

Environmentally conscious de-icers:

Chemical capabilities in the environment and municipalities

Literature review

Ryan Kane, Tufts University

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Executive Summary:

The use of de-icing salt is a ubiquitous and effective means of ensuring passage and safety on many of our nation's roads, but it comes at a cost to the health of our natural environment, in particular our waterways. The high amounts of salt being applied to our roads every winter and, consequently, draining into natural environments has resulted in increased concentration levels that make it difficult for our ecosystems to thrive.

Concentrated amounts of chloride and other components of these road salts cause biochemical imbalances to occur, harming flora and fauna found within freshwater environments that are not adapted to highly saline conditions. As climate change continues to shift seasonal weather patterns and conditions, it has resulted in a staggering increase in road salt application; unsurprisingly, this has further strained local governments tasked with treating environments plagued with salt toxicity and correcting its corrosive damage to both vehicles and infrastructure. Although some areas have begun to implement environmentally conscious alternatives, large-scale adoption of a safe de-icer solution is

necessary to reach goals for protecting green spaces and infrastructure budgets as climate change continues to force human populations to adapt to more variable weather conditions.

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1. Chemistry

Salt

Composed of a positively charged cation bonded to a negatively charged anion, salts are ionic products of acid-alkali reactions. Although dependent on the chemical species, many salts possess a simple composition and a common source of formation that allow for widespread availability. With salt possessing an electrical binary form, society has utilized its reactivity in a myriad of ways, such as clearing our pathways of ice.

Melting

To prevent slick sidewalks and roads, de-icers, such as road salt, work to quickly melt frozen water. When salt interacts with water, dissociation between the salt's cation and anion occurs due to the polarizing ability of water. As these ions become separated in the mass of water, one can think of their identity as inhibitors. By forming intermolecular bonds with molecules of water, ions disrupt the geometric lattice structures of crystallization necessary for solidification. A salt's melting ability highlights the concept of freezing point depression, a phenomenon that occurs when a substance requires lower temperatures to freeze upon the addition of a solute. With salt becoming a component responsible for blocking bonds between water molecules, tight attractive forces become unattainable at previous freezing temperatures. Rather, lower levels of thermal energy, or temperatures, are needed to stabilize these molecules into a rigid solid structure. As our roadways clear of ice to become safe and navigable, aqueous solutions of de-icers are carried through runoff into our nearby bodies of water.

To understand the thermal limits of melting agents, it is necessary to appreciate the difference between eutectic temperatures and practical temperatures. At a certain solute concentration, a solution reaches its lowest possible melting temperature, known as the eutectic temperature [1]. Yet, this behavior is only accomplished at specific and stable conditions, making its application on pavement without laboratory control rather pointless. The lowest practical temperature, which is simply the lowest temperature at which adequate melting is occurring over a reasonable period of time, provides a much more appropriate measure of a de-icer's thermal scope of efficacy [1].

2. Environmental Harm

The application of road salt creates cascading chemical imbalances within environmental systems. The containment of salts and their toxic capabilities is futile. Salt deposits on roadways are able to reach beyond natural bodies of water, into groundwater, soils, and terrestrial food chains. Freshwater ecosystems, like the Upper Mystic River Watershed, possess a low threshold for heightened salinity levels. Most of the resident organisms have evolved in freshwater conditions. As a result, their biochemical response to heightened salinity levels is often ineffective [2]. Further heightening the levels of stress on organisms is the concomitant effect of increased levels of chloride concentrations occurring during winter, a period when the natural culling of freshwater flora and fauna is already taking place. Ecosystem dynamics are further disrupted as invasive species with

greater salt tolerance are supported in such conditions [3]. The current trend of applying de-icers jeopardizes the health of our remaining healthy freshwater ecosystems.

Keeping the composition of rock salt in mind, sodium's environmental impact is much weaker than its anionic counterpart - chloride [4]. Road salt's presence in soil has shown to bring about significant alterations in soil chemistry and composition. Soil conditions are shown to be at the highest risk within 15 feet of a pavement's edge [5]. Considering the high concentration (56%) of impervious surfaces within the Mystic River Watershed, this detail reveals that road salt affects a significant percentage of the remaining natural spaces [6]. Sodium ions generate higher pH levels as hydrogen molecules are exchanged with these metal cations. Basic soil conditions (pH greater than 7) limit the availability of micronutrients necessary for vegetal development [4]. Within the soil, sodium accumulation impairs both permeability and structure; while calcium, magnesium, and potassium ions are capable of replacing sodium ions within the organic media, though are by no means benign at higher concentrations [4].

De-icing salt's influence on water hardness, defined as the amount of dissolved minerals in the water, affects not just the health of an aquatic ecosystem, but its chemical stability. The presence of minerals, such as calcium and magnesium, act as buffering agents and often raise pH. Metal toxicity can also be lessened in such water, as ions can form insoluble precipitates to become unavailable for organism uptake [7].

The potential breadth of damage when chloride ions are present in excessive amounts within an ecosystem is severe. As a result of both osmotic and ionic stress, observations of chloride toxicity in botanicals is similar to that of droughts: browning leaves, loss of foliage, and premature plant death [8]. Splashing from vehicles showers roadside vegetation with highly salted solutions. Coniferous trees are visibly susceptible to this damage compared to grasses and low-lying plants [4]. In Minnesota, stretches of roads lined with conifers now show a distinct skirt of brown needles, defining the range of salt splashing from passing vehicles. It is most threatening to soils in cases of long-term sodium accumulation.

Although adding salt to freshwater ponds and aquariums is a proven way of improving the protective slime coat of fish, unregulated drainage into natural aquatic environments can prove toxic. Freshwater gastropods have displayed acute sensitivity to chloride, with a study revealing a 50% lethal concentration of chloride ranging between 2,540-10,000 ppm [9]. The class of Gastropods, comprised of snails and slugs, contribute significantly to the structure of an ecosystem as well as the survival of local species. Ecosystems are living systems; hence, the extirpation of a species within an environment often leave niche roles vacant, disrupting the stability of a living system. Freshwater fish, macroinvertebrates, nematodes, and amphibians also face biochemical consequences of leaching chloride, consequently presenting the potential for ecological collapse. Beyond just the health of soils and plants, the anionic component of this salt, chloride, induces major chemical stress, known as chloride impairment, to wetland ecosystems [2]. Salinity, a

measurement for the concentration of salt dissolved in water, is a necessary factor in the cellular functions of aquatic organisms, but excessive amounts of chloride can hinder aquatic organisms' osmotic pressure, a cellular process maintaining a balanced concentration of water along with salts and other bodily solutes [10]. At chronic toxicity levels, which may be approached through much of the year in the Aberjona River, Alewife Brook, Mill Brook, and Mystic River, fish exhibit delayed or reduced growth along with ecological shifts [11, 12].

3. Society

Humanity's dependence on salt has created a series of consequences for the safety and structure of municipal infrastructure and environments within watersheds, revealing a damaging relationship with a chemical relied upon for mobility and safety. Today, road salts are draining into waterways at a record high rate [13]. After 20 years of compiling conductivity data from 10 sites within the Mystic River Watershed, MyRWA has successfully illustrated a clear trend in increasing chloride concentrations [11]. Although it is fair to speculate that climate change is the primary contributor to surging road salt applications, the correlation between increasing global temperatures and the use of de-icers across urban landscapes is shown to be minimal [13]. As some cities report continually wetter years while others document periods of drier conditions, a region's relationship with de-icers is dependent on how precipitation responds to increasing global temperatures. In contrast, research conducted through GIS has revealed urbanization to be the main factor

responsible for this steady increase [14]. As populations grow and shift from rural to urban settings, the proliferation of impervious surfaces is an expected consequence of city expansion. Impervious surfaces simply come to mean any surface, whether natural or artificial, that is water-resistant. Common examples are paved surfaces, like roadways, and roofs. Although rooftops do not demand any application of road salt, northern state laws require sidewalks and streets to be de-iced as a public safety measure [15]. As a result of removing permeable surfaces, which partially collect roadway runoff, and creating impervious surfaces, which facilitate the transport of road salts into bodies of water, the increasing concentrations of chloride at MyRWA's testing sites can be viewed as an expected consequence of urban expansion.

The cost analysis of America's current system of road salting has also shown considerable drawbacks and need for revision and/or innovation within the practice [16]. A civil and environmental engineer from Washington State University has spent a considerable amount of time and energy studying the use of de-icers in the United States. He discovered that the nation on average spends \$2.3 billion a year on salting its roadways, plus an additional \$5 billion on correcting its negative impacts, like metal corrosion. Although metal corrosion may seem rather minor and simply aesthetically unappealing to the eye, its occurrence can have considerable effects on public safety and health. In the case of the Flint Water Crisis, there is now substantial evidence by researchers which finds road salt to be the primary culprit for corroding drinking water pipes and releasing lead, a neurotoxin, into domestic water supplies [17]. Cases like this are causing many to push for

reform within road salt application methods and even for severe shifts in industry practices that would demand less maintenance addressing inclement weather, such as developing “ice-free pavements” [16]. Pros and cons exist for each potential solution. However, what cannot be disputed is the need for a timely correction to preserve the health of our natural environments.

4. Solutions

NaCl (Rock salt)

NaCl, or rock salt, has become the ubiquitous de-icer spread on icy pavements as a consequence of its cheap price and effective melting abilities, capable of melting ice at temperatures as low as 15°F [8]. The amount of ice melted per pound of applied salt is dependent on temperature. For example, under eutectic conditions, 1 pound of rock salt can melt up to 46 pounds of ice at 30°F, while only 4 pounds of ice at 1°F [18]. Yet, temperatures commonly remain in ranges appropriate for NaCl application, making the salt a cost-effective tool for maintaining dry roads and sidewalks. With a lower hygroscopic quality and less chloride, NaCl has been experimentally proven to possess less corrosive capabilities with concrete, compared to CaCl₂ and MgCl₂ [19]. Unfortunately, with demonstrated ecological impacts, this de-icer’s application fails to keep environments healthy and chemically balanced [20]. Unlike other common de-icing salts, NaCl is treated with anti-caking agents, sodium ferrocyanide and ferric ferrocyanide, containing cyanide, a chemical group notorious for its lethal potency. Research compiled across multiple studies, however, found these additives possess little potential threat to both terrestrial and

aquatic biota, thus providing no significant change in toxicity [21,22]. Rather the greatest threat towards maintaining ecological systems that NaCl presents is the dissociating sodium and chloride ions, generated upon dissolution. As explained previously in *Ecological Harm*, sodium is not an essential macronutrient for plants, but rather a toxicant capable of competing with potassium along with other vital minerals responsible for major cellular functions. Thus, applying rock salt exacerbates vegetal damage more than other de-icers, as sodium ions spill off impervious surfaces to later leach into soils. Chloride impairment is an additional consequence of applying NaCl. Rock salt is relatively effective and easily the most affordable option, but places considerable strain on environments with its toxic character [23].

CaCl₂

CaCl₂ is widely regarded for its superior melting abilities against common rock salt, as it is capable of melting ice at temperatures as low as -20°F [8]. This can be explained by its differing molecular composition. With each molecule possessing a calcium ion and two chloride ions, it has 50% more ions than NaCl, which when dissociated in water only has one sodium ion and one chloride ion. Additional ions in solution allow for more interactions with water molecules, further disrupting intermolecular structures necessary for freezing. The salt is highly hygroscopic, a chemical tendency to abstract moisture from its surrounding environment, that in turn removes ice from forming on pavements [24]. Its capability for water absorption is so strong that it is able to form a brine within its mass of

collected moisture: a chemical property also known as deliquescence. This characteristic results in corrosive effects on concrete that are greater than NaCl [25]. In terms of its impact on the structure of concrete, this can be explained by first understanding that freezing water expands as it forms a solid structure. The porous surface of concrete allows liquid water from the previously melted ice to fill these pores. CaCl₂ inputs up to 10% more water within these pores, leading to a greater exertion of pressure and further damage if temperatures drop to sub-freezing levels [26]. Yet, this data should be questioned, as it originates from a salt manufacturing site without any reference to any reviewed reports.

The calcium within CaCl₂ possesses its own set of characteristics that impact the environment. In some cases, the calcium application can provide benefits to vegetation suffering from saline soil conditions. The interactions between calcium, sodium, and magnesium within soils and cells and their biological contributions create a complex relationship in vegetal health. Sodium has little biological benefit for plants and rather acts as a competing cation within their cellular functions [23]. Calcium acts as a dominant cation to the negatively charged molecules within the soil, freeing sodium ions to drain out of soils following precipitation, thereby increasing the ratio of magnesium to sodium [27].

While CaCl₂ has numerous benefits to its application compared to other de-icing salts, its cost and environmental damage are not so impressive. Although not the most expensive species of de-icing salt on the market, CaCl₂ is more costly than the inexpensive, omnipresent NaCl. The ecotoxicity achieved by the dissociation of CaCl₂ is, unfortunately,

more potent than NaCl, contributing to greater levels of chloride impairment to freshwater fish [23]. Beyond just hindering osmoregulation, salinity can reduce the development of fish fry. A study found trout growth to diminish at lower chloride concentrations when treated with CaCl₂, compared to the application of NaCl, which exhibited similar growth reductions at chloride concentrations three times greater. Although reductions in growth are not a lethal condition, its gravity in ecological stability is great, as population dynamics would shift if fish were exposed to highly saline environments during early life stages. The melting benefits and lessened impact on concrete structure make CaCl₂ a salt worthy of contemplating to de-ice one's pavements. Yet, its acute ecological effects should be weighed against its positive attributes before implementation.

MgCl₂

In contrast to the widely-used road salts NaCl and CaCl₂, MgCl₂ is a less common de-icer. With -10 °F as its lowest practical temperature effectiveness, it quickly becomes unattractive compared to the much lower priced NaCl and CaCl₂. Also, it is highly corrosive to concrete through a "reaction between Mg²⁺ and the hydrated products in cement paste" [19]. Its lower reactivity also affects its interactions within environmental chemistry. Magnesium is an essential mineral in cells, particularly those of plants. Physiologically, magnesium acts as a contributing element for cellular energetics within chlorophyll molecules, a pigment responsible for photosynthesis. This metal is also found in a number of enzymes critical for maintaining cellular functions [27]. Within aquatic ecosystems, MgCl₂ causes excessive chloride loading. However, despite its chloride impairment,

organism exposure to this salt is less harmful than CaCl_2 . Safety data sheets note highly different acute toxicity levels in rats [28, 29]. 50% of rodents survived after receiving an amount of MgCl_2 130% greater than the amount of CaCl_2 that reached the same percentage in group mortality. Magnesium has a critical role in the cellular processes and energetics responsible for plant growth [30]. As a result of magnesium deficiency, plants typically exhibit stunted growth or necrosis [31]. Introducing magnesium into soil would have a lesser effect on vegetation, which could actually benefit if magnesium levels are deficient due to competing metals, like calcium [27]. Although magnesium is capable of leaching heavy metals from soils, vehicle and industrial sources are greater factors in heavy metal presence from roadway runoff [32]. With the salt's lowest effective melting point at a higher concentration in comparison with NaCl and CaCl_2 , it is often applied in greater amounts than such salts. As a result, increased chloride impairment is a potential drawback of using MgCl_2 if overapplied. Though it would appear that MgCl_2 's lower effective temperature would result in a reduced environmental impact, it commonly pushes greater chloride levels into ecosystems.

NaFo

Sodium formate (NaFo) is an effective road salt, melting ice at temperatures as low as 0°F , that holds similar characteristics to NaCl [33]. It has relatively lower ecotoxicological consequences than NaCl . Because it lacks chloride, chloride impairment is not a concern when applying this salt. However, just like NaCl , NaFo incorporates sodium cations into organic matter that compete with more biologically necessary minerals like potassium and

magnesium. When measuring for IC50 and LC50, this salt's acute toxicity was shown to be much less virulent than NaCl in a study involving seed germination and earthworm survival [34]. Formate, compared to other common ions found in de-icers, shows minor cellular impairment in aquatic mammals [35]. Its de-icing efficiency, in terms of its speed and scope of temperature at which it is functional, is only marginally worse than its chloride counterpart. Even when considering its environmental safety, it is expensive relative to NaCl. Unfortunately, NaFo's high price is unjustifiable in relation to its decent ecotoxicological results, thereby making this salt an expensive alternative unworthy of consideration. Yet, ecologically conscious salts are not out of the question. Other de-icing species are available that can outmatch NaFo in imparting a lesser impact on an environment's health.

CMA

Calcium magnesium acetate, or CMA, is regarded as the most environmentally friendly de-icing salt on the market. Acetate is shown to have poor mobility in soil media, reducing its contamination into groundwater. Studies on its ecotoxicological effects in wetland ecosystems are few, as its presence is often negligible with topsoil immobilizing acetate with only 10% entering into groundwater [36]. Within soils, it is capable of extracting heavy metals with its anionic character. Compared to other de-icers regarded for imposing fewer risks to ecosystems, such as NaFo, CMA is significantly less toxic to terrestrial organisms. Its acute toxicity (LC50) in organic soils is minimal as shown by its effects on earthworm survival during a study [34]. Data on seed germination and

macrophyte growth following repeated treatments of CMA reveal the salt's impact on vegetal health to be minimal in comparison to chloride-based salts, which, as discussed previously with NaCl, CaCl₂, and MgCl₂, are highly impactful in cellular functions by chloride impairment. Unfortunately, it exhibits comparable corrosive attributes to CaCl₂ and MgCl₂ upon contact with concrete, described to "cause significant changes in concrete that result in loss of material and a reduction in stiffness and strength" [37]. The appeal of its low environmental toxicity is greatly compromised by its price, which is over 35 times that of road salt. The median cost per ton of CMA is \$1,492, a formidable price when compared to only \$42 per ton for rock salt [38]. And, unfortunately, its melting capabilities are limited, with the lowest practical temperature at only 20°F, 5°F higher than that of rock salt [8]. Although less environmentally toxic, more salt may be required to reach similar results of NaCl application, potentially reaching similar impacts towards terrestrial health.

Brine de-icers

The use of liquid-based de-icers has become more common in combating ice formation on America's roadways. Such aqueous solutions commonly consist of NaCl concentrations between 20- 30%, equating to approximately 2 pounds of salt per gallon of solution [39]. Two other salts, MgCl₂ and CaCl₂, can also constitute de-icing brines but are less frequently utilized in urban settings due to higher costs. Increased metal corrosion has been observed with brine solutions. Brine's greatest benefit comes with its ability to maximize spread on roadways. Applying brine using motorized sprayers accomplishes more surface contact with roadways and an even spread compared to crystalized salts, and

thus requires less chemical applicant to achieve dry conditions. To reach similar melting effects, on average, brine uses $\frac{2}{3}$ the amount of salt compared to that of rock salt.

However, it should be noted that brine has a limited effect on heavy snowfall and ice coverage compared to solid rock salt.

Bio-based de-icers

New methods of melting ice incorporate the addition of bio-based components to brine solutions, helping to decrease chlorine impairment. Today, many different types of solutions are used across the world. Sugar beet juices are particularly common today, thanks to its relatively low cost and effective melting capabilities. When combined in a brine solution, the high sugar concentration of beets reportedly decreases the melting point of ice more than salt alone [40]. By using less chlorinated salt to melt roadways, municipalities have reported lower chloride concentrations in water bodies. However, by incorporating sugar into aquatic environments, bio-based de-icers have been linked to decreased dissolved oxygen levels through eutrophication [41]. Such aquatic toxicity rather displays this de-icer as another nutrient source to pollute living waters. Further toxic behavior was described in a study revealing increased susceptibility in insects, particularly mayflies, which act as important characters in aquatic ecosystems [42]. Further biochemical research is required to explain the increased blood salt levels found in mayflies exposed to this brine. Bio-based de-icer's smell, color, and sticky residue are common complaints of its utilization. Yet, its color and adhesive nature are qualities that enhance its melting efficacy [43]. Adhering to roadways provides greater contact with ice, allowing for less brine to be

applied to achieve comparable results with solid salt. The red color of beets increases the thermal quality of pavements with the absorption of sunlight [40]. De-icers combined with beet juice have also been shown to be less corrosive to infrastructure and vehicles than road salt [44]. This type of de-icer can be highlighted as a melting method comprising both biologically influenced efficacy with aesthetic issues and eutrophication with chloride consciousness. Such consequences make the practicality of this de-icer rather complex and dependent on the preferences and conditions of a municipality or residence.

5. Comparative Table of De-icers

| | NaCl | CaCl ₂ | MgCl ₂ | NaFo | CMA | Brine | Bio-based Brine |
|--------------------------------------|------------------------------|------------------------------|------------------------------|-------------------------------|------------------------------|----------------------------|--|
| Lowest Practical Melting Temperature | 15°F | -20°F | -10°F | 0°F | 20°F | - | Lower than brine |
| Price (lowest to highest) | 1 | 3 | 2 | 4 | 5 | Cheaper than solid de-icer | Dependent on the brine and conc. ratio |
| Aquatic Quality & Health | Increased chloride impairmen | Increased chloride impairmen | Increased chloride impairmen | Increased salinity, low metal | Minimal depletion of DO, low | Lesser chloride impairmen | Lesser chloride impairmen |

| | | | | | | | |
|------------------------------------|---|---|---|---|---|------|-----------------------|
| | t, low metal toxicity | t, metal toxicity | t, low metal toxicity | toxicity | metal toxicity | t | t, decreased DO |
| Terrestrial Quality & Health | Highest metal toxicity, damages soil structure | Low metal toxicity, improves soil structure | Low metal toxicity, improves soil structure | High metal toxicity, damages soil structure | Low metal toxicity, improves soil structure | - | - |
| Corrosion | Low | High | High | Low | High | High | High |

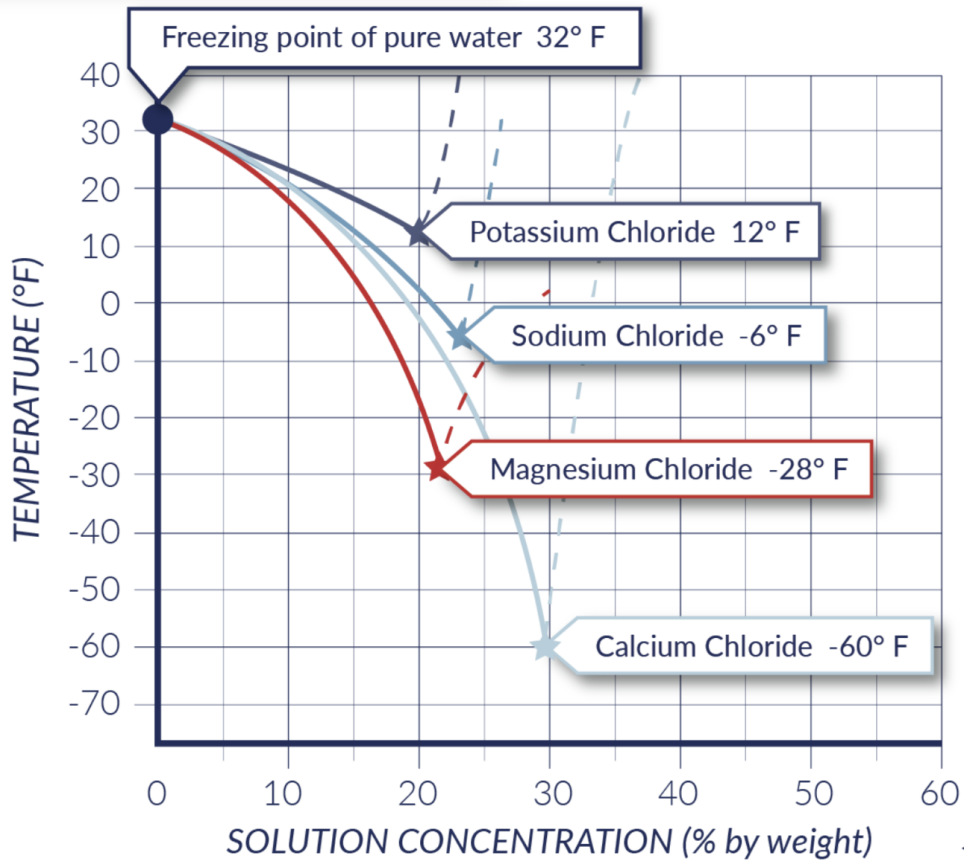


Figure 1. Melting temperature dependence on solution concentration, illustrating the phenomena of eutectic temperature [1].

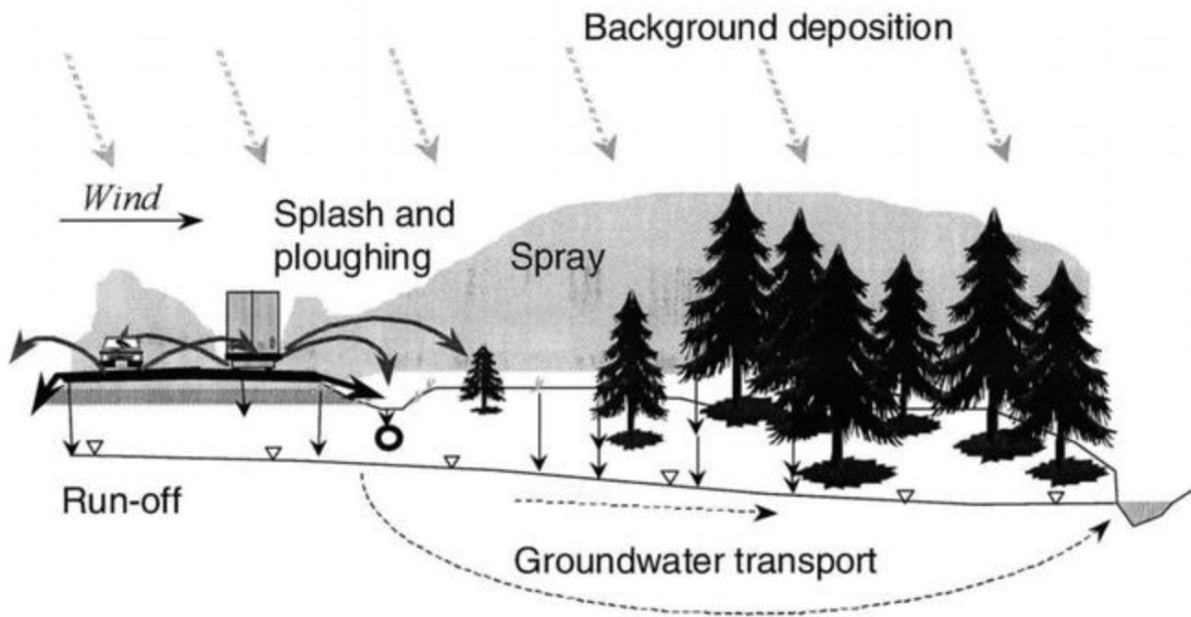


Figure 2. Model of various transport mechanisms for de-icing salts [45].

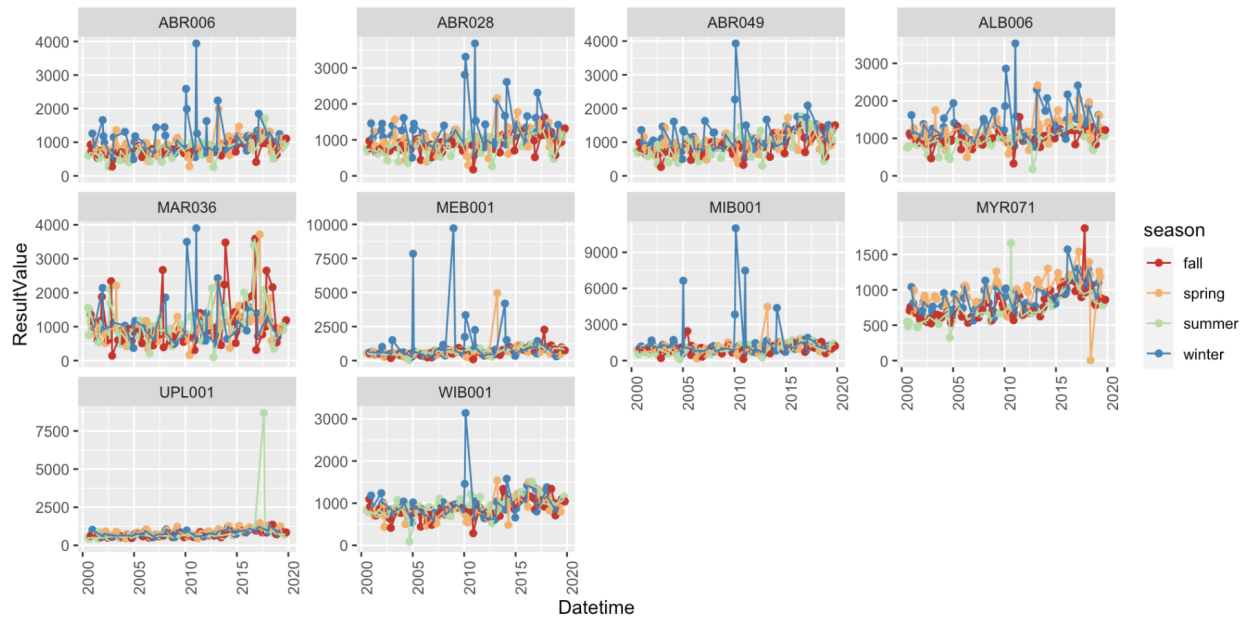


Figure 3. Conductance data measured over 20 years from sampling sites across Mystic River Watershed demonstrating a positive trend in chloride concentrations [11].

Resources

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