

**Base cation loss from road salting with implications for acid
deposition recovery**

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1 **Title: Base cation loss from road salting with implications for acid deposition recovery**

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7 **Abbreviation List:** Adirondack Park (AP)

8 **Core Ideas**

- 9 Acid deposition and road salt are co-occurring stressors in North America and Europe
- 10 Road salt increased soil base cation export in the Adirondack Park of New York
- 11 Road salt may slow ecosystem recovery from acidification

For Review Only

12 Abstract

13 Road salt (NaCl) and acid deposition co-occur across much of North America and Europe. One
14 such region is the Adirondack Park (AP) in New York State, USA, where the effects of acid
15 deposition have been widely studied and the effects of road salt have not. Road salt delivers
16 3,560 Mmol_e of Na to AP roads each year, which has significant potential to displace soil base
17 cations and exacerbate ecosystem recovery from acidification. With this, our objective was to
18 estimate the effect of road salt on soil base cation export for the AP. We used a simple steady
19 state model based on estimated runoff and cation concentrations from lakes in watersheds with
20 (n=84) and without (n=68) paved roads to estimate watershed export of Ca, Mg, K, and Na.
21 Road salting resulted in significantly higher export for all cations, with 28, 15, 2, and 83
22 mmol_e/m²/yr more Ca, Mg, K and Na released, respectively, compared to watersheds without
23 paved roads. Mineral weathering rates are insufficient to replace these lost cations and thus
24 watershed recovery from acidification will be slower in the presence of road salt. Road salt
25 should be included as a co-occurring stressor and accounted for when assessing the impacts of
26 pollutants on ecosystem health, not only in the AP but wherever road salt is applied.

27 **Introduction**

28 Acidification of surface waters and soils from nitrate and sulfate in air pollution is a widely
29 documented environmental stressor in North America and Europe (Garmo et al. 2014; Driscoll et
30 al. 2016). Air pollution controls have resulted in significant reductions in deposition of these two
31 pollutants (Waldner et al 2014; Rattigan et al. 2017), and data from regional lake monitoring
32 networks in North America and Europe shows that surface water chemistry is recovering (Garmo
33 et al. 2014; Driscoll et al. 2016). More limited data from regional soils studies indicates that
34 acidified soils are also recovering (Akselsson et al. 2013; Lawrence et al. 2015).

35 Though air pollution controls have been successful at reversing acidification to some extent,
36 there is a co-occurring stressor that behaves similarly to nitrate and sulfate in terms of its effects
37 on surface waters and soils, road salt (sodium chloride, NaCl). Applied every winter in large
38 quantities to paved roads in North America and Europe, road salt percolates into soils where Na
39 displaces base cations from exchange, increasing soil base cation leaching and concentrations in
40 surface and ground water, much as nitrate and sulfate likely did in the early years of acid
41 deposition (Sullivan et al. 2005).

42 About 50% of road salt is removed annually via overland flow and the remainder
43 accumulates and moves through soils and groundwater (Meriano et al. 2009). A portion of the
44 remaining Na is retained via cation exchange reactions in soils (Sun et al. 2012), displacing Ca,
45 Mg, K, and other cations from exchange and altering soil fertility and water chemistry (Mason et
46 al. 1999). This effect is supported by reports of increased Ca and Mg concentrations in soil
47 solution and ground water adjacent to salted roads (Howard and Beck, 1993; Cooper et al. 2014)
48 and by stream studies reporting significant increases in Ca and Mg fluxes from watersheds
49 receiving road salt (Shanley 1994; Price and Szymanski 2013).

50 Despite their co-occurrence, the environmental effects of road salt have largely been
51 considered separately from acidification. Only recently have authors considered the
52 consequences of these co-occurring stressors; Schweiger et al. (2015) examined road salt effects
53 on cation leaching and acidity in Central Germany, proposed that additional cation leaching from
54 road salting exacerbates watershed recovery from acidification, and urged changes in
55 management practices to reduce the impacts of road salt on acidified watersheds. The geographic
56 extent of road salt impacts on soil base cation fluxes and surface water chemistry in acidified
57 regions may be significant given many of these regions also have salted roads. This argument is
58 supported by Rosfjord et al. (2007) who reported increases in Ca and Mg concentrations in lakes
59 in the northeastern U.S. in watersheds receiving road salt inputs; this was opposite the trend in
60 lakes not receiving road salt, resulting in the authors warning that regional assessments of lake
61 recovery from acidification are complicated by road salt.

62 The focal region for our study was the 2.4 million hectare Adirondack Park (AP) of New
63 York, USA, a largely protected intact landscape dominated by undeveloped forest lands. Acid
64 deposition has been the principal external human stressor in the AP and lakes in this region have
65 served as sentinels for understanding impacts and recovery from acid deposition for decades (e.g.
66 Driscoll et al. 2016). Though primarily undeveloped, the AP does contain an extensive network
67 of 8,000 km of paved roads which represent the primary internal human footprint in this region
68 at the landscape scale; as such the AP provides a unique natural experiment for studying the
69 effects of road salt. Regalado and Kelting (2015) estimated that runoff from this network enters
70 820 lakes (30% of lakes), thus the geographic potential for road salt impacts is significant.

71 About 208,000 metric tons of road salt is applied to AP roads each year (NYSOGS 2013).
72 This annual load represents 3,560 Mmol_c of Na, which is over 2.6 times greater than the annual

73 input of 977 Mmol_c as sulfuric and nitric acids in acid deposition (NADP 2012). When
74 considering that the annual load of Na is more spatially concentrated, the potential for additional
75 base cation losses from soils due to exchange with Na is significant, as is the potential for road
76 salt to exacerbate soil and surface water recovery from acid deposition, not only in the AP, but
77 wherever road salt and acid deposition co-occur in North America and Europe.

78 Given the large geographic areas receiving road runoff, the sheer size of the annual load of
79 road salt added to the AP, and the potential for road salt to exacerbate ecosystem recovery from
80 acidification, the regional significance of road salt as an ecological stressor should be evaluated.
81 As a first step in this evaluation, the objective of this project was to obtain a regional-scale
82 estimate of the effect of road salt on base cation (Ca, Mg, K) export from watersheds in the AP.

83 **Methods**

84 The AP is dominated by Spodosols developed in deposits of glacial till and outwash formed
85 largely from granite gneiss and metasedimentary rocks (Sullivan et al. 2006). Spodosols are
86 naturally acidic (Fanning and Fanning 1989) and AP Spodosols have very low base saturation
87 (Sullivan et al. 2006).

88 The AP paved road network is divided into 1,965 km of state roads and 6,035 km of local
89 roads (Fig. 1a). State roads are those maintained using a standard New York State Department of
90 Transportation winter road management protocol that relies on road salt for deicing. Local roads
91 are those maintained by municipalities who use a variety of winter road management protocols
92 (e.g. sand, sand plus road salt, road salt). Data on use of alternative deicers on paved roads in the
93 AP does not exist, but statewide about 55,000 tons of liquid CaCl₂ and 2,500 tons of liquid
94 MgCl₂ were applied to paved roads in 2008/2009, compared to over 1 million tons of NaCl in
95 this same time period and no other alternative deicers were applied (Kelting and Laxson 2010),

96 thus use of alternatives on paved roads in the AP is likely inconsequential in terms of their
97 impacts on regional scale Ca and Mg fluxes.

98 This analysis was based on median summer Ca, Mg, K, and Na concentrations in lake water
99 determined from monthly (June, July, August) samples collected from 152 lakes over four years
100 (2010 to 2013) in the AP (2470 total water samples). Fifty-four of these lakes were part of the
101 Adirondack Long Term Monitoring (ALTM) program and 98 were part of the Adirondack
102 Watershed Institute (AWI) monitoring program. Water samples from ALTM lakes were
103 collected as surface grab samples or at 0.5 m depth, while AWI water samples were collected as
104 integrated samples of the top 2 m of water. Cation concentrations were determined in ALTM
105 samples using atomic absorption spectroscopy, and in AWI samples using inductively coupled
106 plasma optical emission spectroscopy. Both programs followed QA/QC protocols that included
107 analysis of field blanks and duplicates, laboratory control samples, method blanks and
108 duplicates, and spikes.

109 We delineated the watersheds for these 152 lakes using digital elevation models and the
110 watershed delineation tool in ArcGIS and divided them into two groups, those with no paved
111 roads (n=68) and those with paved roads (n=84) in their watersheds (Fig. 1b). The watersheds
112 with paved roads used in this study contained 736 km of the state road network (37% of total
113 length) and 1,705 km of the local road network (28% of total length) in the AP.

114 The AP has gradients in precipitation, acid deposition, soils, and geology that impact lake
115 chemistry (Driscoll et al. 1991; Ito et al. 2002), and the existence of these gradients could
116 produce spatial bias in our estimates of the effects of road salt on cation export. The 1:250000
117 scale spatial data available for soils and geology and station-level precipitation and acid
118 deposition data were both too coarse for exploring potential bias. So in the absence of suitable

119 data, we tested for spatial bias using multiple regression models with geographic location
120 (latitude, longitude, and elevation) as surrogate independent variables representing the combined
121 effects of precipitation, acid deposition, soils, and geology, with lake cation concentrations as
122 dependent variables. Use of geographic location is supported by Ito et al. (2002) who
123 demonstrated that precipitation and acid deposition were highly correlated with geographic
124 location. Separate regression models for cations with statistically significant geographic location
125 effects ($p \leq 0.10$) were developed to estimate lake cation concentrations and to calculate residuals.
126 Residual concentrations were added to median concentrations for the whole study to obtain
127 adjusted concentration (Equation 1), which normalized the data for location. This process was
128 repeated for each cation.

$$129 \text{ Adjusted Concentration} = \text{Median Concentration} + \text{Residual Concentration} \quad (1)$$

130 After normalizing the data for location, we then examined the relationship between adjusted
131 concentrations and the density of state and local roads using multiple regression, with state and
132 local road density (km road per square-km of watershed area) as independent variables and
133 adjusted lake cation concentrations as dependent variables. State and local road density were not
134 correlated (Pearson $r=0.362$, $p=0.186$).

135 A simple steady state model based on lake cation concentration and watershed runoff was
136 then used to estimate watershed export. We assumed that (a) cation concentrations were well-
137 mixed in the water column such that the surface water samples represented the whole lake
138 concentration, and (b) median summer concentrations were a reasonable estimate of annualized
139 median concentrations. We tested assumption 'a' by comparing surface concentrations to a
140 mixed concentration computed from surface and bottom water samples available for a subset 14
141 lakes in the AWI dataset that were sampled multiple times per summer over 2 to 4 years and had

142 a total of 263 paired observations from surface and bottom waters. We tested assumption ‘b’
143 using twenty years of monthly data collected from the 54 lakes in the ALTM program from 1993
144 to 2013. Median cation concentrations were computed for each lake for the above variables and
145 nonparametric Mann-Whitney U Tests were used to determine if statistically significant
146 differences ($\alpha = 0.05$) existed between mixed and surface concentrations, and between
147 annualized and summer concentrations.

148 Cation export ($\text{mmol}_c/\text{m}^2/\text{yr}$) was estimated by multiplying the adjusted concentration
149 (mmol_c/m^3) by watershed runoff (m/yr) (Equation 2). Since the precipitation gradient was
150 removed in Equation 1, we used a constant runoff value of 0.646 m/yr in this equation to convert
151 concentration to cation export. This value was computed from a US Geological Survey shapefile
152 of average annual runoff for $30 \times 30 \text{m}$ grid cells for the Adirondack region (Gebert et al. 1987)
153 (<http://water.usgs.gov/GIS/metadata/usgswrd/XML/runoff.xml>).

$$154 \text{ Cation Export} = \text{Adjusted Concentration} \times \text{Runoff} \quad (2)$$

155 The nonparametric Mann-Whitney U test was used to test for statistically significant
156 differences between the estimated cation exports from watersheds with no paved roads versus
157 watersheds with paved roads.

158 Our final calculation was to obtain regional scale estimates of road salt impacts on cation
159 export from the Adirondack Park. First, baseline cation exports (Mmol_c/yr) from the entire AP
160 were determined using the following equation:

$$161 \text{ Baseline Cation Export} = \text{Median Cation Export} \times \text{AP Area} \div 1,000 \quad (3)$$

162 where, median cation exports ($\text{mmol}_c/\text{m}^2/\text{yr}$) were obtained for watersheds without paved roads
163 from equation 2, AP Area was the total land area of the AP ($23,558 \text{ km}^2$), and 1,000 was a unit

164 conversion factor (Equation 3). Second, cation exports from road salt (Mmol_c/yr) were
165 determined using the following equation:

$$166 \text{ Cation Export from Road Salt} = \text{Export Difference} \times \text{PR Area} \div 1,000 \quad (4)$$

167 where, export difference was median cation exports (mmol_c/m²/yr) from watersheds with paved
168 roads minus median cation exports (mmol_c/m²/yr) from watersheds without paved roads, PR
169 Area was the total land area of watersheds that receive runoff from paved roads, and 1,000 was a
170 unit conversion factor. The total land area of watersheds that receive runoff from paved roads
171 (PR Area) was determined from Regalado and Kelting (2015) whose GIS based runoff model
172 determined 820 lakes in the AP receive runoff from paved roads. We took the sum of the
173 watershed areas of these 820 lakes as PR Area (15,398 km²). We also compared the estimates
174 from equation #4 to the annual input of Na in road salt (3,560 Mmol_c/yr) as an independent
175 check on the reasonableness of our estimates.

176 Finally, total cation export (Mmol_c/yr) was determined using the following equation:

$$177 \text{ Total Cation Export} = \text{Baseline Cation Export} + \text{Cation Export from Road Salt} \quad (5)$$

178 Results

179 There were no statistically significant differences between mixed and surface water cation
180 concentrations, and relative differences between these two values ranged from -0.6 to 5.2%
181 (Table 1). There were also no statistically significant differences between annualized and
182 summer surface water cation concentrations, and relative differences between these two values
183 ranged from 4.2 to 9.7%. Given the lack of statistically significant differences and small relative
184 differences, our assumptions about a well-mixed water column and using summer concentrations
185 to represent the annualized concentration were both reasonable.

186 Geographic location had a statistically significant effect on the concentrations of all cations
187 except Na (Table 2), explaining 42, 52, and 27% of the variation in Ca, Mg, and K
188 concentrations, respectively. Calcium and Mg had statistically significant interaction terms for
189 latitude×longitude and longitude×elevation. The slope of the interaction term for
190 latitude×longitude was positive, indicating that concentrations of Ca and Mg in lakes increase
191 along a southwest to northeast gradient in the AP. The negative slope interaction term for
192 longitude×elevation for Ca and Mg indicates that higher elevation lakes in the eastern AP have
193 lower concentrations of these two cations. Potassium concentrations decrease from west to east
194 and with elevation, and increase from south to north.

195 Given that location was statistically significant for all cations (except Na) the regression
196 equations in Table 2 were used to adjust concentrations of Ca, Mg, and K using equation #1 prior
197 to calculating exports. Adjusted for location effects or not, the concentrations of all cations were
198 higher in lakes in watersheds with paved roads (Table 3). For lakes in watersheds with no paved
199 roads, Ca had the highest concentration at 88 mmol_c/m³ followed by Na and Mg with the same
200 concentration (26 mmol_c/m³), and K at the lowest concentration (5 mmol_c/m³). Calcium also had
201 the highest concentration for lakes in watersheds with paved roads (179 mmol_c/m³), followed
202 closely by Na (155 mmol_c/m³), then Mg (67 mmol_c/m³), with K at the lowest concentration (9
203 mmol_c/m³). Removing the effect of location resulted in a small increase in Ca concentration with
204 no paved roads and decreased concentrations of Ca, Mg, and K with paved roads. These
205 adjustments reduced the road salt effect (paved roads minus no paved roads) by 25% or 66
206 mmol_c/m³.

207 There were statistically significant positive correlations between adjusted lake cation
208 concentrations and paved road density for all cations (Table 4). Both state and local road

209 densities were statistically significant for Ca, Mg, and K, while only state road density was
210 statistically significant for sodium. State and local road density explained 43, 21, and 33% of the
211 variation in Ca, Mg, and K, respectively, with state road density being the largest contributor to
212 explaining this variation. The slope coefficients for state road density were higher than the slope
213 coefficients for local road density, indicating that state roads have a greater effect on cation
214 concentrations than local roads. State road density alone explained 78% of the variation in Na,
215 showing the overwhelming influence of state roads on lake Na concentrations.

216 There was a statistically significant difference in cation export between watersheds with no
217 paved roads and watersheds with paved roads, with higher export for all cations from watersheds
218 with paved roads (Figure 2). Sodium export was 83 mmol_c/m²/yr (or 494%) higher from
219 watersheds with paved roads. Export for the other cations totaled 45 mmol_c/m²/yr (or 56%)
220 higher from watersheds with paved roads, with 28, 15, and 2 mmol_c/m²/yr more Ca, Mg, and K,
221 respectively, exported from watersheds with paved roads.

222 We estimated baseline cation exports from the AP of 1,399 Mmol_c/yr for Ca, 401 Mmol_c/yr
223 for Mg, 81 Mmol_c/yr for K and 396 Mmol_c/yr for Na (Table 5). Road salting increased cation
224 exports substantially, from 29% for K to 323% for Na. Increased cation export with road salting
225 accounted for 55% of the total annual Na input of 3,560 Mmol_c/yr from road salt, with Na export
226 accounting for 36% of this total annual Na input, leaving the remaining 64% (2,282 Mmol_c/yr) of
227 the added Na retained in AP watersheds. Only 30% (686 Mmol_c/yr) of this retained Na would be
228 required to exchange the additional Ca, Mg, and K exported with road salt.

229 Discussion

230 The objective of this project was to obtain a regional-scale estimate of the effect of road salt
231 on base cation (Ca, Mg, K) export from watersheds in the AP. The results clearly showed

232 significantly higher base cation export with road salting compared to watersheds not receiving
233 road salt. This higher export is significant relative to other ecosystem fluxes and represents an
234 additional and underappreciated source of base cation losses in ecosystems already stressed by
235 and recovering from acidification.

236 The estimates of increased base cation export from road salt in the AP and elsewhere are
237 biogeochemically and regionally significant compared to other ecosystem fluxes (Table 6). The
238 road salt flux is greater than the deposition fluxes for Ca, Mg, and K measured at Huntington
239 Forest located in the central AP and greater than the weathering fluxes for Ca, Mg, and K
240 reported for glacial till soils with granitic geology in New Hampshire, USA. The road salt flux is
241 also greater than the biomass uptake flux for Mg for sites with glacial till soils and granitic
242 geology also located at Huntington Forest. Based on these comparisons it is clear that the road
243 salt fluxes for Ca, Mg, and K are significant relative to other fluxes in the biogeochemical cycle.
244 With 31% more Ca, 58% more Mg, and 29% more K estimated to be exported from the AP with
245 road salting, it is also clear that the road salt flux is regionally significant. This regionally
246 significant effect of road salting on base cation export has a number of potential consequences.

247 The increased base cation export with road salting shown by our study will eventually
248 decline as Na inputs from continued road salting gradually replace exchangeable base cations,
249 resulting in declining base cation concentrations in surface waters (Mason et al. 1999). This
250 phenomenon was observed in the Mohawk River, NY, where Ca concentrations increased
251 initially with the onset of road salting in the 1950s and have subsequently declined while Na
252 concentrations have remained high (Godwin et al. 2003). Where the AP is on this trajectory is
253 unknown, though we do know that road salt has been used in this region since the 1970s and that
254 NY roads receive some of the highest salt loads in North America (Kelting et al. 2012).

255 Weathering is already insufficient to replace base cation losses from forested watersheds in
256 this region and the road salt flux only increases these losses. Weathering rates average 33.8, 16.8,
257 and 13.0 mmol_c/m²/yr for Ca, Mg, and K, respectively, in northern forest ecosystems with glacial
258 till and outwash soils with granitic geology (Ouimet and Duchesne 2005). Based on these
259 averages, it would take 82, 90, and 12% of the weathering fluxes for Ca, Mg, and K,
260 respectively, to replace losses incurred by the road salt flux. Given that mass balance calculations
261 show that base cation exports exceed inputs (deposition+weathering) from forested watersheds
262 without road salt inputs in this region (Watmough et al. 2005), road salt will only magnify these
263 losses in salted watersheds.

264 *Reasonableness of Estimates*

265 Our approach to estimating watershed export and the influence of road salt thereon produced
266 reasonable estimates when considering values reported by others, Na mass balance, supply of
267 exchangeable base cation in AP soils, and other potential sources for elevated base cation
268 concentrations with salted roads.

269 The simple steady state model for estimating watershed export based on average lake
270 concentrations and annual runoff gave reasonable estimates for watersheds without paved roads.
271 Oliva et al. (2003) reported exports of 82.8 mmol_c/m²/yr for Ca (±24.6 at 95% confidence), 50.8
272 mmol_c/m²/yr for Mg (±17.0 at 95% confidence), 7.8 mmol_c/m²/yr for K (±2.2 at 95%
273 confidence), and 44.7 mmol_c/m²/yr for Na (±12.8 at 95% confidence) based on a dataset of 74
274 watersheds with granitic geology. Our Ca export for AP watersheds was within their 95%
275 confidence interval, while exports for Mg, K, and Na were all below their 95% confidence
276 interval. However, our estimates are in closer agreement with Ouimet and Duchesne (2005) who
277 reported watershed release rates of 33.8 (±15.3 at 95% confidence) for Ca, 16.8 (±4.2 at 95%

278 confidence) for Mg, 13.0 (± 5.6 at 95% confidence) for K, and 11.1 (± 3.0 at 95% confidence) for
279 Na.

280 Our estimates of the influence of road salt on base cation exports were consistent with other
281 reports. Road salt increased Ca and Mg fluxes by 75% and 61%, respectively, in the Fever Brook
282 basin in Massachusetts, USA (Shanley 1994). These increases equated to 23 $\text{mmol}_c/\text{m}^2/\text{yr}$ more
283 Ca and 11 $\text{mmol}_c/\text{m}^2/\text{yr}$ more Mg export from this watershed due to road salting. More recently,
284 Price and Szymanski (2013) reported that 14% and 19% of the Ca and Mg fluxes, respectively,
285 from two forested watersheds in Maryland, USA, resulted from road salting. These fluxes
286 equated to 37 $\text{mmol}_c/\text{m}^2/\text{yr}$ more Ca and 23 $\text{mmol}_c/\text{m}^2/\text{yr}$ more Mg export from these two
287 watersheds due to road salting. Mason et al. (1999) reported that stream Ca, Mg, and K
288 concentrations increased by 96, 73, and 80%, respectively, downstream of a highway in Maine
289 where these increases, like in the above studies, were attributed to road salt and the replacement
290 of Ca, Mg, and K from soil cation exchange sites by Na.

291 Our estimates for the effects of road salt on cation export are reasonable when considering
292 the Na mass balance. The additional sum of cation export from road salting (1,964 Mmol_c/yr)
293 represented 55% of the Na applied to AP roads each winter (3,560 Mmol_c/yr). Assuming the
294 additional road salt export of Na (1,278 Mmol_c/yr) was direct runoff, this left 2,282 Mmol_c/yr
295 (3,560 $\text{Mmol}_c/\text{yr} - 1,278 \text{Mmol}_c/\text{yr}$) of Na entering the soil and available for exchange. The sum
296 of the road salt export of Ca, Mg, and K was 686 Mmol_c/yr , leaving a surplus of 1,596 Mmol_c/yr
297 of Na ions, or 70% of the Na available to exchange the other cations. Considering that only a
298 portion of the Na entering the soil would actually participate in exchange (Mason et al. 1999),
299 the large surplus of Na shows that the estimated effects of road salt on base cation export are
300 reasonable.

301 Our estimates of effects of road salt on base cation export are also reasonable when
302 considering the potential supply of these cations on exchange. As mentioned, the AP is
303 dominated by Spodosols that have inherently low exchangeable base cations on a concentration
304 basis but may have ample base cation supply on a content basis to contribute to road salt export.
305 For example, Sullivan et al (2005) reported a median exchangeable Ca concentration of 0.32
306 cmol/kg for B horizons based on 340 soil samples collected from a wide range of soils across
307 the AP. If we assume an average depth of 30 cm, an average bulk density of 1.0 g/cm³, and an
308 average soil fraction of 75% for these soils, median exchangeable Ca content of the B horizon
309 would be 720 mmol/m². Considering our estimated road salt flux of 28 mmol/m²/yr for Ca,
310 based on the above example, there appears to be ample exchangeable Ca content. Johnson and
311 Lindberg (1991) estimated that the top 58 cm of soil (not including the O horizon) for a Spodosol
312 formed in glacial till from granitic rocks located in the central AP contained 3024, 313, and 187
313 mmol/m² of exchangeable Ca, Mg, and K, respectively. With the road salt flux removing 28, 15,
314 and 2 mmol/m²/yr of exchangeable Ca, Mg, and K, respectively, the far greater supply of these
315 cations on exchange lends further support to the reasonableness of our estimates.

316 It is unlikely that the increased cation export from watersheds with paved roads can be
317 explained by other human sources beyond cation exchange. The AP road network traverses
318 undeveloped forest lands, and as discussed by Kelting et al. (2012), given this and low
319 population density there are no other significant sources of Na in the AP above natural inputs.
320 This argument should hold for the other cations as well. However, since road salt does contain
321 some Ca, Mg, and K, part of the increased export of these cations observed in this study could be
322 from the road salt. Road salt is about 97% pure NaCl and along with other impurities it can
323 contain up to 0.5% each CaCl₂ and MgCl₂ by weight (Shanley 1994) and trace amounts of K

324 (Price and Szymanski 2013). Assuming this composition, the 208,000 metric tons of road salt
325 applied to AP roads would deliver less than 1 mmol_c/m²/yr of Ca and Mg, so their contribution in
326 road salt is negligible. Also, as stated in the Methods section, use of alternative deicers that
327 contain Ca or Mg is also likely negligible in the AP (Kelting and Laxson 2010).

328 ***Conclusion***

329 Base cation losses from road salting are biogeochemically significant and should be
330 accounted for when assessing regional impacts of pollutants wherever road salt is applied.

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336 **References List**

337 Akselsson, C., H. Hultberg, P.E. Karlsson, G.P. Karlsson, and S. Hellsten. 2013. Acidification
338 trends in south Swedish forest soils 1986–2008—Slow recovery and high sensitivity to sea-
339 salt episodes. *Science of the Total Environment* 444:271-287.

340 Cooper, C.A., P.M. Mayer, and B.R. Faulkner. 2014. Effects of road salts on groundwater and
341 surface water dynamics of sodium and chloride in an urban restored stream. *Biogeochemistry*
342 121:149-166.

343 Driscoll, C.T., K.M. Driscoll, H. Fakhraei, and K. Civerolo. 2016. Long-term temporal trends
344 and spatial patterns in the acid-base chemistry of lakes in the Adirondack region of New
345 York in response to decreases in acidic deposition. *Atmospheric Environment* 146:5-14.

- 346 Driscoll, C.T., K.M. Driscoll, M.J. Mitchell, and D.J. Raynal. 2003. Effects of acid deposition on
347 forest and aquatic ecosystems in New York State. *Environmental Pollution* 123:327-336.
- 348 Driscoll, C.T., R.M. Newton, C.P. Gubala, J.P. Baker, and S.W. Christensen. 1991. Adirondack
349 Mountains. In: D.F. Charles, editor, *Acid Deposition and Aquatic Ecosystems*, Springer-
350 Verlag, New York, p. 133-202.
- 351 Fanning, D.S., and M.C.B. Fanning. 1989. *Soil morphology, genesis and classification*. John
352 Wiley & Sons, New York.
- 353 Garmo, Ø.A., B.L. Skjelkvåle, H.A. de Wit, L. Colombo, C. Curtis, J. Fölster, A. Hoffmann, J.
354 Hruška, T. Høgåsen, D.S. Jeffries, and W.B. Keller. 2014. Trends in surface water chemistry
355 in acidified areas in Europe and North America from 1990 to 2008. *Water Air and Soil*
356 *Pollution* 225:1880.
- 357 Gbondo-Tugbawa, S.S., C.T. Driscoll, J.D. Aber, and G.E. Likens. 2001. The evaluation of an
358 integrated biogeochemical model (PnET-BGC) at a northern hardwood forest ecosystem.
359 *Water Resources Research* 35:1057–1070.
- 360 Gebert, W.A., D.J. Graczyk, and W.R. Krug. 1987. Average annual runoff in the United States
361 1951-80. US Geological Survey Hydrologic Investigations, Atlas HA-710.
- 362 Godwin, K.S., S.D. Hafner, and M.F. Buff. 2003. Long-term trends in sodium and chloride in the
363 Mohawk River New York: the effect of fifty years of road-salt application. *Environmental*
364 *Pollution* 124:273-281.
- 365 Howard, K.W.F., and P.J. Beck. 1993. Hydrogeochemical implications of groundwater
366 contamination by road de-icing chemicals. *Journal of Contaminant Hydrology* 12:245-268.

- 367 Ito, M., M.J. Mitchell, and C.T. Driscoll. 2002. Spatial patterns of precipitation quantity and
368 chemistry and air temperature in the Adirondack region of New York. *Atmospheric*
369 *Environment* 36:1051-1062.
- 370 Johnson, D.W., and S.E. Lindberg. 1992. *Atmospheric Deposition and Forest Nutrient Cycling*
371 *Ecological Studies* 91. Springer-Verlag, New York.
- 372 Kelting, D.L., and C.L. Laxson. 2010. Review of Effects and Costs of Road De-icing with
373 Recommendations for Winter Road Management in the Adirondack Park. Adirondack
374 Watershed Institute, Paul Smith's College, Paul Smiths, NY, Adirondack Watershed Institute
375 Report# AWI2010-01.
- 376 Kelting, D.L., C.L. Laxson, and E.C. Yerger. 2012. Regional analysis of the effect of paved
377 roads on sodium and chloride in lakes. *Water Research* 46:2749-2758.
- 378 Lawrence, G.B., P.W. Hazlett, I.J. Fernandez, R. Ouimet, S.W. Bailey, W.C. Shortle, K.T.
379 Smith, and M.R. Antidormi. 2015. Declining acidic deposition begins reversal of forest-soil
380 acidification in the northeastern US and eastern Canada. *Environmental Science &*
381 *Technology* 49:13103-13111.
- 382 Mason, C.F., S.A. Norton, I.J. Fernandez, and L.E. Katz. 1999. Deconstruction of the chemical
383 effects of road salt on stream water chemistry. *Journal of Environmental Quality* 28:82-91.
- 384 Meriano, M., N. Eyles, and K.H. Howard. 2009. Hydrogeological impacts of road salt from
385 Canada's busiest highway on a Lake Ontario watershed (Frenchman's Bay) and lagoon City
386 of Pickering. *Journal of Contaminant Hydrology* 107:66-81.
- 387 NADP. 2012. National Atmospheric Deposition Program. NADP Program Office, Illinois State
388 Water Survey, University of Illinois, Champaign, IL 61820.

- 389 NYSOGS. 2013. New York State Office of General Services. Road Salt, Treated Salt, and
390 Emergency Salt. Historical Details. Corning Tower, Empire State Plaza, Albany, NY 12242.
- 391 Oliva, P., J. Viers, and B. Dupré. 2003. Chemical weathering in granitic environments. *Chemical*
392 *Geology* 202:225–256.
- 393 Ouimet, R., and L. Duchesne. 2005. Base cation mineral weathering and total release rates from
394 soils in three calibrated forest watersheds on the Canadian Boreal Shield. *Canadian Journal*
395 *of Soil Science* 85:245-260.
- 396 Price, J.R., and D.W. Szymanski. 2013. The effects of road salt on stream water chemistry in two
397 small forested watersheds Catocin Mountain Maryland USA. *Aquatic Geochemistry*. doi:
398 101007/s10498-013-9193-8.
- 399 Rattigan, O.V., K.L. Civerolo, and H.D. Felton. 2017. Trends in wet precipitation, particulate,
400 and gas-phase species in New York State. *Atmospheric Pollution Research*.
401 <http://dx.doi.org/10.1016/j.apr.2017.04.007>.
- 402 Regalado, S.A., and D.L. Kelting. 2015. Landscape level estimate of lands and waters impacted
403 by road runoff in the Adirondack Park of New York State. *Environmental Monitoring and*
404 *Assessment* 187:510.
- 405 Rosfjord, C.H., K.E. Webster, J.S. Kahl, S.A. Norton, I.J. Fernandez, and A.T. Herlihy. 2007.
406 Anthropogenically driven changes in chloride complicate interpretation of base cation trends
407 in lakes recovering from acid deposition. *Environmental Science and Technology* 41:7688-
408 7693.
- 409 Schweiger, A.H., V. Audorff, and C. Beierkuhnlein. 2015. Salt in the wound: the interfering
410 effect of road salt on acidified forest catchments. *Science of the Total Environment* 532:595-
411 604.

- 412 Shanley, J.B. 1994. Effects of ion exchange on stream solute fluxes in a basin receiving highway
413 deicing salts. *Journal of Environmental Quality* 23:977-986.
- 414 Sun, H., M. Huffine, J. Husch, and L. Sinpatanasajul. 2012. Na/Cl molar ratio changes during a
415 salting cycle and its application to the estimation of sodium retention in salted watersheds.
416 *Journal of Contaminant Hydrology* 137:96-105.
- 417 TRB (2007) Transportation Research Board Guidelines for Selection of Snow and Ice Control
418 Materials to Mitigate Environmental Impacts. NCHRP Report 577 Washington DC.
- 419 Waldner, P., A. Marchetto, A. Thimonier, M. Schmitt, M. Rogora, O. Granke, V. Mues, K.
420 Hansen, G.P. Karlsson, D. Žlindra, and N. Clarke. 2014. Detection of temporal trends in
421 atmospheric deposition of inorganic nitrogen and sulphate to forests in Europe. *Atmospheric*
422 *Environment* 95:363-374.
- 423 Watmough, S.A., J. Aherne, C. Alewell, P. Arp, S. Bailey, T. Clair, P. Dillon, L. Duchesne, C.
424 Eimers, I. Fernandez, N. Foster, T. Larssen, E. Miller, M. Mitchell, and S. Page. 2005.
425 Sulphate, nitrogen, and base cation budgets at 21 forested catchments in Canada the United
426 States and Europe. *Environmental Monitoring and Assessment* 109:1-36.

427 **Figure Captions**

428 Figure 1. State (red lines) and local (black lines) paved road networks (Fig. 1a), and locations of
429 lakes without paved roads (open circles) and with paved roads (solid circles) in their watersheds,
430 larger circles denote centroid of each group (Fig. 1b), Adirondack Park of New York, USA.

431 Figure 2. Median cation export from watersheds with no paved roads (gray bars) and with paved
432 roads (white bars) located in the Adirondack Park of New York, USA. Vertical bars represent
433 95% confidence intervals.

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435

436 Table 1. Summary statistics for mixed, surface, annualized, and summer cation concentrations
 437 used to test assumptions about a well-mixed water column and use of summer concentrations to
 438 estimate cation exports.

Parameter	Ca	Mg	K	Na
<i>Assumption #1: well-mixed water column</i>				
N	14	14	14	14
Mixed Median (mg/L)	3.16(2.74,4.36) [†]	0.96(0.34,1.26)	0.39(0.27,0.47)	1.11(0.76,4.89)
Surface Median (mg/L)	3.18(2.56,4.18)	0.91(0.33,1.22)	0.38(0.27,0.45)	1.11(0.74,4.82)
Relative Difference (%)	-0.6	5.2	2.6	0.0
P value [‡]	0.80	0.63	0.57	0.95
<i>Assumption #2: summer concentration reasonable estimate of annualized concentration</i>				
N	54	54	54	54
Annualized Median (mg/L)	1.55(1.19,2.18)	0.31(0.20,0.46)	0.24(0.15,0.28)	0.57(0.43,0.71)
Summer Median (mg/L)	1.47(1.13,2.08)	0.28(0.17,0.45)	0.23(0.14,0.26)	0.54(0.39,0.67)
Relative Difference (%)	5.2	9.7	4.2	5.3
P value	0.57	0.53	0.28	0.51

439 [†]Values in parentheses are first and third quartiles, respectively

440 [‡]P-value from two-tailed Mann-Whitney U Test

441 Table 2. Regression equations for summer cation concentrations dependent on latitude,
 442 longitude, and elevation in 152 lakes in the Adirondack Park of New York, USA.

Model Terms	Coefficients†			
	Ca	Mg	K	Na
Intercept	52983	30845	-60.9	
Latitude (m)	-1.11×10^{-2}	-6.48×10^{-3}	1.70×10^{-5}	
Longitude (m)	-9.62×10^{-2}	-5.75×10^{-2}	-1.50×10^{-5}	
Elevation (m)	1.26	0.881	-1.47×10^{-2}	
Latitude×Longitude (m ²)	2.11×10^{-7}	1.42×10^{-7}		
Longitude×Elevation (m ²)	-3.00×10^{-6}	-2.00×10^{-6}		
R-square (%)	41.7	51.8	27.3	3.8
Regression P-Value	<0.001	<0.001	<0.001	0.123

443 †Coefficients shown for statistically significant ($p \leq 0.10$) model terms only

444 Table 3. Median cation concentrations in lakes with no paved roads (n=68) and with paved roads
 445 (n=84) in their watershed before and after adjusting for the effects of latitude, longitude, and
 446 elevation on concentration in the Adirondack Park of New York, USA.

Cation	Before (mmol _c /m ³)		After (mmol _c /m ³)	
	No Paved Roads	Paved Roads	No Paved Roads	Paved Roads
Ca	88 (48,128)†	179 (114,249)	92 (59,122)	122 (94,195)
Mg	26 (17,41)	67 (38,95)	26 (15,39)	50 (30,76)
K	5 (4,7)	9 (6,12)	5 (4,6)	8 (5,10)
Na	26 (18,38)	155 (44,283)	26 (18,38)	155 (44,283)
Total	145 (93,206)	410 (233,664)	149 (22,125)	348 (122,468)

447 †Values in parentheses are first and third quartiles, respectively

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448 Table 4. Summary of regression and analysis of variance results of a multiple regression analysis
 449 of adjusted lake cation concentrations (mmol/m^3) versus state and local road density (km/km^2)
 450 for 152 lakes located in the Adirondack Park of New York, USA.

Variable	Regression			Analysis of Variance		
	Coefficient	Standard Error	P-value	d.f.	Sums of Squares	% Contribution
<i>Calcium</i>						
Intercept	91.2	6.6	<0.001			
State Roads	116.9	13.9	<0.001	1	491931	39.1
Local Roads	28.4	9.0	0.002	1	48574	3.9
Regression				2	540505	43.0
Residual Error				149	716981	
Total				151	1257486	
<i>Magnesium</i>						
Intercept	31.9	3.0	<0.001			
State Roads	29.8	6.2	<0.001	1	33742	18.6
Local Roads	9.1	4.0	0.025	1	4978	2.7
Regression				2	38719	21.3
Residual Error				149	143115	
Total				151	181834	
<i>Potassium</i>						
Intercept	5.9	0.2	<0.001	1		
State Roads	3.0	0.5	<0.001	1	370	26.5
Local Roads	1.2	0.3	<0.001	2	87	6.2
Regression				149	457	32.7
Residual Error				151	940	
Total				1	1397	
<i>Sodium</i>						
Intercept	-37.0	8.5	<0.001			
State Roads	381.5	18.0	<0.001	1	4149470	77.7
Local Roads	3.8	11.6	0.745	1	857	0.0
Regression				2	4150327	77.7
Residual Error				149	1191670	
Total				151	5341997	

451

452 Table 5. Estimated baseline and additional cation exports with road salting from the Adirondack
 453 Park, percentage increases in cation export with road salting, and cation exports expressed as
 454 percentage of annual Na inputs with road salting.

Parameter	AP Area (km ²)	Ca	Mg	K	Na	Sum
		Mmol _c /yr				
Baseline Export†	23,558	1,399	401	81	396	2,277
Road Salt Export‡	15,398	430	233	23	1,278	1,964
Total Export		1,829	634	104	1,674	4,240
Percent Increased Export with Road Salting		31	58	29	323	86
Percent of Annual Na Input§		12	6	1	36	55

455 †Baseline Export = Median No Paved Roads × 23,558 km² ÷ 1,000

456 ‡Road Salt Export = Median Difference × 15,398 km² ÷ 1,000

457 §Na input is 3,560 Mmol_c per year

458 Table 6. Biogeochemical fluxes of base cations from road salting compared to atmospheric
459 deposition, weathering and biomass uptake fluxes from other studies.

Flux (mmol _c /m ² /yr)	Ca	Mg	K	Data Source
Road Salt	28	15	2	this study
Atmospheric Deposition	4	1	<1	NADP, 2012
Mineral weathering	17	13	1	Gbondo-Tugbawa et al. 2001
Biomass Uptake	34	4	15	Johnson and Lindberg 1992

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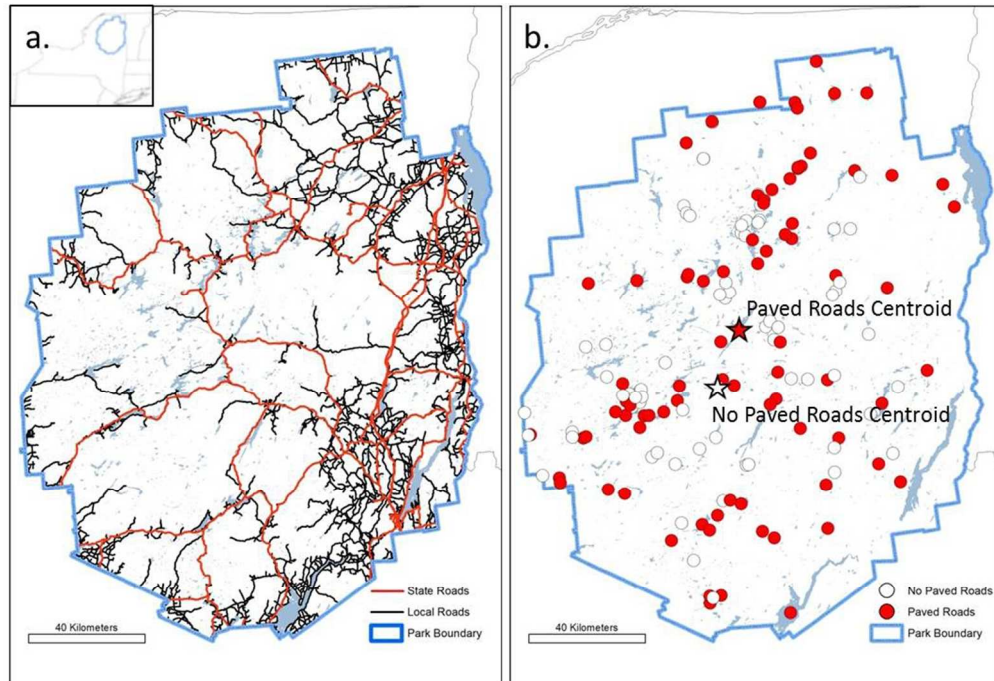


Figure 1. State (red lines) and local (black lines) paved road networks (Fig. 1a), and locations of lakes without paved roads (open circles) and with paved roads (solid circles) in their watersheds, larger circles denote centroid of each group (Fig. 1b), Adirondack Park of New York, USA.

180x122mm (150 x 150 DPI)

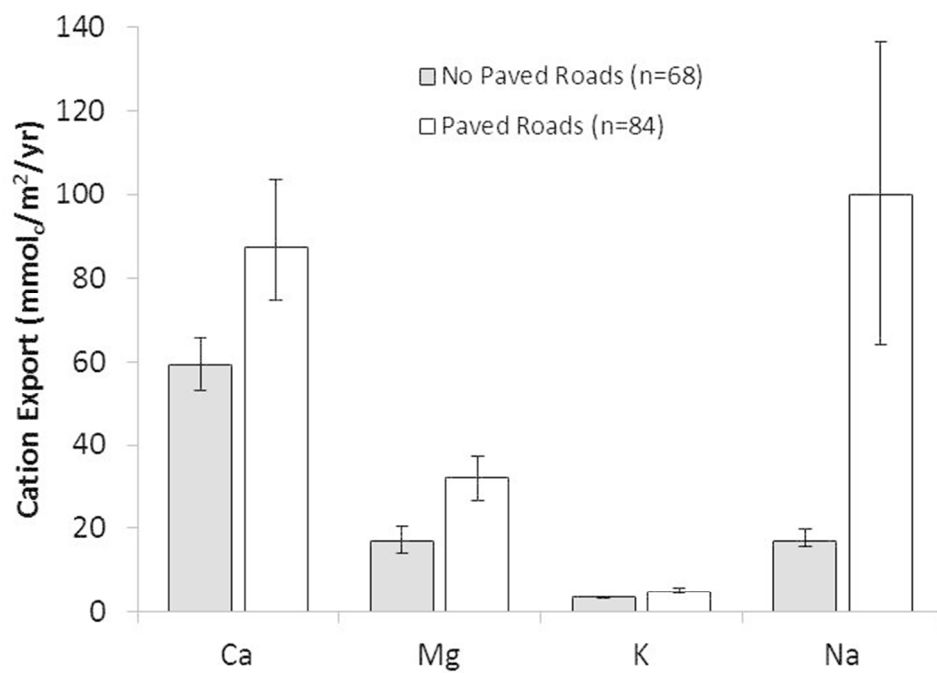


Figure 2. Median cation export from watersheds with no paved roads (gray bars) and with paved roads (white bars) located in the Adirondack Park of New York, USA. Vertical bars represent 95% confidence intervals.

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