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Monitoring Surface Water Chemistry Near Magnesium Chloride Dust Suppressant Treated Roads in Colorado

Betsy A. Goodrich, Ronda D. Koski, and William R. Jacobi* Colorado State University

Magnesium chloride (MgCl_2)-based dust suppression products are commonly used throughout western United States on nonpaved roads for dust suppression and road stabilization by federal, state, and county transportation agencies. The environmental implications of annually applying these products throughout spring and summer months on adjacent stream chemistry are not known. Sixteen streams were monitored biweekly for 1 to 2 yr in two Colorado counties for a suite of water quality variables up and downstream of nonpaved roads treated with MgCl_2 -based dust suppression products. Eight of 16 streams had significantly higher downstream than upstream concentrations of chloride or magnesium over the entire monitoring period ($p \leq 0.05$). Mean downstream chloride concentrations ranged from 0.17 to 36.2 mg/L and magnesium concentrations ranged from 1.06 to 12.8 mg/L. Several other ions and compounds, including those commonly found in dust suppression products such as sodium, calcium, and sulfate, were also significantly higher downstream at some sites. Downstream electrical conductivity (EC), chloride and magnesium concentrations were positively correlated with road surface area draining water toward the stream and yearly amount of MgCl_2 applied ($R^2 = 0.75, 0.51$ and 0.49 , respectively), indicating that road managers can limit the amount of product entering roadside streams by assessing drainage characteristics and application rates in best management practices. Although MgCl_2 -based dust suppressants did move into some roadside streams, the concentrations detected were below those reported to adversely affect fresh water aquatic organisms, but the ultimate fate of these ions in Colorado waterbodies are not known.

SOLUTIONS of MgCl_2 are effective road dust suppressants and help stabilize nonpaved roads (Sanders et al., 1997; Lunsford and Mahoney, 1998; Addo et al., 2004; Piechota et al., 2004). Dust suppressants are also used to control maintenance costs and erosion from nonpaved roads, and have associated economic and safety benefits (Addo et al., 2004). Fugitive dust from nonpaved roads can cause dangerous driving conditions, be detrimental to human health, and contribute to atmospheric particulate matter; therefore dust suppression is important to transportation departments, federal and state forest services, land developers, and private industries (Sanders et al., 1997; Addo et al., 2004; Singh et al., 2003; Piechota et al., 2004). Nearly 25% of the 2.5 million km of public nonpaved roads in the United States are treated with dust suppressants, and usage is increasing due to population growth and the need to suppress particulates in the interest of air quality, especially in arid and semiarid climates (Singh et al., 2003; Piechota et al., 2004).

When mixed with water, chloride salts dissociate into the chloride (Cl^-) anion and the corresponding cation (sodium [Na^+], calcium [Ca^{+2}], potassium [K^+], or magnesium [Mg^{+2}]). Organisms require these elements for optimal health, however, excessive amounts can disrupt normal metabolic processes (Evans and Frick, 2001; Environment Canada and Health Canada, 2001; Fischel, 2001; Lewis, 2001). Previous research has shown that repeated applications of sodium chloride (NaCl) for deicing control on paved roads can lead to elevated concentrations of chloride and sodium in the surface waters adjacent to roads (Howard and Beck, 1993; Evans and Frick, 2001; Environment Canada and Health Canada, 2001; Fischel, 2001; Bossong et al., 2003; Godwin et al., 2003; Capesius et al., 2005; Kaushal et al., 2005; Panno et al., 2006; Collins and Russell, 2009). Dissolved salt may alter the physical properties of surface water by increasing the density, resulting in salt accumulation in deeper waters (Environment Canada and Health Canada, 2001; Fischel, 2001; Lewis, 1999). The impact of MgCl_2 -based dust suppression product application on roadside adjacent surface water resources are not fully known, and determining if these products move into streams that pass under or are parallel to treated nonpaved roads in the western United States has not been studied (Addo et al., 2004).

Natural chloride inputs to Colorado streams through precipitation are minor, with concentrations ranging from 0.05 to 0.20 mg/L

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Abbreviations: EC, electrical conductivity; MgCl_2 , magnesium chloride.

(Bossong et al., 2003; Stevens, 2001; National Atmospheric Deposition Program/National Trends Network, 2007). In general, background concentrations of chloride in Colorado streams are <5.0 mg/L, depending on the geology of the area, but where human inputs have altered stream chemistry, concentrations have been measured up to 400 mg/L (Musselman et al., 1996; Bossong et al., 2003; Fischel, 2001; Stevens, 2001; Jassby and Goldman, 2003; Capesius et al., 2005). In other areas of North America, higher concentrations (more than 4000 mg/L chloride in winter months) have been measured in various watersheds, presumably from deicing salt inputs (Environment Canada and Health Canada, 2001; Kaushal et al., 2005).

The USEPA has set the Secondary Maximum Contamination Level (SMCL) for chloride in drinking water at 250 mg/L based mainly on palatability (USEPA, 1992). Due to differences in salt types and experimental methods between reports, there are rarely consistent toxicity ranges on the effects of chloride on aquatic systems, but lethality data summarized by Environment Canada, modeled for chronic exposure, indicated that 5% of freshwater aquatic species would be affected at chloride concentrations of about 210 mg/L, and 10% would be affected by approximately 240 mg/L chloride (Environment Canada and Health Canada, 2001). A literature review of NaCl exposure studies summarized chloride toxicity thresholds (LC_{50} and EC_{50}) of various aquatic organisms as ranging from 874 to 30,300 mg/L chloride depending on exposure time (Evans and Frick, 2001; Environment Canada and Health Canada, 2001).

The effects of summer applied chloride-based dust suppression products on surface water chloride concentrations are not currently known (Environment Canada and Health Canada, 2001). The quality of roadside stream water along nonpaved $MgCl_2$ treated roads will depend on several factors including dust suppression application rate, type and intensity of precipitation, stream flow, and the drainage from the road system (Addo et al., 2004). This study was initiated to determine if $MgCl_2$ -based dust suppressant products affected the chemistry of surface waters adjacent to treated nonpaved roads in two Colorado counties.

Materials and Methods

Sampling Sites

Stream sampling sites were established from May to June 2004 with seven and nine sites at 2200 to 2730 m elevation in Grand and Larimer Counties, Colorado, respectively (Fig. 1). Streams were selected if they crossed under, or were adjacent to, a nonpaved road treated with $MgCl_2$ -based dust suppressant and there were roadside ditches that discharged road surface water directly into or within 10 m of the stream. We hypothesized that the surrounding area and road topography would influence $MgCl_2$ runoff into the streams directly from the road and roadside ditches, so the amount of surface area that potentially diverted water into a stream (surface area index) was measured (Fig. 2). The surface area of all road sections, the length and slope of all roadside ditches, and the area of all embankments (surface area directly off the road shoulder) that would divert road water runoff toward the stream

were combined to calculate the surface area index, a measurement with no units as it combined percentage and area measurements (Fig. 2; Supplemental Information, Table S1). If a roadside ditch discharged onto the embankment before the stream, the ditch length was reduced by the distance from the stream. Thirty-year (1971–2000) average monthly precipitation at each site was obtained from spatially gridded 800 m data (PRISM Group at Oregon State University, 2006) and seasonal precipitation was totaled for the months streams were sampled: May to October (see Supplemental Information, Table S1).

Average anhydrous $MgCl_2$ application amounts ($kg\ km^{-1}\ yr^{-1}$) for each road were calculated from dust suppression application records ($gal\ mi^{-1}$ of $MgCl_2$ solution applied), using 368.59 g anhydrous $MgCl_2$ per liter of dust suppression solution applied as the active ingredient weight/solution ratio (D.L. Miller, personal communication, 2006; A. Green, personal communication, 2006) (see Supplemental Information, Table S1). Various formulations of dust suppressants have been applied to some roads, specifically 1:1 mixtures of $MgCl_2$ and lignin sulfonate solutions (see Supplemental Information, Table S2). The volume of lignin was not included in application rate calculations. Dust suppression products are initially applied to nonpaved roads after snow melts in the spring and are typically applied one to three times per road each season (see Supplemental Information, Table S1). Stream sampling was conducted every other week at each site, with no previous knowledge of the timing or frequency of $MgCl_2$ application on nonpaved roads adjacent to each stream sampling site. Both $MgCl_2$ and lignin based products were sampled directly from application trucks or tanks and analyzed for chemical content (see Supplemental Information, Table S2).

Biweekly Stream Water Sampling

Two permanently marked water sampling locations were established at each stream, one 20 to 50 m upstream and another 20 to 50 m downstream from the road (Fig. 2). Upstream collection locations were above any possible area where road drainage water could enter the stream, except for two sites as noted in the discussion. Downstream collection locations were below the output of all ditches, embankments, and road sections that could divert water toward the stream (Fig. 2). Both sides of the stream were marked with wooden stakes and measurements of stream width, average depth, and velocity were collected twice in May and twice in October to quantify the range of stream characteristics in the spring to fall (see Supplemental Information, Table S1). Stream width was measured from edge to edge of the current water channel, and two to eight depth measurements were averaged across each cross-section depending on stream width. Velocity was determined using a hand-held flow probe equipped with a water velocity meter (Global Water Instrumentation, Inc., Gold River, CA.), averaged across the width of each stream, measured at approximately half the vertical distance between the stream bottom and surface of the stream. Velocity measurements were taken at each point until three consistent readings were obtained in a row. Two measurements each in May and October of stream area ($m^2 = \text{depth} \times \text{width}$) and velocity (m/s) were averaged to obtain average spring and fall stream flow (m^3/s) (see

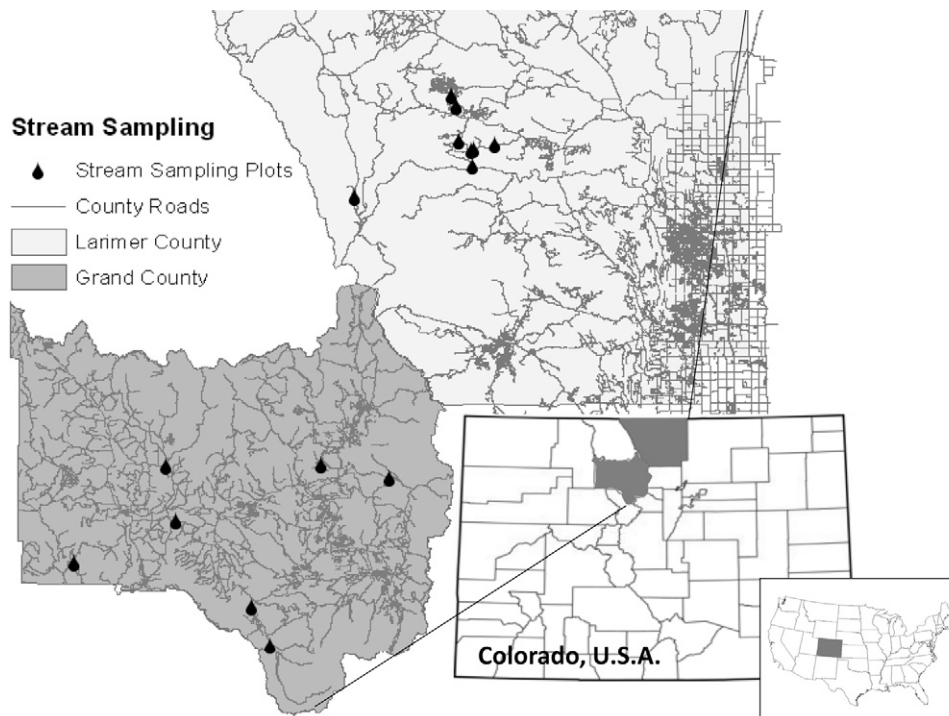


Fig. 1. General locations of 16 stream sampling sites in Larimer and Grand Counties, Colorado along MgCl_2 - based dust suppression product treated roads, sampled for surface water chemistry in 2004–2005 up and downstream of MgCl_2 treated roads.

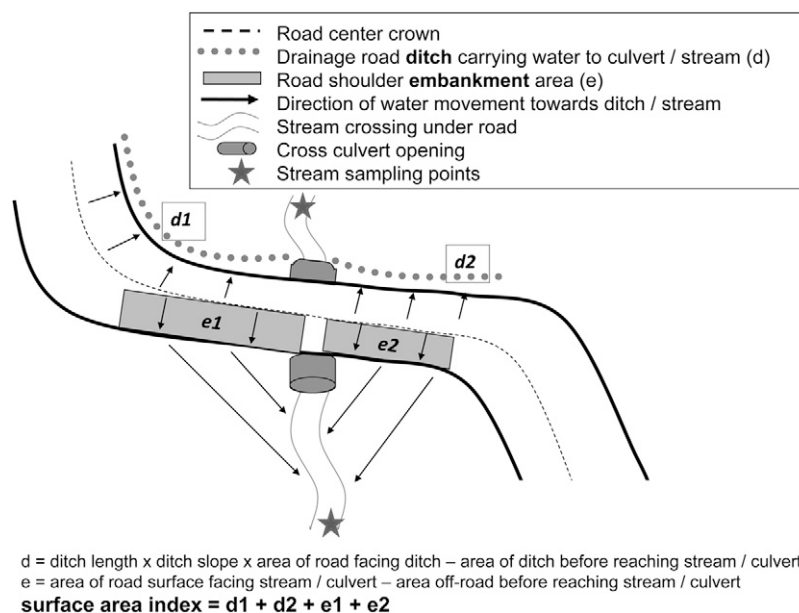


Fig. 2. Measurements and equations used to calculate surface area index values for use in statistical models to predict downstream electrical conductivity (EC), chloride and magnesium concentrations of 16 stream sampling sites in Larimer and Grand Counties, Colorado sampled for surface water chemistry up and downstream of MgCl_2 treated roads in 2004–2005.

Supplemental Information, Table S1). Water samples were collected upstream and downstream at each stream site once every 2 wk from 12 May to 16 Oct. 2004 in Grand County ($n = 4$ –11 per site) and from 7 May to 8 Oct. 2004, and 18 May to 2 Nov. 2005 in Larimer County ($n = 22$ per site). Water was collected in 125-mL Nalgene (Nalge Nunc International Corp., Rochester, NY) containers that were triple-rinsed with stream water just before collections.

Chemical Analyses

Each stream water sample and three replicates of both dust suppression products were analyzed for chemical content. Alkalinity (CaCO_3) was determined via acid titration. Boron (B^-), calcium (Ca^{+2}), iron (Fe^{+2}), magnesium (Mg^{+2}), manganese (Mn^+), phosphorus (P), potassium (K^+), sodium (Na^+), and sulfate (SO_4^{-2}) concentrations were determined us-

ing inductively coupled plasma (ICP) spectrometry. Nitrate (NO_3^-) was determined using the cadmium reduction colorimetric method (USEPA, 1984) and ammonia was determined with flow-injection analysis (FIA). An acid titration method was used to determine bicarbonates (HCO_3^-) and carbonates (CO_3^{2-}). Electrical conductivity (EC) was determined using a Duraprobe Model 152A (Thermo Scientific, Waltham, MA). Chloride (Cl^-) was determined using the cadmium reduction colorimetric method (AOAC International, 1995; Gavlak et al., 1994; K. Klink, personal communication, 2008). Duplicate water samples were sent in for one stream sample and all major ions were within <1.0 mg/L of the duplicate.

Statistical Analyses

We used a generalized linear mixed model to fit fixed and random effects in statistical analyses (The GLIMMIX Procedure, SAS Version 9.1 [SAS Institute, Cary, NC]). The GLIMMIX Procedure fits models to data with correlations or nonconstant variability and assumes normal random effects (SAS Institute, 2008). Fixed effects included stream site (each stream site was treated as a group of samples so variance was pooled over sites [$n = 4$ –22 collections per site]) and position from road (upstream or downstream). Random effects in the model were date of sample collection and the date by site interactions. This model compared upstream and downstream ion concentrations for each stream site averaged over all sampling dates using $p \leq 0.05$ as statistical significance. Ion concentrations had to be logarithmically transformed to equalize variances and normalize skewed data, and were back-transformed to present means in a biologically relevant manner. Pearson Correlation Coefficients (r) were used to compare simple linear regressions of site parameters with mean downslope ion concentrations. An analysis of covariance (ANCOVA) model was used to determine if the upstream concentration, surface area index, total precipitation, average rate of MgCl_2 application, and month of collection could explain mean downstream EC and concentrations of chloride and magnesium by using the coefficient of determination (R^2) for each model.

Results

Water Chemistry

Mean upstream concentrations of chloride ranged from 0.15 to 31.5 mg/L and downstream concentrations ranged from 0.17 to 36.2 mg/L over all 16 streams monitored in both counties (Table 1). Upstream concentrations of magnesium ranged from 1.15 to 12.8 mg/L and downstream concentrations were 1.06 to 12.8 mg/L. Over all sampling dates, significantly higher downstream concentrations of chloride ($p \leq 0.05$) occurred in 7 out of 16 streams and higher downstream magnesium occurred in 5 out of 16 streams (Table 1). Electrical conductivity was higher downstream from the road in 4 of 16 streams and ranged from 0.04 to 0.84 dS/m in downstream samples (Table 1). Stream flow was variable across the 16 stream sites, ranged from 0.0003 to 0.38 m^3/s , and was higher at all sites in May compared to October, with the exception of two sites in Grand County (see Supplemental Information, Table S1).

At a few Grand County sites significant differences occurred between up and downstream water samples for alkalinity, aluminum, boron, calcium, potassium, sulfate, and sodium (see Supplemental Information, Tables S3 and S4). Several streams in Grand County (Sites 3, 4, 6, and 7) had high concentrations of sodium, sulfate, and alkalinity in both up and downstream samples (see Supplemental Information, Tables S3 and S4). Significant differences between up and downstream measurements of alkalinity, aluminum, boron, calcium, pH, potassium, sodium, and sulfate occurred at some sites in Larimer County (see Supplemental Information, Tables S3 and S4).

Relationships between Site Factors and Downstream Electrical Conductivity, Chloride, and Magnesium

After accounting for ion concentrations in upstream waters, the site factors measured at each stream site explained the variability of downstream EC, chloride and magnesium concentrations fairly well ($R^2 = 0.49$ – 0.75) (Table 2). The MgCl_2 application rate, surface area index, precipitation, and month of water collection were all significant factors in ANCOVA models to predict downstream ion concentrations with the upstream equivalent used as a covariate (Table 2).

As the average MgCl_2 application rate increased along study roads, downstream EC, chloride and magnesium concentrations increased (Table 2). The average MgCl_2 application rate on study roads ranged from 1790 to 5910 kg MgCl_2 per km per year and mean average application rate was 4280 kg $\text{km}^{-1} \text{yr}^{-1}$ ($\text{SD} = 982$ kg $\text{km}^{-1} \text{yr}^{-1}$). When compared using simple linear correlations, average MgCl_2 application rate was positively correlated with downstream chloride ($r = 0.42$, $p < 0.001$) and magnesium ($r = 0.41$, $p < 0.001$) concentrations (Table 3). Increases in downstream values of all variables were also significantly related to increases in the surface area draining water into each stream site (Table 2). Surface area indices ranged from 18,600 to 634,000 across stream sampling sites and were as dramatically different in the field as these numbers indicate (see Supplemental Information, Table 1). In simple linear regression, surface area index alone was positively related to chloride concentrations ($r = 0.45$, $p < 0.0001$) and had significant but weaker correlations with all other values (Table 3).

Total May to October 30-yr average precipitation ranged from 19.8 to 27.2 cm at stream sampling sites over both study counties, with an average of 23.0 and 26.2 cm for Grand and Larimer Counties, respectively (see Supplemental Information, Table 1). Precipitation was significantly negatively correlated only with EC ($r = -0.58$, $p < 0.0001$) (Table 3). The 30-yr average precipitation was also a significant variable in modeling EC and magnesium concentrations with ANCOVA models (Table 2). The month stream water was collected (May through October) was a significant variable in all models (Table 2). The highest EC, chloride, and magnesium concentrations were measured in October and were lower in spring months (Table 2). In simple linear regressions, an increase in stream flow decreased all concentrations (Table 3).

Table 1. Mean chloride (Cl⁻) and magnesium (Mg⁺²) concentrations (mg/L) and electrical conductivity (EC, dS/m) from 16 streams adjacent to MgCl₂-treated nonpaved roads in Grand (2004) and Larimer (2004–2005) Counties, Colorado. NOTE: Concentrations shown are back-transformed log₁₀ mean concentration data. Concentrations were averaged over all months.

County	Site	Upstream Cl ⁻	Downstream Cl ⁻	P > t †	Upstream Mg ⁺²	Downstream Mg ⁺²	P > t †	Upstream EC	Downstream EC	P > t †	No.‡
		mg/L			mg/L			dS/m			
Grand	1	0.85	0.66		1.38	1.06	**	0.05	0.04		11
Grand	2	0.87	1.30		2.07	2.50	*	0.21	0.24		9
Grand	3	2.63	2.90		12.83	12.83		0.42	0.42		4
Grand	4	2.01	2.63		4.62	5.23		0.33	0.37		11
Grand	5	0.15	0.35		1.86	1.86		0.08	0.08		12
Grand	6	2.83	3.11		1.50	1.50		0.84	0.84		10
Grand	7	6.14	10.80	**	4.00	5.76	***	0.26	0.26		11
Larimer	1	2.06	2.07		2.42	2.24		0.07	0.07		22
Larimer	2	0.89	24.47	***	2.77	5.72	***	0.09	0.19	***	22
Larimer	3	0.51	10.09	***	2.38	4.63	***	0.08	0.15	***	23
Larimer	4	2.37	19.81	***	2.64	8.02	***	0.09	0.24	***	22
Larimer	5	1.06	3.89	***	2.46	3.04		0.08	0.11	*	22
Larimer	6	9.66	13.79	*	4.15	5.03		0.17	0.21		22
Larimer	7	31.52	36.24		6.92	7.98		0.22	0.25		22
Larimer	8	2.34	3.67	*	2.21	2.57		0.07	0.09		22
Larimer	9	0.30	0.17		1.15	1.19		0.04	0.04		22

† P < |t| = differences significant between upstream and downstream means at $p \leq 0.0001$ (***), $p \leq 0.01$ (**) and $p \leq 0.05$ (*) appear in bold text.

‡ No. = number of collection days at each site.

Table 2. Best regression equations (highest R²) for downstream electrical conductivity (EC), chloride and magnesium concentrations values using upstream values and site variables as covariates in Grand and Larimer Counties, Colorado, 2004–2005 ($n = 15$ streamst, 504 observations). NOTE: all parameters except months are significant covariate effects (using Type III SS) at $p < 0.05$ unless denoted not significant by NS; monthly italic numbers indicate value is not significantly different from the baseline October [zero] when used in the equation#.

Downstream variable (Log ₁₀)	R ²	Intercept	Log ₁₀ upstream variable	Log ₁₀ surface area‡	MgCl ₂ application rate§	Month of stream sampling					
						Precipitation¶	May	June	July	Aug.	Sept.
EC, dS/m	0.75	0.4179	0.6977	0.0454	2.61×10^{-5}	-0.0389	-0.0993	-0.1353	-0.0699	-0.0427	-0.0297
Cl ⁻ concentration, mg/L	0.51	-1.8634	0.5658	0.4722	12.59×10^{-5}	-0.0295(NS)	-0.1249	-0.3246	-0.0620	-0.1640	-0.1507
Mg ⁺² concentration, mg/L	0.49	-0.0044	0.5831	0.1031	4.40×10^{-5}	-0.0178	-0.1117	-0.1661	-0.0833	-0.0433	-0.0552

† County 1: Site 3 dropped due to disrupted sampling at stream mid-season.

‡ Surface area = measured for each stream site through road width, drainage length and slopes, and embankment width and lengths (see Fig. 2).

§ MgCl₂ application rate = kg km⁻¹ yr⁻¹.

¶ Precipitation = 30-yr average May–Oct. precipitation (cm) (Table 1).

Log₁₀ Downstream Variable = $\beta_a + \beta_{\text{upstream}}(\text{Log}_{10}\text{Upstream Variable}) + \beta_{\text{surface}}(\text{Log}_{10}\text{Surface Area}) + \beta_{\text{application}}(\text{Average MgCl}_2\text{ Application}) + \beta_{\text{precip}}(\text{Seasonal Precipitation}) + \beta_{\text{month}}$

Table 3. Pearson correlation coefficients for stream water electrical conductivity (EC), chloride and magnesium concentrations vs. site variables in Grand And Larimer Counties, Colorado, 2004–2005 ($n = 15$ streamst, 521 observations).

Downstream variable	Upstream equivalent variable‡	Stream flow§	Surface area¶	MgCl ₂ Application rate#	Precipitation††
EC, dS/m	0.82	-0.12	0.09	0.18	-0.58
Cl ⁻ concentration, mg/L	0.64	-0.21	0.45	0.42	0.06 (NS)
Mg ⁺² concentration, mg/L	0.65	-0.16	0.39	0.41	0.04 (NS)

† County 1: Site 3 dropped due to disrupted sampling at stream mid-season.

‡ All variables significantly correlated to upstream equivalent variable at $p < 0.0001$.

§ Stream flow (m³/s) = stream velocity (m/s) × stream area (m²). All variables significantly correlated to stream flow at $p < 0.05$.

¶ Surface area = measured through road and embankment areas and drainage length and slopes. All variables significantly correlated to surface area at $p < 0.05$.

MgCl₂ application rate = kg km⁻¹ yr⁻¹. All variables significantly correlated to application rate at $p < 0.001$.

†† Precipitation = 30-yr average total May–Oct. precipitation (cm). Electrical conductivity only significantly correlated to precipitation at $p < 0.05$.

Discussion

Ion Concentrations in Roadside Streams and Relevance to Other Colorado Waterbodies

We did not find a consistent regional stream water response associated with the application of MgCl₂-based dust suppression

products to nonpaved roads throughout northern Colorado. However, MgCl₂ products did move into some streams and the ions occurred in measurable concentrations in flowing streams throughout spring, summer, and fall. Chloride concentrations measured (0.15–36.2 mg/L) were similar to those in the Roaring Fork (1.0–43.0 mg/L) and the Big Thompson (0.16–22.0 mg/L) rivers in Colorado, both in drainages where deicing chloride

compounds are used on adjacent paved roads (Fischel, 2001; Jassby and Goldman, 2003). Concentrations were at the low end of the range measured in Turkey Creek, CO (5.41–390 mg/L), where chloride inputs had presumably occurred from deicing compounds (Bossong et al., 2003). Magnesium concentrations in northern Colorado streams (1.06–12.8 mg/L) were also on the low end of the 1.83 to 70.9 mg/L range measured in Turkey Creek (Bossong et al., 2003) and similar to those measured in the Guanella Pass, CO watershed (Stevens, 2001). Compared to surface water concentrations of streams impacted by winter deicing practices, ion concentrations measured in study streams adjacent to nonpaved roads were low (Environment Canada and Health Canada, 2001; Kaushal et al., 2005). Chloride concentrations have been measured above 1000 mg/L during winter months in watersheds impacted by chloride salts used for snow and ice control (Environment Canada and Health Canada, 2001; Kaushal et al., 2005), and the effects of NaCl deicing agents can also persist past winter months. Ponds within 60 m of treated secondary roads or highways have been measured with more than 500 mg/L chloride in spring and more than 400 mg/L in late summer months (Collins and Russell, 2009).

Other Sources and Elements of Surface Water Concentrations

We assumed that any increases in ion concentrations from upstream to downstream surface waters were effects of the MgCl_2 treated road that separated them, hence the upstream control for the downstream section at each stream site. We assumed that dust movement off roads containing MgCl_2 was negligible since we did not measure significantly higher soil concentrations of these ions upslope from roads past the road shoulders in previous sampling (Goodrich et al., 2009). Background, or natural, concentrations of chloride in surface water are generally low (Jassby and Goldman, 2003; Godwin et al., 2003; Panno et al., 2006; Collins and Russell, 2009), and high upstream concentrations at three of our stream sites indicate chloride was introduced into the surface water above the adjacent study road (Table 1). Other human inputs besides road treatment products can be measurable in adjacent roadside water bodies and include agricultural chemicals, effluent from septic systems, animal waste, and municipal landfills (Panno et al., 2006). Grand County Site 7 was located approximately 1 km downstream of a large mine spoils pile that might have caused relatively high upstream and downstream concentrations of several ions and compounds, including chloride (6.14 and 10.8 mg/L, respectively) (see Supplemental Information, Tables S3 and S4). Grand County Site 6 had high concentrations of sodium and sulfate in the upstream surface waters, which may have been due to extensive cattle grazing in the area (i.e., Panno et al., 2006). Larimer County Site 6, which had a mean upstream chloride concentration of 9.66 mg/L, had approximately 1 km of nonpaved road area draining into the stream above the upstream collection site as the stream ran parallel with the road. Larimer County Site 7, with an upstream mean chloride concentration of 31.5 mg/L, was further downstream from Site 2, which had 24.5 mg/L chloride downstream

from the road. Grand County Site 3 had higher than average concentrations of magnesium both up and downstream (both 12.8 mg/L) from the road, of which we do not know the source. The remaining sites did not have additional ion inputs into the upstream sampling sites and represent background concentrations of chloride (0.15–2.83 mg/L) and magnesium (1.15–4.62 mg/L) in these areas of Colorado.

Larimer County Sites 2 to 4 had higher calcium, sodium, and sulfate concentrations downstream compared to upstream waters (see Supplemental Information, Tables S3 and S4). These chemicals occur in small quantities in MgCl_2 -based dust suppression products (see Supplemental Information, Table S2) and were higher in streams where magnesium and chloride inputs were detectable (see Supplemental Information, Tables S3 and S4). Aside from these noted changes, MgCl_2 inputs did not drastically alter water chemistry in northern Colorado streams (see Supplemental Information, Tables S3 and S4).

Ion Concentrations Relevant to Aquatic Life

Chloride concentration estimates of acute and chronic lethality of aquatic organisms, although not always consistent between reports, are generally high. Predictive lethality models estimate 5 to 10% changes in aquatic organisms at the EPA SMCL of 250 mg/L chloride (Environment Canada and Health Canada, 2001). The ranges of short-term LC_{50} , summarized by Environment Canada for the Canadian Environmental Protection Act) included 6060 to 30,330 mg/L chloride for fish and benthic organisms in <24 h; 4990 to 8550 mg/L chloride for 24-h tests, 1400 to 13,100 mg/L chloride for 3 to 4 d tests; and 874 to 3660 mg/L for 7 to 10 d tests (Evans and Frick, 2001; Environment Canada and Health Canada, 2001). In a 1988 EPA assessment of various chloride salt toxicities, raw acute (24–96 h) LC_{50} or EC_{50} values ranged from 86.0 mg/L chloride for the most sensitive genus, *Daphnia* spp. to 13,100 mg/L chloride for *Anguilla rostrata* (American eel) (USEPA, 1988). Mean concentrations of chloride and magnesium ions found in surface water samples in northern Colorado streams over the summers of 2004 and 2005 are well below the ranges considered to be deleterious to aquatic life, based on previous research and standards set by Environment Canada and Health Canada (2001) and USEPA (1988), but there is limited research on acute, chronic, or seasonal impacts of chloride-based salts on population levels or mortality thresholds of aquatic life in Rocky Mountain watersheds.

Ion Concentrations Relevant to Road and Stream Site Factors

We hypothesized that the water quality of roadside streams adjacent to MgCl_2 -treated roads would be related to several interacting factors. The amount of MgCl_2 that moves off treated roads and into roadside streams should be a function of the annual or total MgCl_2 application rates, composition, and type of roadside or streambank soils, the type, intensity, and amount of precipitation and the drainage of the road system (Addo et al., 2004). Stream characteristics, such as depth, width, and stream flow will also influence the measurable amount of these ions in

moving water, as the slower the water moves the higher the ion concentrations will occur. We chose to measure several of these factors that ANCOVA indicated did interact with one another and influenced downstream concentrations (Table 2). Delineating easily measurable site factors at streams adjacent to or crossing under treated roads can help road managers focus on areas with a high risk of MgCl_2 inputs. These high risk streams can be monitored for environmental impacts or transportation officials can use better management practices to reduce runoff from roads at those road sections. Equations can be used to calculate how much surface area, MgCl_2 application rate, and month of sampling will affect downstream concentrations by inputting some background concentration (0.15–2.73 mg/L for chloride and 1.15–4.62 mg/L for magnesium) for the upstream coefficient (Table 2). Our ANCOVA model indicated that increased annual MgCl_2 application rate along nonpaved roads will increase the downstream concentration of ions in roadside streams. In addition, the higher surface area a stream site was associated with (longer or steeper ditches channeling water toward the stream or more road surface area angled toward the stream) the more chloride and magnesium was measured downstream. We speculate that these factors need to occur together for MgCl_2 ions to move into roadside streams and the effects of runoff may be limited by reducing MgCl_2 application in areas with a high surface index. By measuring these site factors, road managers can, with some confidence ($R^2 = 0.49\text{--}0.75$), determine if a stream adjacent to a treated road will increase in EC, chloride, or magnesium concentrations when MgCl_2 is applied.

Thirty-year average precipitation data from PRISM models were a significant variable in most ANCOVA models, but are not the most accurate measurements of how precipitation may affect MgCl_2 movement into streams. Precipitation can cause runoff from fairly impenetrable surfaces such as paved or well stabilized nonpaved roads and move into roadside environments (Mason et al., 1999; Addo et al., 2004). Using daily site specific precipitation data and sampling streams during or directly after rainfall would be useful in determining if ions move into streams and peak during or directly after precipitation events, neither of which were measured in this study. The twice-monthly sampling of stream sites was designed to measure mean concentrations over a season, and does not necessarily indicate maximum fluxes that may occur in downstream areas (see Supplemental Information, Table S5). We speculate that during precipitation events, streams with higher surface area indices (i.e., longer, steeper ditches or more road surface angled toward the downstream site) would have greater road water runoff moving more chloride and magnesium ions into the stream. However, higher stream flow from precipitation and snowmelt may dilute the ions, making concentrations lower. Based on our monthly sampling data, it is clear that chloride concentrations are lower in spring months and higher in the fall in most streams sampled (see Supplemental Information, Table S5), while stream flow is lowest in fall months (see Supplemental Information, Table S1). While consistent amounts of MgCl_2 ions may be moving off treated roads throughout the 6 mo sampling period, the lower concentrations measured dur-

ing the spring months were most likely due to higher rates of stream flow (see Supplemental Information, Tables S1 and S5). Using machines to monitor hourly or daily measurements of EC, chloride, magnesium, and precipitation at each stream site could have helped better explain the daily and seasonal changes in MgCl_2 movement into roadside streams, but were not feasible in this study. Knowing this information may be critical, as the total ion loads, or yields (e.g., mg Cl⁻/s, kg Cl⁻/d), increase with higher stream flow and may be carried downstream to standing lakes or ponds and intensify—affecting both water quality and aquatic life (Environment Canada and Health Canada, 2001; Collins and Russell, 2009). The ultimate fate of MgCl_2 ions in northern Colorado waterbodies was not determined in this study.

The precise physical processes of ion movement from treated roads were not quantified in this study, although through personal observation we speculate that during large precipitation events ions are washed from the crown of the upper road surface toward the road edges and into roadside ditches, where they are carried downslope with water toward roadside culvert or stream systems. The differences in physical and chemical properties of magnesium and chloride ions most likely affected the amount that were washed from the road base and entered streams below treated roads. Chloride ions do not readily precipitate or form complexes with other ions and move fairly easily through soil solutions, while magnesium may remain in the soil matrix and exchange and interact with other cations on exchange complexes (Mason et al., 1999; White and Broadley, 2001). Chloride, in general, was in higher concentrations than magnesium in downstream surface waters (Table 1) but does not occur in higher amounts in natural systems (White and Broadley, 2001). There was twice the amount of chloride as magnesium in the application solution, and more chloride was introduced to the environment with MgCl_2 -based dust suppressant application (see Supplemental Information, Table 2). Other factors, including unaccounted variations in MgCl_2 application rates from one section of road to another, pulses of rain, and the ability of chloride and magnesium ions to move vertically and horizontally in different soil types, may help to explain some of the unexplained variation in our prediction models.

Conclusions

Chloride and magnesium ions from MgCl_2 -based dust suppression products did move into several streams passing under or adjacent to treated nonpaved roads, but not all downstream concentrations were significantly different than those measured upstream. We did not find a strong water quality response to the application of MgCl_2 -based dust suppression products to adjacent nonpaved roads throughout two northern Colorado counties. The input from MgCl_2 ions did not alter other elements in or characteristics of surface waters to a substantial degree, although several additional ions and compounds found in dust suppression products were measured in downstream surface waters affected by road runoff. Surface area potentially draining water into the stream, average yearly amount of

MgCl₂ applied, month of sampling, and total May to October total precipitation partially explained the variation in EC, chloride, and magnesium concentrations found downstream of treated roads. The mean concentrations of chloride and magnesium ions found in stream water samples collected over the sampling season in 2004 and 2005 are well below the ranges considered to be deleterious to aquatic life based on previous research and standards set by Environment Canada and Health Canada (2001) and USEPA (1988), although the lack of continuous water quality monitoring in this study may not accurately represent the pulses of maximum concentrations which could occur during, or directly following, precipitation events.

Supplemental Information Available

Supplemental Information tables contain more detailed information on stream sampling locations, site information, magnesium chloride product information and ranges of chloride and other element concentrations measured throughout the periods of stream sampling. Stream sampling locations and site information, including stream sizes (width, depth, and seasonal velocity) and magnesium chloride application rates are included for road managers intending to utilize this information in best management practices and compare stream characteristics, magnesium chloride application rates and precipitation conditions to those in their areas of interest. Supplemental Information also includes detailed concentration data on several ions and compounds that are of interest to surface water quality and did significantly differ downstream compared to upstream in streams affected by magnesium chloride application. The final Supplemental Information table illustrates the changes in chloride concentrations throughout the months of stream sampling. This detailed information is also meant for road managers or others utilizing the information in this manuscript in magnesium chloride dust suppression application best management practices. It is available free of charge at <http://jeq.sciijournals.org>.

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