

# POTENTIAL IMPACT OF SODIUM CHLORIDE AND CALCIUM CHLORIDE DE-ICING MIXTURES ON ROADSIDE SOILS AND PLANTS

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De-icing salts are applied to highways at rates as high as 30 tons/lane-mile/year or 120 tons/mile of four-lane highway. The quantity of salt required to maintain bare pavement can be minimized partly by applying chemicals, such as sodium chloride and calcium chloride mixtures, that melt ice faster per unit applied and by allowing adequate time after application for bare pavement. At high salt loadings, salt pollution is being traded for time to bare pavement at the rate of two or three times more salt than is required for slower de-icing. Laboratory data indicate that NaCl, if used between 0 and 10 F for de-icing within 1 hour, can introduce fivetimes more  $\text{Cl}^-$  than  $\text{CaCl}_2$  and 10 times more moles of  $\text{Na}^+$  than moles of  $\text{Ca}^{++}$  from  $\text{CaCl}_2$ . However, both can melt roughly similar quantities of ice if sufficient time is allowed for equilibrium. Potential salt loadings in roadside soils and drainage waters were compared with published field data by use of hypothetical constructs, and potentials for producing saline (high salt) and alkali (high sodium) soils were estimated. Although considerable de-icing salt damage to plants is reported in the literature, the damage does not appear to be so extensive as guidelines for agricultural soils in the arid West tend to suggest. Use of  $\text{CaCl}_2$  and NaCl mixtures should avoid the need for adding materials like gypsum to periodically decrease the  $\text{Na}^+$  content of roadside soils and at the same time should offer the potential for improved de-icing efficiency.

\*THREE MAJOR STUDIES have been published recently on the environmental impact of highway de-icing (1, 2, 3). Taken together, these studies represent a fairly complete and comprehensive analysis of the problem. The specific characteristics of calcium chloride for de-icing, however, are not considered in detail by these reviews because calcium chloride commands less than 5 percent of the total de-icing salt market, the rest being sodium chloride.

This paper was prepared to identify differences between  $\text{CaCl}_2$  and NaCl in terms of their potential environmental impact and to further understand environmental effects of de-icing salt. The potential for broadscale contamination of the environment is considered along with the comparative amounts of  $\text{CaCl}_2$  and NaCl necessary to perform equivalent tasks. Hypothetical constructs are devised to compare potential salt loadings in roadside soils and drainage waters with published field data and to relate these salt loadings to established guidelines used in agriculture.

## SALT LOAD FROM DE-ICING

Hanes, Zelazny, and Blaser (1) conclude that chloride concentration in major rivers in northcentral and northeast United States is not seriously affected by de-icing salts applied to highways and that it is the immediate roadside areas that are most seriously affected by salt. They present data for the chloride content of major rivers draining the portion of the United States receiving the bulk of de-icing chemicals. Approximate total annual salt loads as calculated from their chloride data and approximate average flow data are given below for the Delaware, Hudson, Mississippi, Missouri, Ohio, and

Potomac Rivers for 1958 through 1963. ( $\text{Cl}^-$  concentration values were converted to NaCl equivalent.)

<u>River</u>	<u>NaCl/Year</u> <u>(million tons)</u>
Delaware	0.122
Hudson	0.122
Mississippi at East St. Louis, Ill.	1.810
Missouri at Kansas City	0.967
Ohio at Cairo, Ill.	0.725
Potomac at Great Falls, Md.	0.181
Total	3.927

The total of 3.927 million tons of NaCl equivalent per year omits some drainage from the northcentral and northeast United States, notably the St. Lawrence River, but includes a major portion of the runoff from the area.

Use of NaCl for de-icing within the region during the winter of 1966-67 is reported as 1.975 and 2.146 million tons for the northeast and northcentral United States respectively. Combined, this is approximately 4.12 million tons. However, reported use is estimated to represent about 75 percent of the total de-icing salt usage in the region (2). This cursory analysis indicates that the amount of salt being lost from the northeast and northcentral United States in drainage waters is somewhat less than the amount of salt added annually for de-icing purposes in the same region. Because de-icing salts represent only 11 percent of the salt introduced into the environment (2), a substantial quantity of salt appears to be accumulating somewhere within this region, apparently in roadside areas and in groundwater. This proportion of salt retention is considerably greater than has been reported in the literature (2). Obviously, salt distribution and movement through the environment will have to be more thoroughly understood in the near future.

The quantity of salt required to maintain bare pavement can be minimized partly by applying chemicals that melt more ice in less time. This can be accomplished by mixtures of  $\text{CaCl}_2$  and NaCl, particularly at low temperatures. But we need to know the characteristics of each and the number of ions of the mixtures necessary to accomplish equivalent de-icing jobs.

Dickinson (4) compared the ice-melting capacities of NaCl and  $\text{CaCl}_2$  at times ranging from 15 min to equilibrium and at temperatures ranging from 0 to 26 F. His data, as adapted for use in this analysis, are plotted in Figures 1 to 4. One gram of ice can be melted by varying millimolar quantities of NaCl. Time elapsed and temperature significantly influence the quantity of salt required (Fig. 1). A single curve in Figure 1 represents the millimolar concentration of NaCl or of the individual  $\text{Na}^+$  or  $\text{Cl}^-$  ions. Data are presented for elapsed times of 15 min, 30 min, 1 hour, and 6 hours and for equilibrium. Similar data are shown for  $\text{CaCl}_2$  in Figure 2, except that the millimolar concentrations of  $\text{Ca}^{++}$  and  $\text{Cl}^-$  ions are represented by separate curves and the  $\text{CaCl}_2$  concentration corresponds to the  $\text{Ca}^{++}$  curves. Furthermore, only 15-min and equilibrium data are plotted for  $\text{Ca}^{++}$ . At 0 F, between two and three times more  $\text{CaCl}_2$  is required to melt 1 gram of ice than is required at 25 F. At temperatures below 10 F and elapsed times of less than 1 hour, NaCl melts ice very inefficiently, whereas at equilibrium it is nearly equivalent to  $\text{CaCl}_2$ . Calcium chloride melts ice faster at lower temperatures because it can attract hygroscopic water at the low partial pressures of water in equilibrium with ice at 0 F and also because it produces considerable heat when dissolved. Sodium chloride, on the other hand, is unable to attract hygroscopic water at low partial pressures of water and absorbs heat while it is being dissolved.

The influence of elapsed time on the quantity of  $\text{CaCl}_2$  required is shown by the insert in Figure 2. The vertical axis of that insert represents the increase in  $\text{CaCl}_2$  required to melt 1 gram of ice in 15 min, 30 min, 1 hour, and 6 hours as compared to the quantity required at equilibrium. The time effect is more pronounced than the temperature effect noted above: three times more  $\text{CaCl}_2$  required at 15 min and two times more at 1 hour as compared to the equilibrium melting capacity.

Figure 1. Amount of  $\text{Na}^+$  and  $\text{Cl}^-$  interjected into environment when  $\text{NaCl}$  melts 1 gram of ice (4).

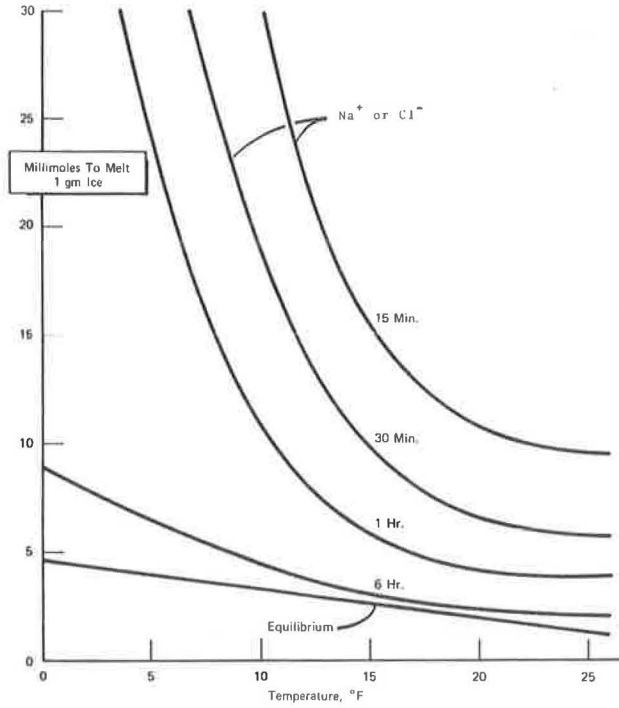
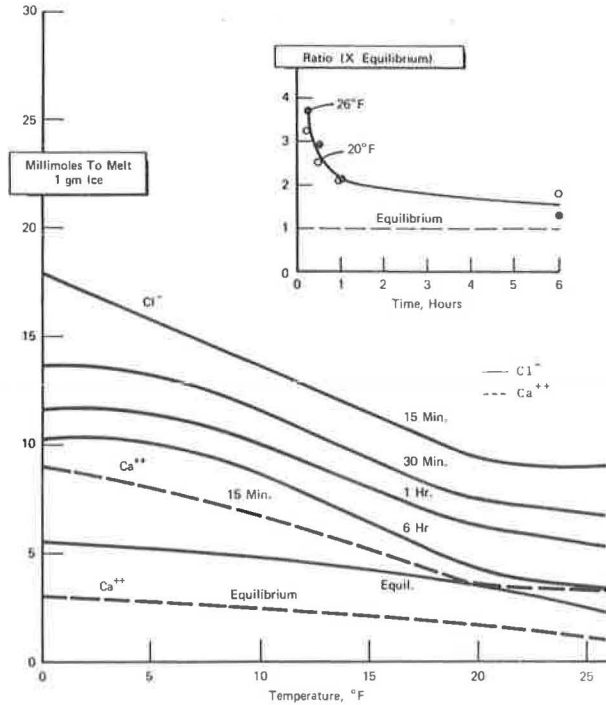


Figure 2.  $\text{Ca}^{++}$  and  $\text{Cl}^-$  interjected into environment when  $\text{CaCl}_2$  melts 1 gram of ice.



The differences between NaCl and CaCl<sub>2</sub> can be elaborated further by comparing the ratio of chloride introduced from the two different sources at varying melting times and at varying temperatures (Fig. 3). At temperatures below 10 F and times of less than 1 hour, much more chloride is introduced into the environment from NaCl than from CaCl<sub>2</sub>. Above 20 F the reverse is true; NaCl contributes less chloride than CaCl<sub>2</sub>. The temperature effect for 1 hour's de-icing is shown by the insert in Figure 3.

The molar ratios of sodium to calcium can also be compared (Fig. 4). Less calcium than sodium is introduced into the environment on a molar basis regardless of melting time and temperature. However, if the ratio were expressed on an equivalent charge basis, the relationships between Na<sup>+</sup> and Ca<sup>++</sup> would be the same as for chloride from the two sources shown in Figure 3. Nonetheless, at short times and cold temperatures, CaCl<sub>2</sub> interjects much less total salt into the environment than NaCl.

The relationships described were determined under ideal laboratory conditions and can be extrapolated to the field only if the same relative de-icing activity of CaCl<sub>2</sub> and NaCl also applies to the field environment. Major differences between field and laboratory appear to be heat contributed by radiant energy, heat loss due to chill winds, heats of solution, and solubility as a function of temperature. The effect of these variables needs to be assessed in future work.

The above analysis demonstrates that there is a trade-off between the amount of de-icing salt applied and the time that elapses between spreading and ice breakup—the less salt used, the more time required. If conditions are such that bare pavement is not required for 6 hours after spreading, then nearly equivalent amounts of CaCl<sub>2</sub> and NaCl can be introduced into the environment. However, if bare pavement is required in less than 1 hour after spreading and the temperature is below 10 F, CaCl<sub>2</sub> is preferable to NaCl. At temperatures between 1 and 10 F, five times more Cl<sup>-</sup> and 10 times more Na<sup>+</sup> than Ca<sup>++</sup> can be introduced into the environment on a mole-for-mole basis. At temperatures above 10 F, more Cl<sup>-</sup> is introduced by CaCl<sub>2</sub>, but more Na<sup>+</sup> is contributed by NaCl than Ca<sup>++</sup> by CaCl<sub>2</sub>. So there is an additional trade-off if Na<sup>+</sup> and Cl<sup>-</sup> are equally harmful.

## POTENTIAL FOR SALINIZATION AND ALKALIZATION OF SOILS

For many years, agricultural scientists (5, 6) have studied soils affected by salt. Salt-affected (halomorphic) soils develop under imperfect drainage conditions in arid regions. In nature, salt accumulates in soils when water is lost primarily through evaporation rather than drainage. This natural process is quite different from the process of de-icing salt accumulation along highways in the northcentral and northeast United States because rain moves salts away with surface runoff and through soil profiles. Nonetheless, many useful concepts and benchmarks can be borrowed from the natural salt-affected soil technology and used to understand the de-icing salt problem along highways. This section reviews characteristics of naturally saline and alkali soils, estimates the potential salt accumulation in soils along highways from de-icing, estimates the potential salt content of drainage waters, and examines the potential benefits from use of varying mixtures of NaCl and CaCl<sub>2</sub> for de-icing.

### Characteristics of Saline and Alkali Soils

Saline soils contain soluble salts in the surface horizons that compete with plants for available water. Salts common in saline soils include sodium, calcium, magnesium, and potassium in the form of chlorides, sulfates, bicarbonates, and carbonates. The exchangeable ions are dominantly calcium and magnesium with small amounts of sodium. As a result, saline soils generally have a pH below 8, and the high salt contents prevent dispersion of soil grains. Saline soil is also called solonchak or white alkali that often has white, salty crusts. Salinization refers to the process of accumulating soluble salts in the surface soil layers.

Alkali soils, also called solonetz soils or black alkali, can be formed by leaching soluble salts from saline soils that use sodium-rich irrigation waters; this causes the exchange capacity to become predominantly saturated with sodium and depleted of calcium and magnesium. The pH of alkali soils sometimes increases to as much as 10.

Figure 3.  $\text{Cl}^-$  pollution potential for  $\text{CaCl}_2$  as compared to  $\text{NaCl}$  expressed as melting rate and temperature-dependent function (4).

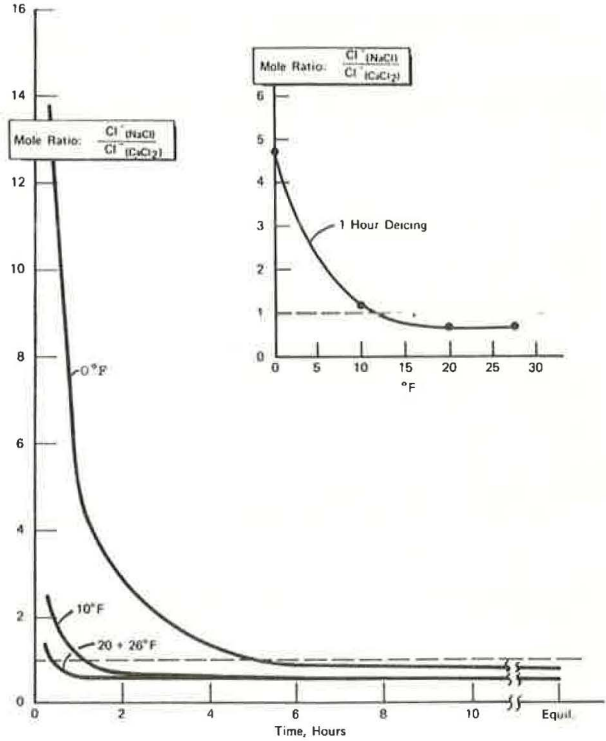
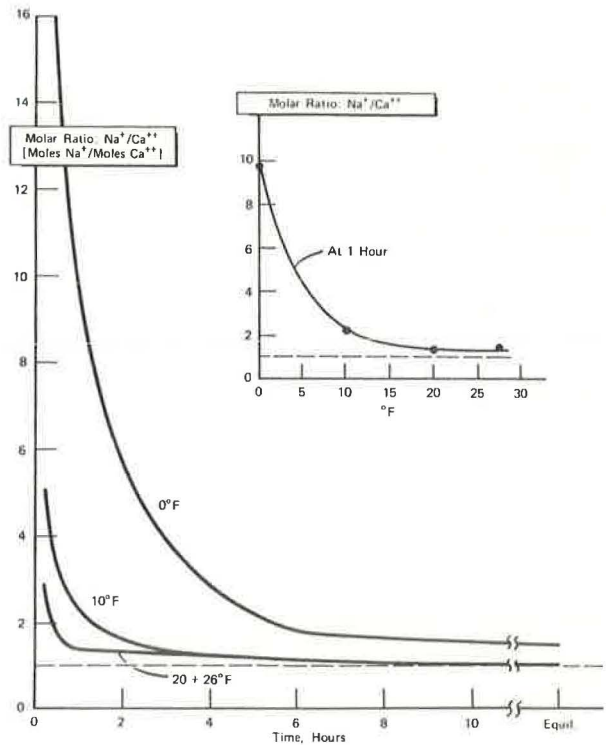


Figure 4.  $\text{Na}^+$  and  $\text{Ca}^{++}$  pollution potential for  $\text{CaCl}_2$  and  $\text{NaCl}$  (4).



The high sodium content and high alkalinity disperse both inorganic and organic colloids, which tend to move down the soil profile. Soluble organic matter also moves to the soil surface from evaporation, making the soil surface dark and contributing the term black alkali. These soils have very poor aeration and low water availability because their structure is destroyed.

Alkali soils can be subdivided into two categories, saline-alkali and non-saline-alkali. Saline-alkali soils are high in soluble salts and exchangeable sodium, whereas non-saline-alkali soils are low in soluble salts but contain over 15 percent exchangeable sodium on the colloids. A further description of saline and alkali soils is given elsewhere (5).

Alkali soils can be reclaimed by adding soluble calcium salts like  $\text{CaCl}_2$  and gypsum. Of these two additives or amendments, gypsum is preferred because of low cost; however,  $\text{CaCl}_2$  is much more soluble and, as a result, should replace sodium more rapidly. Several other amendments can be used to reclaim alkali soils including sulfur, sulfuric acid, iron sulfate, aluminum sulfate, lime sulfur, and ground limestone (5).

The salt content of saline soils is determined by measuring the conductivity of soil extracts and relating this to standard solution concentrations. Accordingly, the osmotic pressure of soil solutions can be determined from conductivity of the extract. Plant response is then related to salt levels in soils as shown in Figure 5, which interrelates conductivity of saturation extracts, osmotic pressure, percentage of salt in soil, and soil moisture content. The reference conductivity along the horizontal axis in Figure 5 is determined on saturation extracts from soil, i.e., extracts taken from soils with pores completely filled with water. A saturation extract producing a conductivity of 3 millimhos per centimeter indicates that the soil contains 0.2 percent salt. At that salt level and saturation, only a few crops are affected detrimentally. However, for a soil that will retain only 25 percent of saturation moisture content under field conditions, 0.2 percent salt produces a conductivity of about 12 millimhos per centimeter at 25 percent of saturation and would be very detrimental to crop growth. These plant responses are described in the salinity scale shown in Figure 5.

#### Potential Salt Levels From De-Icing

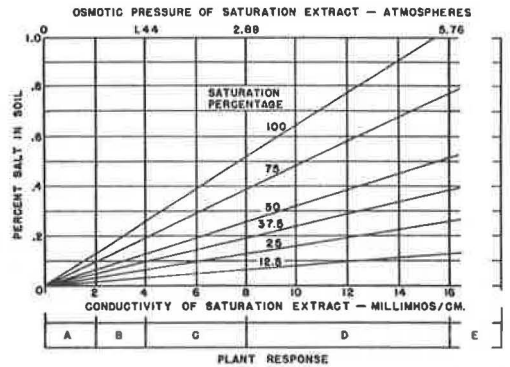
Data can be extracted from existing publications on de-icing salts and their environmental effects to determine how much salt might potentially accumulate along roadways as compared to how much has been observed in some cases. Then, these salt levels can be compared to the tolerance levels shown in Figure 5 for saline soils.

The quantities of de-icing salt applied per single lane-mile per year by state highway departments and toll authorities are presented by Hanes, Zelazny, and Blaser (1). The average salt use was calculated for key states during five winters. Average application rates range between 3 tons per single lane-mile for Virginia and as much as 28 tons per single lane-mile for Pennsylvania.

The potential salt levels that could accumulate in roadside soils are given in Table 1. The salt levels in soils were calculated by assuming that all the salt for one winter season stays on site, when, in fact, much of the salt will be carried away in runoff waters. The resulting salt concentrations in that table only indicate a maximum achievable salt level.

Potential salt levels were calculated for varying roadside areas along two- and four-lane highways treated with as much as 30 tons of salt per single lane-mile. The table lists the pounds salt applied per acre per year and the resulting percentage of salt that could accumulate in soil. Roadside widths of 30 and 60 ft were assumed to calculate total roadside areas. The percentages of salt from Table 1 are shown in Figure 6 for three roadside widths. Also, states are grouped by average level of salt use (1). The figure can be used to estimate the salt that might be expected in roadside soils under the assumptions used in this hypothetical construct. For example, the Massachusetts highway department uses 10 to 15 tons of salt/lane-mile/year (1), which converts to 0.1 to 0.3 percent salt in roadside soils. Salt levels of this magnitude will produce varying plant responses, depending on the soil-water content and plant sensitivity. For example, at 100 percent saturation, crop responses are expected to range from A to C on the salinity scale (Fig. 5), whereas at 25 percent of moisture saturation the same

Figure 5. Plant response related to salt level, soil moisture, and conductivity of saturation extracts (5).



**SALINITY SCALE \***

SPECIFIC CONDUCTANCE OF SATURATED EXTRACT OF SOIL (MICROMHOM/CM)									
0	A	2,000	B	4,000	C	8,000	D	16,000	E
NONSALINE		VERY SLIGHTLY SALINE		MODERATELY SALINE		STRONGLY SALINE		VERY STRONGLY SALINE	
Salinity effects mostly negligible.		Yields of very sensitive crops may be restricted.		Yield of many crops restricted. Alfalfa, cotton, sugar beet, cereals, and grain sorghums adapted.		Only tolerant crops yield satisfactorily. Bare spots because of injury to germination.		Only a few very tolerant crops yield satisfactorily. Only salt-tolerant grasses, herbaceous plants, shrubs, and some trees grow.	
0		0.1		0.3		0.5		1.0	
Salts in Moisture Saturation Extract (%)									

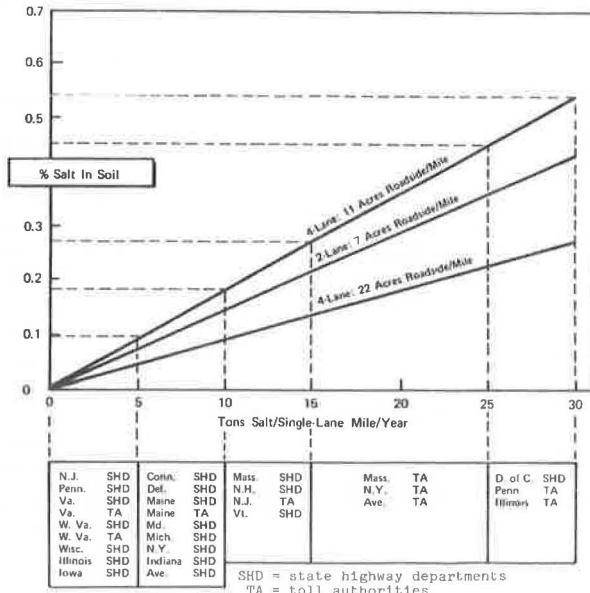
Table 1. Potential salt level accumulations in roadside soils.

Pavement	No. of Lanes	Area* (acres of roadside/mile)	Width (ft)	Salting Rate			Salt in Soil <sup>b</sup> (percent)	meq/Liter NaCl in Runoff
				Ton/Lane-Mile	Ton/Roadway-Mile	Lb/Acre		
2	7	60		5	10	2,850	0.07	16.0
				10	20	5,700	0.14	32.1
				20	40	11,400	0.29	64.2
				30	60	17,200	0.43	96.8
4	11	60, 30-ft median		5	20	3,640	0.09	18.5
				10	40	7,280	0.18	37.0
				20	80	14,560	0.36	73.6
				30	120	21,800	0.55	110.7
4	22	120, 60-ft median		5	20	1,820	0.05	11.5
				10	40	3,640	0.09	23.1
				20	80	7,280	0.18	46.2
				30	120	10,900	0.27	69.3

\*Approximation.

<sup>b</sup>Calculated for 12-in. layer weighing about  $4 \times 10^6$  lb/acre.

Figure 6. Average de-icing salt use by state (assuming that 1 year's salt all remains on site).



salt concentrations are expected to produce plant responses ranging from C to D on the salinity scale and to significantly inhibit plant growth.

Salt levels actually measured in the field by investigators fall within the range indicated as achievable by this construct. Zelazny, Hanes, and Blaser (7) reported sodium levels ranging from below 0.01 percent to about 0.1 percent for a roadside area in Vermont. They measured sodium and chloride levels at varying times and depths in soils on each side of a highway, one side being uphill and the other collecting the drainage water on the east side of the highway. They reported decline of silver maples on the downhill side, whereas trees were quite healthy on the uphill side. When these sodium concentration levels are converted to total salt (NaCl) concentrations in the soil, the maximum salt concentrations observed by Zelazny, Hanes, and Blaser (7) approach 0.25 percent, fully within the range predicted by the above construct. However, they reported gradually increasing salt levels with time as well as considerable leaching of salt from the profile, neither of which was considered in the construct.

Nonetheless, the predicted salt levels approach those observed in the field and the construct apparently can be used to approximate the salt levels that can be expected in roadside soils. Additionally, salt levels comparable to those reported by Zelazny, Hanes, and Blaser are clearly indicated as being harmful by previously established guidelines for salt levels in arid western soils.

#### Potential Runoff Composition and Impact on Soils

The above analysis has serious limitations, so it is desirable to approach the problem of salt impact on roadside areas from a different direction to further elaborate the potential impact of salts on roadside soils and crops. This can be accomplished by estimating the salt content of runoff waters from salted roadways and then applying water quality criteria to irrigation waters to predict the potential long-term impact of these salt-laden waters on roadside soils.

Potential salt levels in runoff water are estimated for varying right-of-way widths and salt application rates as given in Table 1. These concentrations were calculated by assuming that the applied salt is dissolved by 9 in. of water dropped on the roadway and roadside areas. This precipitation level was determined as nearly average for Michigan, New York, Maine, Chicago, and Minneapolis during the months of December, January, February, and March (1). The salt concentrations in the runoff range from about 10 to a high of 110 meq NaCl per liter.

Sodium adsorption ratios (SAR) are given in Table 2 for various NaCl and CaCl<sub>2</sub> formulations covering the range of total salt (CaCl<sub>2</sub> + NaCl) levels up to 120 meq per liter. SAR is a major criterion for irrigation water quality and can be determined from nomograms (5). SAR is calculated by the equation

$$\text{SAR} = \frac{\text{Na}^+}{\sqrt{(\text{Ca}^{++} + \text{Mg}^{++})/2}}$$

The concentrations of sodium and calcium in the drainage water as given in Table 2 are used in conjunction with the nomograms to determine the SAR.

Conductivity was estimated for the various solutions in Table 2 by using established relationships between salt concentration and conductivity (5). In this way, SAR and conductivity were determined for five salt formulations including NaCl containing only CaCl<sub>2</sub> as an impurity; mixtures containing 1:3, 1:2, and 1:1 blends of CaCl<sub>2</sub> to NaCl; and an anhydrous CaCl<sub>2</sub> containing NaCl as an impurity.

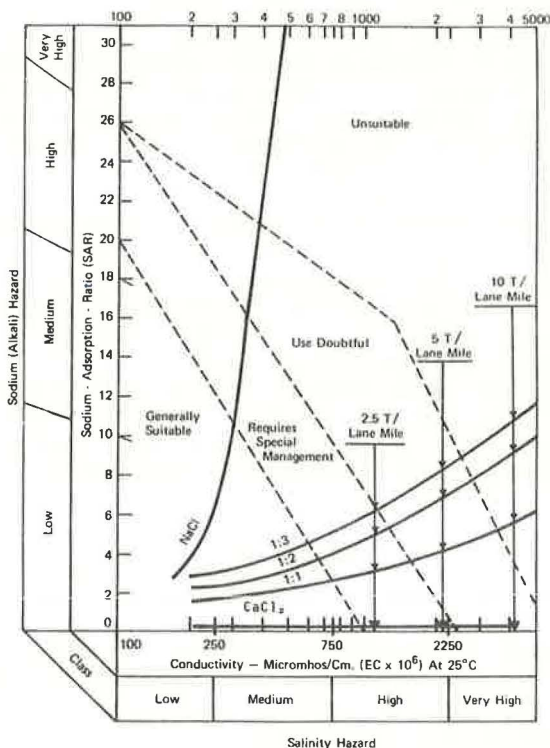
SAR and conductivity are shown in Figure 7 for each of the above formulations to demonstrate the potential impact of de-icing salt mixtures on plants and soils. For example, for NaCl containing only CaCl<sub>2</sub> as an impurity, SAR increases rapidly as salt concentration increases. The curve for NaCl intersects four hazard zones, the hazard changing with salt level or the quantity of water available for diluting the salt. High runoff and low salt applications create the least hazard. Similarly for blends of CaCl<sub>2</sub> and NaCl, the plots for SAR and conductivity will be followed as salt levels and dilutions



**Table 2. Sodium adsorption ratios for various NaCl and CaCl<sub>2</sub> formulations.**

CaCl <sub>2</sub> to NaCl Mixture (weight ratio)	meq Ca <sup>++</sup> / meq Na	meq Na <sup>+</sup> / Liter	meq Ca <sup>++</sup> / Liter	SAR	Estimated Conductivity (mmho)
0.0055:1 (NaCl)	0.0058	2.5	0.0145	10	0.3
		5	0.029	40	0.6
		10	0.058	60	1.2
		30	0.174	110	3.4
		60	0.348	150	6.5
1:3	0.352	2.5	0.88	3.6	0.33
		5	1.76	5.3	0.8
		10	3.52	7.5	1.6
		30	10.6	11	4.5
		60	21.1	18	8.5
1:2	0.528	2.5	1.32	3.0	0.38
		5	2.64	4.3	0.9
		10	5.28	6.2	1.8
		30	15.8	10	5.0
		60	31.7	15	9.5
1:1	1.055	2.5	2.64	2.2	0.5
		5	5.28	3	1.2
		10	10.55	4.3	2.3
		30	31.7	7.5	6.5
		60	63.4	11	12.0
0.9457:0.0146 (anhydrous CaCl <sub>2</sub> )	68.4	0.036	2.5	0	0.3
		0.073	5	0	0.6
		0.145	10	0	1.2
		0.435	30	0	3.4

**Figure 7. Irrigation water quality criteria adapted to characterize drainage waters from roads treated with various de-icing formulations.**



**Table 3. Composition of drainage water in the field.**

Location	Cl <sup>-</sup> in Roadside Runoff (ppm)			meq Na <sup>+</sup> /Liter		
	High	Low	Mean	High	Low	Mean
Chippewa Falls, Wisc.	10,250			289		
Madison, Wisc.	3,275			92		
Lake Menona, Wisc. <sup>a</sup>	1,130	77.5	285	32	2	8
I-95, Maine <sup>b</sup>	844.9	38.1	570.2	24	1	16
	264.9 <sup>c</sup>	70.4 <sup>c</sup>	168.2 <sup>c</sup>	12	3	7
Chicago, Ill.	25,000	1,300	11,000	705	37	310

<sup>a</sup>Large snow pile near lake.

<sup>b</sup>Culvert draining.

<sup>c</sup>Na<sup>+</sup>.

change. The anhydrous  $\text{CaCl}_2$  alone contains very little sodium and will increase salinity but not contribute to SAR. Consequently, it falls along the horizontal axis.

Water quality zones are superimposed on Figure 7 to indicate the suitability of water for irrigating crops (5). Waters in the first zone are generally suitable for irrigation. Waters in the second zone require special management for their use, whereas waters in the third zone can be used only in special cases and under special management. The last zone contains waters largely unsuitable for irrigation and use by plants except under unusual circumstances.

The potential impact of various salt usage levels is also shown in Figure 7 for the various de-icing formulations. Average drainage water composition was calculated for applications of 2.5, 5, and 10 tons per lane-mile, which can be expected along a standard four-lane highway (30-ft roadside, median, and pavement widths, receiving 9 in. of rainfall during 4 winter months of December, January, February, and March). Even at 2.5 tons per lane-mile,  $\text{NaCl}$  cannot be applied alone to such a highway without producing drainage water that is highly unsuitable for roadside areas. The potential hazard to roadside areas is considerably reduced by applying blends of  $\text{CaCl}_2$  and  $\text{NaCl}$ . This contention is further supported by the fact that  $\text{CaCl}_2$  is considered to be a suitable amendment for reclaiming alkali (sodium-rich) soils (5).

The drainage water compositions developed by this hypothetical construct need to be compared to salt levels measured in drainage water from snowmelts in the field (Table 3). Many of the values given in the table are reported in the literature as chloride, so the sodium levels were assumed to be similar on an equivalent-for-equivalent basis. These measured values are both lower and higher than the values given in Tables 1 and 2 of the hypothetical construct, suggesting that the analysis presents a reasonably valid approximation of average salt levels in roadside runoff.

## DISCUSSION AND CONCLUSIONS

All of the preceding analyses indicate salt damage should be observed along almost all roads on which de-icing salts are used. This is obviously not the case. Even though roadside damage to plants is reported in the literature, the damage is not so extensive as suggested by the constructs developed in this paper. Consequently, we have to conclude that the criteria developed for the arid West regarding irrigation waters and salt accumulation levels do not directly apply to soils located along highways in more humid and colder regions.

Several major differences are apparent. First, infiltration of salt waters is significantly impeded during the winter months when soils are frozen. Second, the criteria were established for long-term agricultural productivity. Third, much of the salt is carried away in runoff water and does not affect the soils on site but rather collects in nearby water bodies and is carried away in streams. Each of these would tend to diminish the observed damage to roadside vegetation. On the other hand, damage to roadside areas would seemingly be enhanced by the fact that drainage waters will alternate from brine to fresh throughout the winter months and will be quite low in salt through the summer months. Such variation of salt levels in the water would tend to disperse soils more strongly than a constant quality of water. Furthermore, salt dissolved in the soil solution would become concentrated in the unfrozen phase as soils are frozen. This phenomenon may expose perennial plant roots to disproportionately high osmotic forces in the soil solution.

Obviously, more detailed knowledge of the processes of salinization and alkalization as they apply to the use of de-icing salts in the northcentral and northeast United States is needed before roadside salt damage can be accurately understood. Nonetheless, one can conclude that mixtures of  $\text{CaCl}_2$  and  $\text{NaCl}$  will decrease the potential for damage, particularly to soil physical properties.

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## DISCUSSION

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The hypothesis studied in this paper is a significant factor in projecting future use of de-icing compounds on highways, and the conclusion that mixtures of calcium chloride and sodium chloride will decrease the potential for damage to physical properties of soils as compared to application of sodium chloride singly is valid. The data presented in the report thoroughly justify this conclusion.

The implication of this conclusion is primarily of significance for those situations where de-icing compounds are applied long after a snow or ice storm begins, because under those conditions the chemical agent is used to melt ice that has already formed and that is strongly bonded to the pavement. This situation might most frequently occur in small towns and cities where the municipal capacity for snow removal is limited.

Most highway departments plan to apply the de-icing chemical to the pavement when precipitation begins, thereby preventing the bonding of snow to the pavement. Thus the snowplow is able to push the unfrozen mass to the side of the highway. Under this latter condition the potential difference between sodium chloride and calcium chloride in endangering environmental contamination is minimized because the time factor is less important. One is not attempting to melt a 1-in. layer of ice in less than 1 hour.

Technically, any soil that has more than 15 percent of its cation exchange capacity occupied by sodium is termed alkali (8). In a recent study conducted in Maine (9) only one soil site out of 27 sampled randomly along major highways contained enough sodium to be properly termed alkali. However, it was also noted that at most sites sodium and chloride values decreased consistently with increasing distance from the edge of the highway over a distance of approximately 40 to 50 ft. Also, sodium and chloride levels in the soil increased with number of years over which highway salting had occurred. These data are in general agreement with the assumption made in Table 1 of this paper, where salt concentration on bands of 30 to 60 ft on both sides of the highway were calculated for several rates of application.

The assumption made in Table 1 that the salt applied to a highway is dissolved in the precipitation occurring during the winter months may not be entirely valid because much of the salt is frozen into the snowbank at the edge of the road and is not released to the surrounding environment until snowmelt occurs at the end of the winter period. Published data (9) indicate that most of the salt is contained in the snow within 10 ft of the edge of the pavement.

It appears valid to conclude that salt toxicity to some plant species can be predicted by interpreting data from several publications produced in the arid western areas of the United States. However, there are not yet sufficient data on conditions in the northeastern and northcentral states to safely predict when toxicity levels will be reached at a given site unless soil and water samples are monitored frequently. Some of the variables that negate a generalization on this point are as follows:

1. Texture of surface soil and subsoil,
2. Surface and internal drainage,
3. Rate and repetition of salt application, and
4. Type of vegetation on the site.

Reference is made in this paper to a number of compounds that have been used to replace sodium ions in alkali soils in order that they may be leached from the profile. Most of those chemicals, namely gypsum, calcium chloride and various sulfate compounds, have been proved successful. However, it does not appear that ground limestone is a suitable material, although it would be much cheaper than gypsum in many of the northeastern states. The calcium from gypsum or limestone is equally effective in entering the cation exchange sites of a sodium-affected soil, but the resulting sodium sulfate formed from gypsum is highly soluble, and the sodium carbonate formed from limestone is relatively insoluble. In one recent experiment (11) where limestone and gypsum were applied to high sodium soils along three highways, the latter compound reduced the sodium level by one-third, whereas the limestone was ineffective.

In summary, the data and conclusions presented in this paper are pertinent to the present issue confronting highway departments concerning the potential hazard of adding greater quantities of both sodium and chloride ions to the environment. Proper interpretation of these findings made at the local level in accordance with existing conditions could well decrease the environmental threat to some degree.

My comments are intended as an additional interpretation of the findings rather than as criticisms.

#### References

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Robert L. Westerman, University of Arizona

Salt-affected soils develop not only under imperfect drainage conditions but also with poor management. In the Southwest, evaporation can cause significant accumulation of salts, but salts accumulate in many soils as a result of leaching inadequate to move the harmful salts out of the root zone. This often occurs because of the poor quality or amount of irrigation water used. The only difference is that in northcentral and northeastern United States rainfall is adequate for leaching of soluble salts through the profile. During periods of rainfall, the drainage ways collect water from the paved surfaces, which increases leaching of soils. As suggested by the author, the soils are frozen during the winter, and most of the salt is lost in runoff waters, which leaves very little to move through the soil profile. During spring more rain falls and leaching appears to be adequate.

The guidelines that have been established for crops grown in the arid Southwest are based on the electrical conductivity of the soil extract, and I disagree with the author's statement that the levels do not apply in soils located along highways in more humid and colder regions. These criteria were established to preserve agriculture and are conservative, but the basic guidelines do apply. In the author's case very little of the salt load is passing through the soil profile. If, however, salts were accumulating in the soils, the rise in the salinity level in the soil solution would affect plant growth. The extent of damage to the plants would depend on the plant's tolerance to salinity and the osmotic pressure in the soil solution.

However, I do agree with the author that mixtures of NaCl and CaCl<sub>2</sub> would reduce the potential pollution hazard from de-icing solutions.

E. J. Rubins, University of Connecticut

Brandt's thesis is that salt mixtures containing calcium chloride not only are superior to sodium chloride alone for de-icing purposes but also have the additional advantage of providing calcium ions to overcome the deleterious effect of sodium on contaminated roadside soils. Arguments in favor of anhydrous calcium chloride as a component of highway de-icing mixtures are based on the observation that heat is evolved when it dissolves and that it can attract hygroscopic water to form a brine at low partial pressures of water. But these advantages are often lost in the translation from laboratory to field.

It has been pointed out (12) that partial hydration of calcium chloride during handling will reduce the exothermic effect when it reaches the road surface and that wind chill can remove heat otherwise available for the melting process, particularly when application is made at the onset of a storm and there is no opportunity for the calcium chloride particle to become embedded in ice or packed snow. When embedment does occur, the favorable effect of a calcium chloride brine in triggering solution of sodium chloride will be lost if the distribution pattern of the brine is such that dry sodium chloride does not fall within its effective radius.

The dual problem of a high level of soluble salt (salinity) and a buildup of exchangeable sodium (alkali) is of serious concern wherever soils of arid regions are irrigated for crop production. This problem is not general to humid regions such as the north-eastern United States, but it can assume local importance where soils are being reclaimed from the sea, where brackish water has been used for supplemental irrigation, or where excessively high rates of fertilizer have been applied. Roadside soils subjected to salt from de-icing operations can also be presumed to be vulnerable.

Criteria for irrigation water quality have been based on two measurements: the sodium adsorption ratio (SAR) derived from molar concentration values for sodium, calcium, and magnesium

$$\left( \text{SAR} = \frac{\text{Na}^+}{\sqrt{\text{Ca}^{++} + \text{Mg}^{++}}} \right)$$
 and the soluble salt concentration measured by electrical conductivity. The former provides an estimate of sodium (alkali) hazard, the latter an estimate of salinity hazard. An overall estimate of water quality is based on the interaction between the two (5).

This approach has been used widely in arid regions. The pH value of these soils is 7 or more, and the only exchangeable cations that need be considered are sodium, calcium, and magnesium. But the application without modification to salt-containing runoff waters in the humid regions is open to serious question. In the humid regions soils are acid to varying degrees, and as the pH value falls aluminum takes over from calcium as the predominant exchangeable cation. It is relatively difficult for a monovalent cation like sodium to exchange divalent calcium, although, of course, this does take place. It is even more difficult for sodium to exchange the trivalent aluminum ion. If SAR is to be considered for soils of the humid regions, molar relations such as

$$\frac{\text{Na}^+}{\sqrt[3]{\text{Al}^{+++}}}$$
 should also be considered.

Figure 7 of Brandt's paper has been adapted from another publication (5) in which water quality zones are identified on a plot of sodium (alkali) hazard against salinity hazard. The zones defined in this version are far from identical to those in the original publication, but the rationale and the details of the derivation are not given.

Both versions do show clearly that the presence in water of calcium ions from whatever source will lower sodium (alkali) hazard to soil through which it percolates by lowering SAR. Plots for various calcium chloride-sodium chloride ratios are given in Figure 7, but the plot for sodium chloride used alone is unrealistic. Because the SAR of pure sodium chloride is infinite, it has been necessary to assume a small impurity of calcium in order to make the plot!

Actually in humid regions a pure solution of sodium chloride percolating through the soil would not remain so very long. There would be some exchange by sodium ions of various ions such as calcium and aluminum. A series of ratios between sodium and these ions would be quickly established in the percolate depending on salt concentration and soil pH value. It is not unreasonable to speculate that the actual plot for sodium chloride solutions in Figure 7 would be different from that given.

Soil application of relatively inexpensive gypsum is a favored treatment for soils adversely affected by sodium in both the arid and the humid regions. Some experimental work has been carried out on the use of gypsum on soils bordering highways (11). If the use of gypsum is clearly indicated for this purpose, further studies including cost analyses should be established to compare this material applied to the soil with calcium chloride applied in de-icing operations.

### Reference

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Avery E. Rich, University of New Hampshire

Brandt's paper is of great interest to me, and I am sure that others will find it equally interesting. I do not claim to be a chemist, and some of the paper delves into chemistry a bit too deeply for me to comprehend completely. However, I understand most of it and agree with a good portion of it.

The University of New Hampshire initiated research on the effect of de-icing compounds on roadside vegetation about 12 years ago. Until that time limited observations and research reports indicated that salt caused little if any harm to the vegetation. No one seemed to know or care what became of the salt after it performed its task of melting the ice and snow except for the constant complaints of car owners concerning their rusted and corroded automobiles. However, about that time our state highway department and others started receiving complaints about salt from the highways contaminating wells that were in close proximity to the highways. When samples of water from the wells were tested, some of the samples were found to be too salty to drink. While we continued our investigations on vegetation, Fred Hutchinson of Maine and others studied the movement of salt into and through the soil and into the water.

I am afraid I must question Brandt's statement that "Even though roadside damage to plants is reported in the literature, the damage is nowhere so extensive as would be indicated." I can only conclude that we have done a poor job of publicizing our research. We have shown that NaCl is very injurious to roadside trees and that CaCl<sub>2</sub> is slightly less toxic.

Brandt has made a good case for using a mixture of 1 part CaCl<sub>2</sub> and 3 parts NaCl. Our research has shown that NaCl is more toxic to tree seedlings than CaCl<sub>2</sub>. However, CaCl<sub>2</sub> alone at high rates is rather toxic. He states that 2.5 tons of NaCl per lane-mile may produce unsuitable water quality but the same rate of 1:3 CaCl<sub>2</sub> to NaCl mixture can produce acceptable drainage water. What happens if the amount of the mixture is increased, due to frequency or severity of storms or faulty equipment? Will the water still be potable? I doubt it.

Let's look at the arguments for the use of CaCl<sub>2</sub> over NaCl:

1. More effective ice melter at certain critical temperatures,
2. Less injurious to physical structure of soil,
3. Slightly less injurious to vegetation, and
4. Less objectionable as a pollutant of drinking water.

Now let's look at the arguments against the use of CaCl<sub>2</sub>:

1. Much more expensive to purchase,
2. Much more difficult to store,

3. More difficult to handle and apply, and
4. May be irritating to handler.

I am not sure which side wins. I am very much in favor of using a mixture of the two salts if the mixture will do what Brandt suggests, if economics will allow it, and if the mechanics of storage and application can be worked out. I think more research, development, and testing are needed, but the bright hope is worth the effort.

## AUTHOR'S CLOSURE

Exchangeable aluminum content certainly ranks among major differences in soils of the humid regions and of the arid West, as pointed out by Rubins. This point alone may explain why Hutchinson found only one soil in 27 samples from Maine highways that contained over 15 percent exchangeable sodium or could be termed alkali. The exchangeable aluminum content will tend to be more significant for older, more highly weathered residual soils but less significant for geologically younger alluvial soils or glacial deposits. However, of equal significance is the fact that most soils along highways are subsoils or parent material rather than weathered A or B horizons as classified by agronomists. Subsoils in humid regions frequently are calcareous rather than high in exchangeable aluminum. Nonetheless, Rubins' point that all the exchangeable cations must be considered to properly apply the sodium adsorption ratio (SAR) concept is certainly valid.

Water quality zones in Figure 7 were drawn to approximate those from the original plot (5). The zones identified in the original plot are not meaningful to most people dealing with highway de-icing salt. Consequently, the simplified version was devised for this paper. It should not be used by more serious investigators in place of the original version. The plot for NaCl was derived from a typical analysis for commercially available NaCl rather than arbitrarily assuming an impurity level.

Rubins first points out that trivalent aluminum ions will be difficult for sodium ions to replace but later contends that specific ratios will be established in the percolate, and he is right in both cases. However, we must also remember that salt loadings can range between 1 and 10 tons of salt per roadside acre per year, assuming 11 acres of affected roadside per mile of four-lane freeway. Such high salt loadings strongly suggest that we need to quantify the exchange equilibria. It may be that exchangeable aluminum effectively prevents formation of alkali soils or that excessive exchangeable  $\text{Na}^+$  in the presence of exchangeable  $\text{Al}^{+++}$  does not destroy soil structure or that calcareous subsoils are only very slowly converted to alkali soils. Extensive tree damage reported by Rich and others suggests that we need to work toward quantifying the hazard.

Adams pointed out in the oral discussion that ions retained by bed load sediment escape detection when only water analyses are used to calculate total salt leaving a watershed as was assumed in the paper. The exchangeable salt transported with sediment can account for a significant portion of the suggested deficit. Adams indicated that the salt transported as bed load is very hard to quantify. This is obviously a very important consideration in examining total salt movement through the environment.