoff. These two examples were chosen as pessimistic, involving small streams potentially receiving relatively large amounts of CMA biochemical oxygen demand. The method predicts that the oxygen degradation in the stream may be severe under the worst conditions, which involve the largest number of small successive snowfalls since records have been kept, after each of which CMA is assumed to have been applied, as well as stream ice cover, which prevents reaeration. Both example streams are predicted to go anaerobic over part of their length. However, if only the stream ice cover is assumed not to exist, thus allowing aeration, the dissolved oxygen impact is, although significant, insufficient to violate the prevailing stream standard of 5 mg/L. The results suggest that in Illinois streams the oxygen-depletion impact of CMA may be severe but that such instances will be relatively uncommon; more often the impact will be well within that which can be assimilated by the stream.

Highway administrators currently face a dilemma in choosing a method to deice winter roads. Direct costs of salting, usually with rock salt (sodium chloride), are relatively low, but these costs exclude damage to vehicles, highways, bridges, and the environment. If external costs are included, the total cost of salting increases considerably. In 1976, for example, this larger cost for the United States was estimated at nearly $3 billion—15 times the costs for materials, storage, and application (*1*). On the other hand, the public demands safe roads throughout the year, requiring that a deicing agent be used to clear winter roads. Past attempts to lower the total costs of deicing have focused on reducing the amount of salt applied on roads; these strategies often either failed to reduce significantly total salt applications or resulted in an inferior level of winter road safety.

Some alternative deicers are less corrosive than salt, but they have higher initial costs. In another paper in this Record, Gingrich et al. address whether the increase in the initial cost of alternatives is less than the savings in vehicle, highway, and bridge damage that would result from their widespread use. The environmental effects of these alternatives may be qualitatively different, rendering comparison difficult. The most popular of such deicers is calcium magnesium acetate (CMA). Although it is a salt, its potential environmental effects are generally different from those of salt. It damages vegetation and soil to a much lesser extent than salt (*2*), causes less ion mobility (*3*), but may have a somewhat greater impact on phytoplankton, invertebrates, and fish (*2,4,5*). Additionally, it will deplete oxygen from streams and lakes by aerobic biochemical degradation of the acetate ion, which is readily and rapidly used by aerobic bacteria (*6*). Reviews of environmental effects of alternative deicers are presented by D'Itri (*7*), TRB (*8*), and Goldman and Malyj (*9*). A number of papers assess the biological degradation and potential oxygen-depleting effects of CMA-laden runoff in sewage treatment works (*10,11*), ponds and lakes in which complete mixing is assumed (*2,6*), and soil (*3,12*). However, the authors are unaware of any studies of these problems in natural streams.

This paper reports on a quantitative modeling study focusing on the oxygen-depleting effect of CMA in two Illinois streams: the Kaskaskia River and several tributaries and a stretch of the (southeastern) Vermilion River. The next section presents a modeling-based method for assessing the potential impact of CMA on the dissolved oxygen (DO) in streams through biodegradation.

OXYGEN-DEPLETION EFFECTS OF CMA FOR ILLINOIS EXAMPLE CASES

In this section, we describe a modified Streeter-Phelps (*13*) model that is used to predict the DO in a stream. The model

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uses the standard method of characterizing aerobically biodegradable waste in terms of its biochemical oxygen demand (BOD), the amount of oxygen it would consume under microbial action in a sealed container. The model is applied to two example cases in Illinois. The Streeter-Phelps model is quite venerable and simple, although the modifications to accommodate other effects besides point sources of BOD are more recent and add to its sophistication. Nevertheless, it remains one of the most useful tools available to estimate the impact on water quality of BOD discharges, because it requires the evaluation of so few parameters. More sophisticated models were available to the authors, but calibrating such models was beyond the scope of the research project.

Modeling Method

The model, which accounts for tributary flow and multiple point sources of BOD along the length of the stream, is given by the following recursive equations. Let D_j be the DO deficit, that is, the difference between the DO and the saturation DO, at the downstream end of any segment of the stream (referred to as a reach) j. Then

$$D_j = \frac{L_{j-1}Q_{j-1} + \ell_j(Q_j - Q_{j-1})}{Q_j} h_j + \frac{D_{j-1}Q_{j-1} + d_j(Q_j - Q_{j-1})}{Q_j} g_j$$

where

$$L_j = \frac{L_{j-1}\,Q_{j-1} + \ell_j\,(Q_j - Q_{j-1})}{Q_j} f_j$$

$$f_j = e^{-k_{rj}t_j}$$

$$g_j = e^{-k_{aj}t_j}$$

$$h_j = \left(\frac{k_{dj}}{k_{aj} - k_{rj}}\right)(e^{-k_{rj}t_j} - e^{-k_{aj}t_j})$$

k_{dj}, k_{rj} = BOD decay and removal coefficients in reach j, respectively;
t_j = travel time;
k_{aj} = reaeration coefficient in reach j (the four previous parameters are assumed uniform within reach j);
Q_{j-1} = streamflow at downstream end of reach j, so that $(Q_j - Q_{j-1})$ is the combined flow of all tributaries entering reach j;
L_j = BOD concentration at downstream end of reach j; and
ℓ_j, d_j = BOD and DO deficit concentrations in combined tributaries to reach j, respectively.

The model assumes that the BOD decay is a first-order reaction and, combining that assumption with the principle of superposition, allows multiple point sources of BOD along the length of the stream. Longitudinal mixing in the receiving stream is assumed negligible, which allows the use of this steady-state model for what is an inherently unsteady process. This assumption, though not entirely justified for a slug input such as is modeled here, is chosen because it is pessimistic. Furthermore, data on longitudinal dispersion coefficients were unavailable for the streams modeled.

The principal mechanisms for the effect of CMA on DO are (a) the rate of biodegradation by microorganisms in the stream, (b) the rate of replenishment of oxygen from atmospheric reaeration, and (c) the amount of CMA entering the stream. These mechanisms are represented by the model, and parameters are associated with each.

Selecting Model Parameters

Connolly et al. (*6*) report on a laboratory batch reactor experiment showing that the decay coefficient, k_d, of CMA in water (and presumably microorganisms) from a small stream tributary of the Scituate Reservoir in Rhode Island is 0.0326 per day at 2°C. However, Wright and McDonnell (*14*) report a streamflow-dependent formula for the decay coefficient that yields decay coefficients of the same order of magnitude or slightly larger than those reported by Connolly et al. (*6*). The Wright and McDonnell estimate was adopted as pessimistic (*14*).

The rate of atmospheric reaeration is characterized by the reaeration coefficient, k_a. The model estimates the reaeration coefficients by the O'Connor and Dobbins formula (*15*). The model adjusts both the decay and the reaeration coefficients for variations in water temperature according to the exponential formula (*16*). The temperature correction factors are taken as 1.047 for the decay coefficient and 1.024 for the reaeration coefficient.

Estimating Delivery Rate of CMA

The quantity of CMA entering the stream depends on (a) the area of treated roadway that drains to the stream, (b) the rate and frequency of application of the deicer, (c) the route and the rate of transport from the roadway to the stream, and (d) the extent of biodegradation along the route of transport.

When CMA is transported from the treated roadway to the stream, some CMA may be biodegraded in soil between the road and the stream. To be pessimistic, however, the model assumes no degradation to occur between the road and the stream. This assumption, admittedly pessimistic, might be accurate during rapid snowmelt events during which the CMA-laden runoff predominately travels rapidly over land and through ditches rather than slowly through soil.

The model uses a factor of 0.72 to convert initial CMA concentration to ultimate BOD (*2*). The streamflow data are extracted from the records of streamflow compiled by the U.S. Geological Survey. Ungauged flow rates are estimated from flow rates at nearby gauging stations in proportion to the drainage area. The model also requires a description of the hydraulic geometry along the length of the stream. The hydraulic parameters are adopted from Stall and Fok (*17*).

The would-be CMA concentration after a snowmelt event is estimated as follows: It is assumed that the mass of CMA on the road just before the snowmelt event is known. Because the streamflow upstream of the uppermost stream gauge is unknown, minimal biodegradation of CMA between its point of origin and that point is assumed. Hence, it is assumed that biodegradation commences at the uppermost stream gauge. From topographic maps, the amount of CMA in each stream catchment can be determined. A snowmelt event is identified from the record as a period in which the air temperature increased above freezing, the snowpack decreased, and the streamflow of the receiving stream increased.

The snowmelt hydrograph (Figure 1) is decomposed as follows: The streamflow before the snowmelt event is attributed to groundwater accretion and is called the base flow, B. The excess streamflow during that period is attributed to snowmelt and is assumed to carry a constant concentration of CMA. Therefore, the concentration of CMA in the CMA-laden water flowing into the stream during the entire snowmelt event is calculated as the mass of CMA on the roads in the basin, M, divided by the volume of water in the hydrograph above the base flow. This volume, V, is mathematically the integral of the streamflow Q minus the base flow B over time. The actual concentration of CMA in the stream, then, varies over time, depending what fraction of its flow is from the snowmelt containing CMA and what fraction is from groundwater, which is assumed not to contain CMA. Thus, the concentration of CMA in the stream at any time is given by

$$C = (Q - B)M/[Q \int (Q - B)\mathrm{d}t]$$

To be pessimistic, the maximum value of this concentration, which occurs at the peak of the hydrograph, is used in determining the headwater BOD in the modified Streeter-Phelps equation. Under the assumption of zero longitudinal dispersion, the minimum DO would occur as this slug of water passed through the stream system.

Occasionally, the streamflow in the hydrograph does not return to its antecedent (pre-snowmelt event) value. (It is likely that some of the water is being held up in shallow groundwater.) In such cases, the base flow is taken as the antecedent flow and the streamflow is artificially returned to this value at the time of the first occurrence of a zero-depth snowpack. This is a pessimistic approach in that it assumes the CMA to be delivered to the stream more rapidly than it actually is.

This method assumes that the snow containing CMA melts at the same rate as other snow, which may not be an accurate assumption. The roadside snowpack contains a melting agent that lowers its melting point and might cause it to melt more quickly. It is assumed, however, that this will not occur to any significant degree, since in any such melting the CMA solution would mix with more unmelted snow, thus preventing its progress toward the stream until the air temperature is high enough to melt all the snow. Instead, the roadside snowpack, because it has a much lower surface-to-volume ratio, may actually melt more slowly than a uniform snowpack covering the land, despite containing a melting agent. Thus the assumption of a uniform rate of melting for all snow is seen as pessimistic in that it overestimates the rate at which CMA is delivered to the stream. If the peak CMA concentration occurs either before or after the peak streamflow, the concentration throughout the snowmelt event will be less than estimated by this method.

Example Cases

Both example cases are chosen to represent worst-case scenarios for the oxygen depletion effects of CMA and are characterized by small streams being polluted by relatively large amounts of BOD associated with CMA use in an urban area. Figure 2 shows the locations of the two cases. The first is an upper reach of the Kaskaskia River in Illinois. Within this example, two scenarios were simulated; the first includes CMA BOD from urban sources in west Champaign, Illinois; rural sources in the Kaskaskia basin; and sewage BOD from the southwest treatment plant of the Urbana-Champaign Sanitary District. The second includes only the sewage plant and rural portions, excluding the urban runoff.

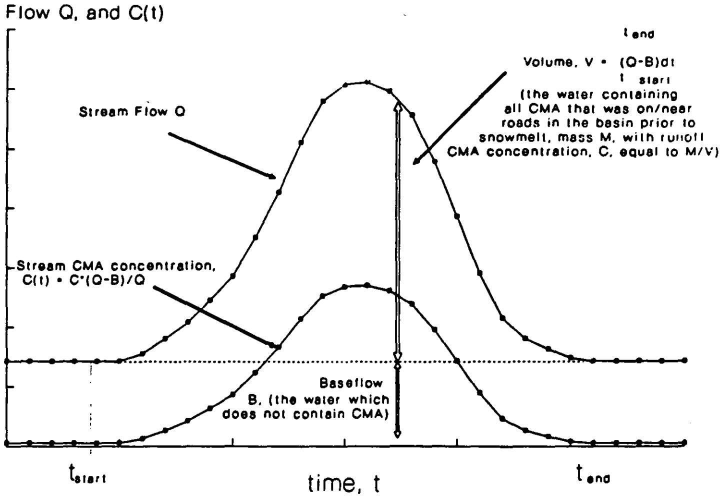

FIGURE 1 CMA delivery determined from decomposition of snowmelt hydrograph.

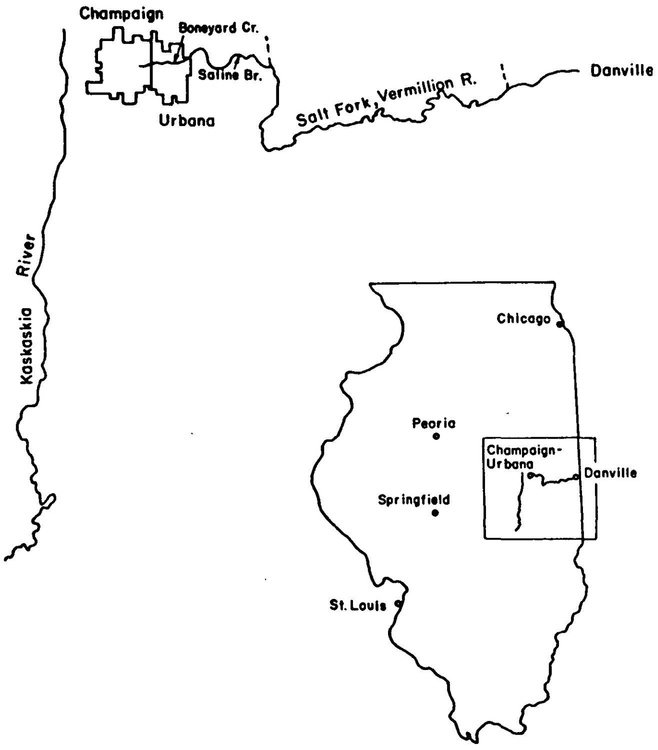

FIGURE 2 Locator map of example cases.

The second case is the Vermilion River in the Wabash River Basin in Illinois. It includes Boneyard Creek, Saline Branch, Salt Fork, and Middle Fork Vermilion River. Boneyard Creek, which is a small stream passing through Champaign-Urbana, Illinois, receives a large portion of the street runoff from those cities. For this example, only one scenario was simulated, which included the urban, rural, and sewage portions of runoff for this basin.

For both cases, the worst period of snowmelt from the historical record was December 1, 1983, through January 5, 1984. During this time, there were five relatively light snowfalls, interspersed with and followed by closely spaced melting events, resulting in what would have been a high concentration of deicer in the melt runoff. Each snowfall was assumed to have been followed by the application of deicer at the equivalent salt rate of 250 lb/lane-mi (71 kg/lane-km). This is the rate used by most counties in Illinois and most Illinois Department of Transportation districts. On the basis of the substitution rates discussed earlier, a CMA application rate of 1.5 times that of road salt, or 375 lb/lane-mi (107 kg/lane-km), is assumed.

Results

During a thawing period, it is possible to have both delivery of water from snowmelt and an ice-covered stream. This is considered the worst case; there is no atmospheric reaeration, and replenishment of oxygen is entirely due to DO in the tributaries. Thus, for both the Kaskaskia and Vermilion cases, two conditions of atmospheric reaeration were analyzed in the BOD modeling: aerated and ice-covered.

Kaskaskia River

Figure 3 illustrates the modeling results as DO profiles for the Kaskaskia River. Because of the high spatial density of deicer-treated highways and the low flow in the river, the BOD in the stream due to CMA is highest near the head of the river (near Bondville and Ficklin). The maximum CMA BOD entering the river occurs near Bondville; it is about 20 mg/L, depending on the scenario. The DO in the river is completely depleted under the most pessimistic conditions of full urban runoff and ice cover. The DO profile of the river when it is aerated is higher than that when it is ice-covered, and it is particularly significant near Bondville and Ficklin. This shows that the potential oxygen depletion of CMA in the river may be substantially reduced by atmospheric reaeration. The figure also shows that the urban portion of CMA runoff contributes substantially to the BOD load. The effect of the sewage discharge was included, but it was not substantial.

Boneyard–Saline Branch–Salt Fork–Vermilion Basin

Figure 4 illustrates the results of the BOD modeling for streams in the Boneyard–Saline Branch–Salt Fork–Vermilion basin.

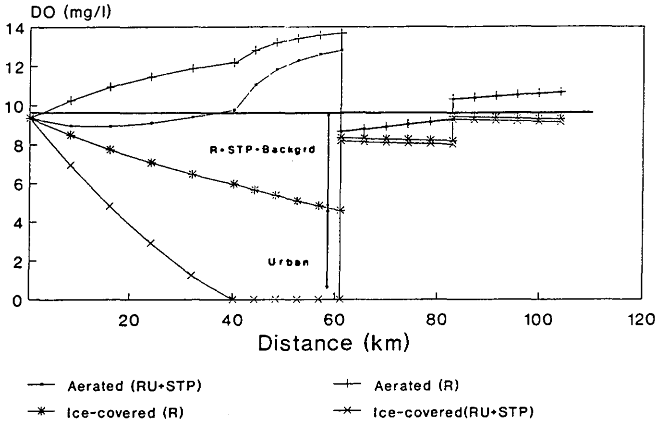

FIGURE 3 DO profiles for Kaskaskia River.

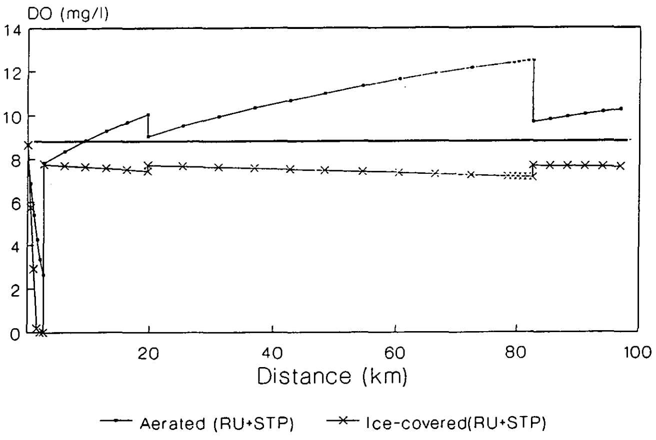

FIGURE 4 DO profiles for Boneyard–Saline Branch–Salt Fork–Vermilion system.

Because of the high density of roadways from which Boneyard Creek receives CMA, the CMA BOD entering the Boneyard Creek at Champaign-Urbana is as high as 124 mg/L. This high BOD has the potential of complete oxygen depletion at certain locations when the streams are ice-covered. When they are aerated, there is substantial DO depletion in Boneyard Creek (DO falls from 8.6 to 1.4 mg/L), but the DO increases to above 7.8 after Boneyard Creek enters the Saline Branch.

FINAL REMARKS

The modeling results presented in this paper suggest that under certain circumstances, CMA may deplete oxygen in streams substantially. The scenarios evaluated were deliberately crafted to be quite pessimistic. The examples were thought to be the most pessimistic in Illinois. Both involved the same urban area, Champaign-Urbana, discharging street runoff to a small stream. Such a case—that is, a relatively large city located on a small stream—is generally the most critical for deicer impact on the water quality of the stream.

The pessimistic assumption of ice cover during a snowmelt event is somewhat unlikely, since snowmelt is often accompanied by ice breakup. Nevertheless, after particularly severe winters with thick stream ice cover, snowmelt runoff can increase streamflows while the ice remains intact. Moreover, even when stream ice is gone, ice cover on lakes may remain.

The assumption of no degradation of acetate between the road and the nearest gauged stream is somewhat pessimistic in a rural setting. Soil microbial activity may significantly reduce the amount of CMA that will actually reach the streams. However, this effect is less pronounced in urban areas where a large portion of the flow is on streets and in storm sewers, where little such rectification occurs.

The assumption of zero longitudinal dispersion is pessimistic, but it is more accurate for the smaller upstream reaches of streams in which the greatest DO loss was predicted. The model did not include sediment oxygen demand, parameter values for which were unavailable for the two Illinois streams modeled. Accounting for this effect would decrease the amount of CMA-laden runoff that the stream can accommodate without violating the DO standard. An analytical mathematical model for DO that accommodates longitudinal dispersion is readily available but the dispersion parameter is not, and evaluating it was beyond the scope of this project.

Although a definitive verdict on the effect of CMA on DO in streams will have to await further, and probably empirical, study, the results presented here suggest that the oxygen-depletion effects of CMA in natural streams may be of concern, but primarily in cases of urban areas on small streams.

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