Changes in water quality in an urban stream following the use of organically derived deicing products[1, 2]

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ABSTRACT

Willow Brook receives runoff from Cooperstown, NY and flows into Otsego Lake, a phosphorus limited, mesotrophic waterbody. Between 1992 and 1998, the Village of Cooperstown's winter road management policy included plowing and applying abrasives (particulate material intended to increase traction) mixed with enough salt to minimize clumping. Between 1998 and 2002, Ice Ban Magic™ and Magic Minus Zero™, both organic deicers mixed with magnesium chloride, were applied experimentally in conjunction with abrasives and salt. During the winter of 2002/2003, road treatment consisted solely of applications of salt which had been treated with Magic Minus Zero™. Precipitation-based monitoring on Willow Brook conducted between 1991 and 2003 revealed significant declines in the export of total phosphorus, despite elevated phosphorus levels in Ice Ban Magic™ and Magic Minus Zero™, and suspended sediment as the volume of abrasives applied to roads was reduced. Chloride levels are increasing, however. The implicit trade-offs between potential pollutants and the cost of road management in cold climates are acknowledged for management of transportation safety .
Key Words: phosphorus, suspended sediment, chloride, winter road management, abrasives, Ice Ban

INTRODUCTION

Otsego Lake (Otsego County, NY; 42°40'N-74°55'W) is a deep (50.5 m max) dimictic waterbody of glacial origin, which forms the headwaters of the Susquehanna River. It is generally considered mesotrophic, based upon transparencies and rates of hypolimnetic oxygen depletion, and its production is limited by phosphorus (Harman et al. 2002). Willow Brook drains 375 ha (927 ac) of Otsego Lake's 18,820 ha (46,480 ac) watershed. With the Village of Cooperstown located near the stream's mouth, it is the only drainage basin typifying urban runoff. Research conducted between 1991-93 indicated that the export rates of total phosphorus and suspended sediment (units per area of drainage basin) were substantially higher from Willow Brook than from any other tributary of Otsego Lake (Albright 1996). By comparison, the drainage basin of Gimmerglen Creek, adjacent to that of Willow Brook and of almost identical size, but having almost no urban component and receiving minimal applications of deicers, delivered approximately 20% as much total phosphorus and 15% as much sediment as did Willow Brook.

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During 1991-93, winter road management depended upon the use of abrasives. Though commonly referred to as "sand", the abrasives used locally contain high fractions of clay and silt (particles < 0.06-2 mm). Because research suggested that most of the phosphorus and sediment load from Willow Brook was associated with winter and springtime runoff events which included snowmelt, these materials were suspected as being a major source. Investigations showed that the abrasives being used for winter road management had a large fraction of easily suspendable particulates and associated phosphorus (Albright et al. 1994), further implicating them as important sources of these pollutants.

While phosphorus and sediments are pollutants of primary concern to Otsego Lake (and, presumably, to other phosphorus-limited water bodies), other issues related to various winter road management strategies, such as highway safety, costs, human health and environmental concerns, warrant attention. The use of salt (sodium chloride) as a road deicer began in the 1940s and was widespread by 1970, when many communities adopted a "bare pavement policy" (Bubeck at al. 1971). Since 1970, approximately 9 million metric tons (10 million tons) of salt have been applied annually to roads in the United States (Transportation Research Board 1991). New York State is among the heaviest users of salt, applying, on average, 9.3 metric tons· lane $km^{-1}\cdot year^{-1}$ (16.6 tons· lane $mile^{-1}\cdot year^{-1}$). The widespread use of salt is a function of its low cost and general effectiveness at moderate temperatures. However, because the deicing action of salt diminishes below -12^{o} C (10^{o} F), additives or abrasives are typically used to enhance traction and/or melting (Transportation Research Board 1991). Temperatures well below -12^{o} C are common in the Cooperstown area (Blechman unpubl.).

One drawback associated with road salt is its corrosivity to vehicles, bridges and concrete (Transportation Research Board 1991; Burtwell 2001). When expenses related to protection from damage by salt (anti-corrosive measures), as well as actual damage caused by it, are incorporated into its overall cost, salt prices increase from about $30 to $385-$735 (1990 US dollars) per ton (Transportation Research Board 1991).

Numerous articles have inferred substantial negative environmental implications of using road salt (Horner and Brenner 1992; Environmental Protection Agency 1999; Ormsby 1999; Dionysiou et al. 2000). However, evidence of the scope of this claim seems unsubstantiated. For example, accumulated sodium has been demonstrated to decrease permeability and increase the alkalinity of soils, reducing fertility (Transportation Research Board 1991), but this is generally confined to within a few m of the road edge and within 1 m depth (Prior and Berthouex 1967). Similarly, while salt-induced damage to roadside vegetation through osmotic stress in the root zone and by dehydration of foliage and branches by salt spray has also been documented (Hanes et al. 1970; Transportation Research Board 1991), research by Gidley (1990) suggests that these effects are confined to 3-12 m of the roadside (depending primarily on slope).

Chloride concentration spikes from road runoff in aquatic environments are generally limited to small roadside streams. Although several studies in New York and Illinois have documented chloride concentrations exceeding 500 $mg\cdot L^{-1}$ (Transportation Research Board 1991), the duration of these spikes is generally limited to the early stages of snowmelt events, after which they are diluted by increased flow (Hutchinson 1970). While concentrations of several thousand mg·L^{-1} chloride have been reported, these are believed to be attributable to improper salt storage rather than its actual application (Hanes 1970). Runoff from uncovered salt piles can reach 134,000 mg·L^{-1} chloride (Bertram and Wolf 2001).

Given the above, there seems to be little evidence that salt, when used responsibly, poses a wide ranging threat to aquatic life. Blasius and Merritt (2002) conducted field and laboratory research on the effects of salt on benthic macroinvertebrates, and reviewed similar research provided in the literature. They compared the benthic communities upstream and downstream from point sources of road salt in two Michigan streams. Differences in the communities were deemed attributable to siltation by road abrasives and erosion rather than by salt. The lowest chloride concentration that elicited behavioral responses by invertebrates in their laboratory studies was 1,000 mg·L^{-1} NaCl (606 mg·L^{-1} chloride). This triggered increased drift (wherein organisms left benthic refuges) by the amphipod *Gammarus pseudolimnaeus*. The LC_{50} (concentration causing death in half the study animals) for this organism was 7,700 mg·L^{-1} NaCl (4,670 mg·L^{-1} chloride). The lowest salt concentration resulting in 50% mortality of any invertebrate species in studies they reviewed was 2,400 mg·L^{-1} NaCl (1,450 mg·L^{-1} chloride) for the mayfly *Hexagenia limbata*. However, this was at 26^{o}C, a temperature much higher than that likely to be encountered during periods of road salt runoff. At 18^{o}C, the LC_{50} for this species was 6,300 mg·L^{-1} NaCl (3,800 mg·L^{-1} chloride).

Concerns have also been raised regarding salt contamination of groundwater as it relates to human health. Hulling and Hollocher (1972) estimated steady-state concentrations of salt in groundwater in a suburban area near Boston, Massachusetts based on aerial salt application rates, estimating an infiltration rate of 35% and a residence time exceeding one year. Despite application rates near Boston being among the highest in the nation, at 12.4 metric ton·lane km^{-1}·year^{--1} (22 ton·lane mile^{-1}·year^{--1}), their steady state estimate was only 160 mg·L^{-1} NaCl (100 mg·L^{-1} chloride). Concentration guidelines for consumption of both chloride and sodium are 250 mg·L^{-1} (US Public Health Service 1962; France 1996), which are based upon aesthetic (i.e., taste) rather than health reasons (though for those on low-sodium diets, water having < 20 mg·L^{-1} sodium is recommended (American Heart Association 1957)). Because sodium intake from all beverages account for 1-2% of total human intake (Transportation Research Board 1991), adverse health effects from groundwater seem unlikely.

In the 1980s, the Federal Highway Administration initiated research to investigate alternative road deicers having lower costs, corrosivity and/or environmental impacts than sodium chloride (Transportation Research Board 1991; Horner and Brenner 1992). The one considered most promising was calcium magnesium acetate (CMA), produced by reacting dolomitic lime with acetic acid. Research on environmental implications of CMA indicate that, at concentrations well beyond those expected in runoff, soils would experience only negligible changes in permeability and fertility and no negative effects would be imparted on terrestrial vegetation and aquatic organisms (including *Daphnia magna*, rainbow trout (*Salmo gairdneri*) and fathead minnow (*Pimephales promelas*)) (Transportation Research Board 1991; Horner and Brenner 1992).The only recognized potential threat to aquatic organisms is oxygen loss through the decomposition of acetate should it accumulate in poorly flushed waterbodies. No human health issues have been linked to CMA.

Despite a lack of environmental concerns, use of CMA is currently limited due to: 1) its slower, more limited deicing action at lower temperatures (< -5^{o}C; 23^{o}), necessitating the use of 1.7 times that of salt to achieve comparable melting, and 2) its substantially higher cost, at $925-$2450 (2000 dollars) per ton, making the effective cost-per-ton equivalent of CMA to salt approximately $1575-$4165 per ton (year 2000 dollars). Even after factoring in the associated costs of using salt (protection from corrosivity and damage by it), its overall cost is considerably less. Because of these reasons, the Committee on the Comparative Cost of Rock Salt and Calcium Magnesium Acetate for Highway Deicing recommended that CMA not be considered for a general replacement of salt (Transportation Research Board 1991). It is worth noting that research on advances in the production methods of generating acetate, both by a gasification/fermentation process of domestic waste and by cheese whey fermentation process, have resulted in a predicted cost reduction to approximately 20% of that currently available (Ormsby 1999). If those cost reductions are realized, CMA might be an attractive deicer in environmentally –sensitive areas.

Recently, mixtures of magnesium chloride and organic byproducts of either fermentation or processing of corn (or, less commonly, barley or milk; Environmental Technology Evaluation Center 1999), have been used as deicers. The organic derivative is generally mixed with equal parts of 26-30% magnesium chloride solution and is purported as being an anti-corrosive deicer which can be applied directly as a liquid or used to pre-wet salt, the latter designed to lower the effective temperature range of salt. This product was originally marketed under the name of Ice Ban Magic™ , more recently as Magic Minus Zero™ (hereafter, both products will be referred to as Magic™). An independent evaluation by the Highway Innovative Technology Evaluation Center (1999) found that Magic™, when used as a pre-wetting agent to salt, melted ice faster, penetrated ice deeper, and worked at lower temperatures than did straight salt. Field tests suggested enhanced performance of the mix, even when used at one-half the recommended rate (63 kg·lane km^{-1} (225 lb·lane mi^{-1}) vs 126 kg·lane km^{-1} (450 lb·mi^{-1})).

The primary concern among watershed managers for using Magic™ involves highly elevated phosphorus levels in the raw product (originally 2,500-5,500 mg·L^{-1}, more recently 70-100 mg·L^{-1}). However, most of the phosphorus reportedly is in the form of phytic acid (derived primarily from corn; HITEC 1999) which readily chelates divalent cations (Fe^{+2}, Ca^{+2}), forming compounds that are largely insoluble in water (Weast 1968; Graf 1986). It has therefore been suggested that most of the phosphorus in the product is not prone to runoff or to biological uptake upon reaching a waterway, though there is a paucity of information on this product in the literature. After conducting 96-hour static growth tests using Magic™ as a potential phosphorus source, Toxikon Environmental Sciences (1997) reported inhibition of growth, relative to dilution water controls, of the algae *Sekenastrum capricornutun* and *Microcystis aeruginosa* at all concentrations tested. Similar work using the same organisms, conducted by Auer and Heppelmann (unpublished), differed in that the assays were allowed to continue for several weeks. They also observed an early inhibitory effect on growth by Magic™, where test cultures lagged the control for about 14 days; following that, test cultures commenced growing and stabilized by day 25. This was interpreted as the phosphorus in the product being originally in an unavailable form, but over time was released by microbial action.

Locally, some additive to salt is necessary to achieve acceptable deicing action because temperatures < -12°C (10°F) prevail during winter months. Because the abrasives being used for road management were likely a major contributor of phosphorus and sediments to Otsego Lake, the Village of Cooperstown reassessed its winter road management practices. An experimental design was approved whereby, over time, the use of abrasives would be reduced and supplemented with Magic™ .

In order to characterize the efficacy of such an approach, this study evaluated total phosphorus and suspended sediment export, and mean event runoff, by Willow Brook during winter precipitation events involving snow melt. During this work, three different approaches were employed by the Village of Cooperstown regarding winter road management: 1) reliance upon abrasives having just enough salt to avoid clumping, 2) a reduction in abrasives and increased salt, coupled with liquid Magic™ spot applications and 3) complete reliance on salt that had been pre-wetted with Magic™. Comparing mean event export rates to mean event runoff between the three management strategies allowed for insight into which strategy will most reduce phosphorus and sediment to sensitive water bodies.

METHODS

Throughout the study, a Sigma 800SL™ programmable automated water sampler was stationed near the outlet of Willow Brook. A pressure transducer type integral flowmeter provided for sampling initiation and, along with data logging capabilities, for constant hydrological monitoring. Every effort was made to collect samples during each runoff event which included snowmelt during the study periods. However, weather conditions occasionally precluded this, a result of prolonged cold which would cause excessive ice buildup in the culvert which housed the pressure transducer. Damming by the ice produced erroneously high flow recordings, and cold temperatures disabled the sampler due to freezing intake lines. Therefore, although attempts were made to clear ice and thaw lines in preparation for a predicted event, data were restricted to somewhat milder conditions when the ice could be cleared.

During each runoff event (defined here as a discharge increase from pre-storm conditions by at least a factor of three for a duration of at least 0.25 days) a series of discrete samples (12-24) was collected. Sampling intensity was greatest (at 15 minute intervals) during the ascending phase of the hydrograph to address the "first flush" phenomenon. This situation is reflected by quicker responses in flow and nutrients during the earlier stages of an event, particularly in more urban settings (Beaulac and Reckhow 1982; Livingston and Cox 1985). Samples were composited in a flow- and time-weighted manner, resulting in one sample that reflected each runoff event. Total phosphorus concentrations were measured by single reagent ascorbic acid technique following persulfate digestion (APHA 1989); suspended sediment levels were assessed using the gravimetric method (APHA 1989).

Water quality data were compared over three time periods, each representing different strategies for winter road management in Cooperstown. Table 1 summarizes the mean annual volumes of salt, abrasives and Magic™ applied to the roads during each period (Coleman 2003). Mean runoff ($m^3 \cdot ha^{-1} \cdot day^{-1}$) during each storm event was considered the independent variable, which describes event intensity. Export rates of total phosphorus ($g \cdot ha^{-1} \cdot day^{-1}$) and suspended sediment ($kg \cdot ha^{-1} \cdot day^{-1}$) were considered to be dependent upon runoff. Applying a Kolmogorov-Smirnov one-sample test using the standardized residuals from the linear regression model showed that residuals were normally distributed ($p>0.05$). Therefore, correction for skewness was not necessary. Results of regression analysis between time periods were compared (ANOVA analysis) using Statgraphics Plus™ (Manugistics™ 1998).

Period	Salt (kg)	Abrasives (kg)	Magic™ (kg)
Period 1			
1992/93, spring 1998	28,700	1,413,300	0
Period 2			
1998/99, 2001/02	68,000	635,000	7,100
Period 3			
2002/2003	662,000	0	26,800

Table 1. Annual mean volumes (kg) of salt, abrasives and Magic™ applied to roads in Cooperstown during the three periods during which total phosphorus and suspended sediment export rates and runoff were evaluated in Willow Brook.

RESULTS AND DISCUSSION

Figure 1 compares runoff and total phosphorus export rates for the three time periods considered. Similarly, Fig. 2 compares runoff and suspended sediment export rates. Both regression analyses indicate sequential reductions in slope over time; that is, as the use of abrasives declined, a storm event of given intensity (defined by mean runoff) delivered less total phosphorus and sediment to Otsego Lake. Reductions in export of both total phosphorus and suspended sediment between those sequential time periods are significant (ANOVA, $p<0.01$), except for the change in total phosphorus export between time period 1 and 2 (ANOVA, $p>0.10$). Those reductions from period 1 to period 3 are highly significant (ANOVA, $p<<0.01$). The slope of the total phosphorus regression line in the most recent period (3) is about 30% of that which it had been during heavy abrasive use (period 1); for suspended sediment, period 3 dropped to about 15% of what it had been in period 1.

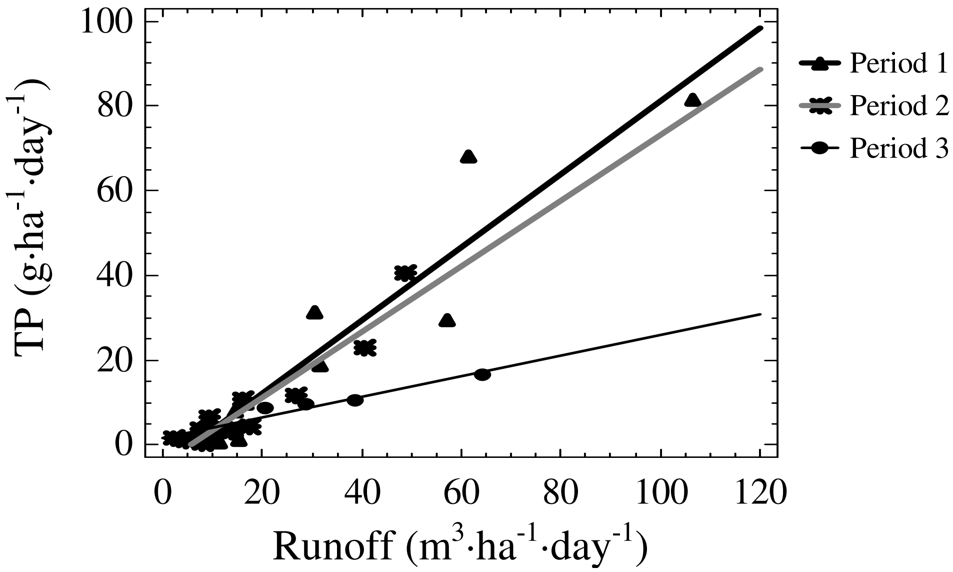

Figure 1. Comparison of mean storm event total phosphorus export (g·ha^{-1}·day^{-1}) and runoff (m^{3}·ha·$^{-1}$day^{-1}) between the three time periods studied. Period 1= abrasives+salt, Period 2= abrasives+salt+Magic^{TM} and Period 3= salt+ Magic^{TM}. The slope of Period 2 is not significantly different from Period 1 ($p>0.10$). Slope of Period 3 is significantly lower than Period 1 and Period 2 ($p<0.01$).

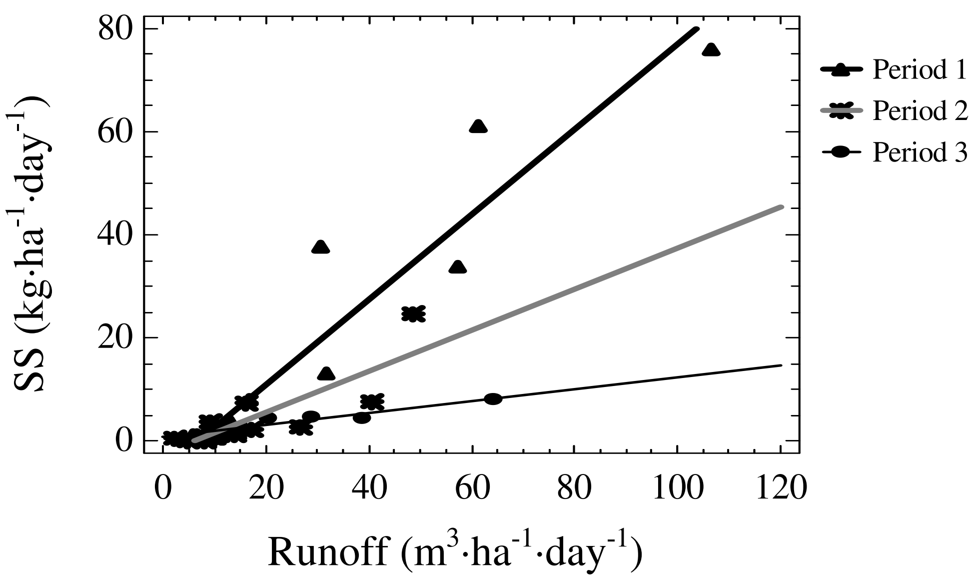

Figure 2. Comparison of mean storm event suspended sediment export (kg·ha^{-1}·day^{-1}) and runoff (m^{3}·ha·$^{-1}$day^{-1}) between the three time periods studied. Period 1= abrasives+salt, Period 2= abrasives+salt+Magic^{TM} and Period 3= salt+ Magic^{TM}. The slope of Period 3 is significantly lower than Period 2, which is significantly lower than Period 1 ($p<0.01$).

The management of Otsego Lake primarily focuses upon limiting phosphorus loading. Research presented here clearly implicates abrasives conventionally used for winter road maintenance as a significant source of that nutrient. Because Otsego Lake's algal production is limited by phosphorus, and because relatively small increases in phosphorus can stimulate algal production (Oglesby and Schaffner 1975), increasing salt use in lieu of using abrasives seems a wise management strategy. The addition of Magic™ (or, potentially, other salt additives) increases the melting effectiveness of salt at low temperatures, allowing for acceptable treatment at lower application rates than if only salt were used.

While not of concern locally in the short term, the excessive use of salt as a deicer is of potential consequence. Since 1996 the mean concentration of chloride of Otsego Lake has increased by approximately 1.0 $mg \cdot L^{-1}$ annually (Fig. 3) (Albright 2003), representing the addition of 640,000 kg (700 tons) of sodium chloride to the lake each year. Chloride concentrations in Willow Brook during winter thaws has exceeded 1,000 $mg \cdot L^{-1}$ for brief durations (Albright 1996), with unknown ecological ramifications. Also, groundwater samples in the watershed, which are expected to have had background concentrations similar to historic lake concentrations of 1-2 $mg \cdot L^{-1}$ (Fig. 3), from some near-lake wells have recently have been tested at 40-60 $mg \cdot L^{-1}$, presumably due to road salting.

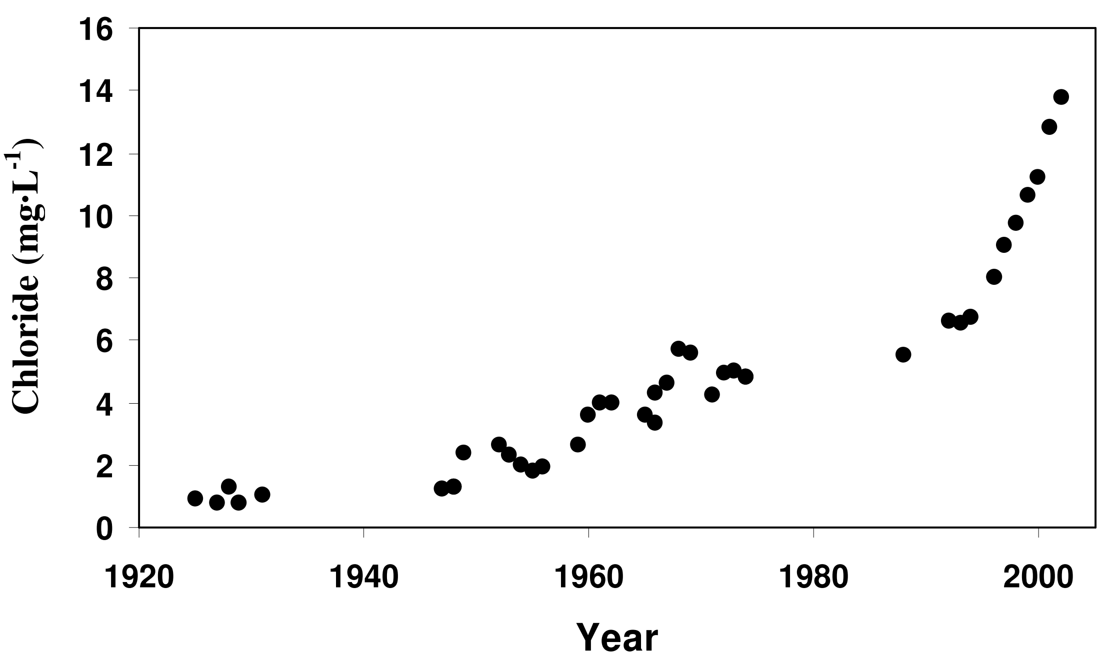

Figure 3. Mean chloride concentrations of Otsego Lake, 1925-2003. Points later than 1990 represent yearly averages (Albright 2003).

The benign nature of salt (compared, at least, to phosphorus) can be further exemplified by two other upstate New York Lakes, Seneca and Cayuga. Both are of similar origin to Otsego Lake, having been formed during Pleistocene glaciation, have similar morphology (though deeper, having maximum depths of 198.4 m and 133 m, respectively), and are phosphorus limited oligo-mesotrophic water bodies (Oglesby 1978; Schaffner and Oglesby 1978). However, a striking difference is notable in the chloride concentrations of these lakes, with Seneca having 160-165 $mg \cdot L^{-1}$ and Cayuga 81 $mg \cdot L^{-1}$. The bulk of the salt content is of natural origin, by the intrusion of saline groundwater and/or the actual intersection of salt strata by the lake basins. Despite chloride concentrations of up to an order of magnitude higher than that of Otsego, the communities of vascular plants, zooplankton and fish (Oglesby 1978; Schaffner and Oglesby 1978) are remarkably similar to those found in Otsego (Harman et al. 1997).

MANAGEMENT IMPLICATIONS

Currently, options for highway deicers are limited. While environmentally benign, CMA is prohibitively expensive for general use, though it may be appropriate in extraordinarily sensitive areas. A review of the literature does not suggest negative environmental impacts of aquatic communities by salt at concentrations expected from responsible handling and applications, which can substantially reduce waste and excessive runoff. This includes proper storage, the lack of which has been implicated for the loss of 5% of the total used in the US and is most often faulted for gross contamination of localized groundwater and small streams (Environmental Protection Agency 1999), as well as the maintenance and calibration of spreading equipment. Pre-wetting salt allows for better adhesion to road surfaces, and has allowed for an 18% reduction of salt in the UK (Burtwell 2001). Similarly, products such as Magic™ allow for improved action of salt, facilitating a reduction in the amount used, while eliminating the phosphorus and sediment inputs associated with abrasives.

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