Road Salt Forensics:

Using Cl^-/Br^- Ratios and Other Indicators to Differentiate Road Salt and Other Impacts in Groundwater

Outline

- A Road Salt “Primer”
- Environmental Impacts
- The Regulation of Road Salt
- Using Road Salt Forensics

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Road Salt

- Granular sodium chloride was first used to de-ice roads on an experimental basis in 1938.
- Many municipalities across Canada use sodium chloride (Halite or Rock Salt) as an economical means of de-icing roads
- 5,000,000 tonnes per year across Canada on roadways alone
  - City of Calgary uses 30,000-40,000 tonnes per year
  - City of Toronto uses 130,000-150,000 tonnes per year
- NaCl enters the environment during snowmelt runoff, also from wastewater plants as it is not removed during treatment
- Adverse effects on plants and aquatic life
- Na and Cl regulated in groundwater in Alberta

'You can taste it': Road salt making GTA rivers, streams as salty as seawater

Scientists warn high chloride level in GTA waterways is damaging ecosystem, wildlife, ground water sources

Trevor Dunn · CBC News · Posted: Feb 02, 2018 4:00 AM ET | Last Updated: February 2

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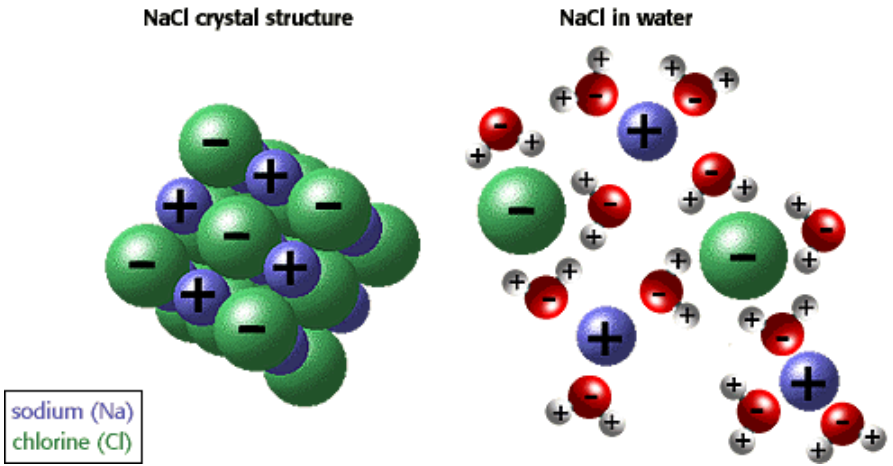
How Road Salt Works

- At 0°C / 32°F water molecules organize themselves into crystal, becoming ice.
- Salt ions (Na^+ & Cl^-) move between the water molecules, taking up space, preventing them from organizing into crystals.
- Water molecules now need to be colder before they can overcome the Na^+ and Cl^- interference to crystalize.



- Limitation…< -18 °C the capacity for salt to de-ice is diminished

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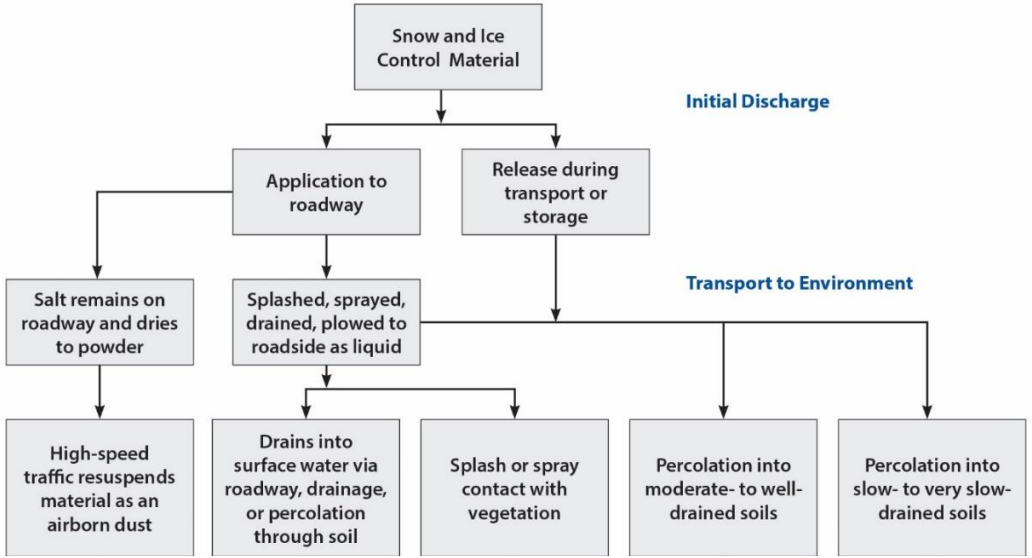
Environmental Impacts

Water:

- Dissolved Na^+ and Cl^- washed into storm sewers and surface water systems
- Seepage into groundwater supplies
- 10% of aquatic species are affected by Cl^- concentrations ≥ 240 mg/L (Health Canada)
- 4 separate Toronto creek samples:
  - 1,390-4,310 mg/L
  - Affects oxygen and nutrient distribution in the aquatic ecosystem

Soils:

- Plants that thrive on salt-rich soils can become invasive
- High salt content can be deadly to some animal life



Reprinted from:
National Cooperative Highway Research Program Report 577: "Guidelines for the Selection of Snow and Ice Control Materials to Mitigate Environmental Impacts

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Regulations

Parameter	BC	AB	SK	MB	ON	CCME
Drinking Water						
Sodium (mg/L)	200	200	200	200	NV	200
Chloride (mg/L)	250	250	250	250	NV	250
Groundwater						
Sodium (mg/L)	NV	200	200	200	490	NV
Chloride (mg/L)	100	100	250	250	790	NV
Surface Water (protection of freshwater aquatic life)						
Sodium (mg/L)	NV	200	NV	NV	NV	NV
Chloride (mg/L)	1500	100	120	NV	NV	120
Soil						
Sodium (ug/g)	150	NV	NV	NV	NV	NV
Chloride (ug/g)	100	NV	NV	NV	NV	NV

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Salinity and Sodicity

- Salinity – assessed through electrical conductivity (EC) measurements

- Sodicity – assessed through Sodium Absorption Ratio (SAR) which measures the proportion of sodium to calcium and magnesium in soil solution

$$SAR = \frac{[Na^+]}{\sqrt{1/2\,([Ca^{2+}] + [Mg^{2+}])}}$$

- Sodicity and Salinity in Alberta measured on a saturated paste extract vs. set ratio in Ontario

Alberta Guidelines

Table 2.2 Soil Quality Guidelines for Unrestricted Land Use

Parameter		Rating Categories			
		Good	Fair	Poor	Unsuitable
Topsoil[c]	EC dS/m (salinity)	<2[a]	2 to 4	4 to 8	>8
	SAR (sodicity)	<4	4 to 8	8 to 12	>12[b]
Subsoil[c]	EC dS/m (salinity)	<3	3 to 5	5 to 10	>10
	SAR (sodicity)	<4	4 to 8	8 to 12	>12

a Some plants are sensitive to salts at EC < 2 dS/m (e.g., flax, clover, beans, wheat, peas, some garden crops).

b Material characterized by SAR of 12 to 20 may be rated as poor if texture is sandy loam or coarser and saturation % is less than 100.

c Topsoil: surface A horizons on the control area, or the equivalent surface soil on the reclaimed site. Subsoil: B and C horizons and the upper portion of the parent material.

SAR, EC and Salinity can be impacted by sodium and chloride from road salt

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Elevated Sodicity & Salinity

- EC, SAR and Chloride are often included in a metals/inorganics lab package
- Hits can be problematic when it wasn't identified as a COPC in the Phase I
  - Is it background?
  - Is it road salt?
  - Is it mine?

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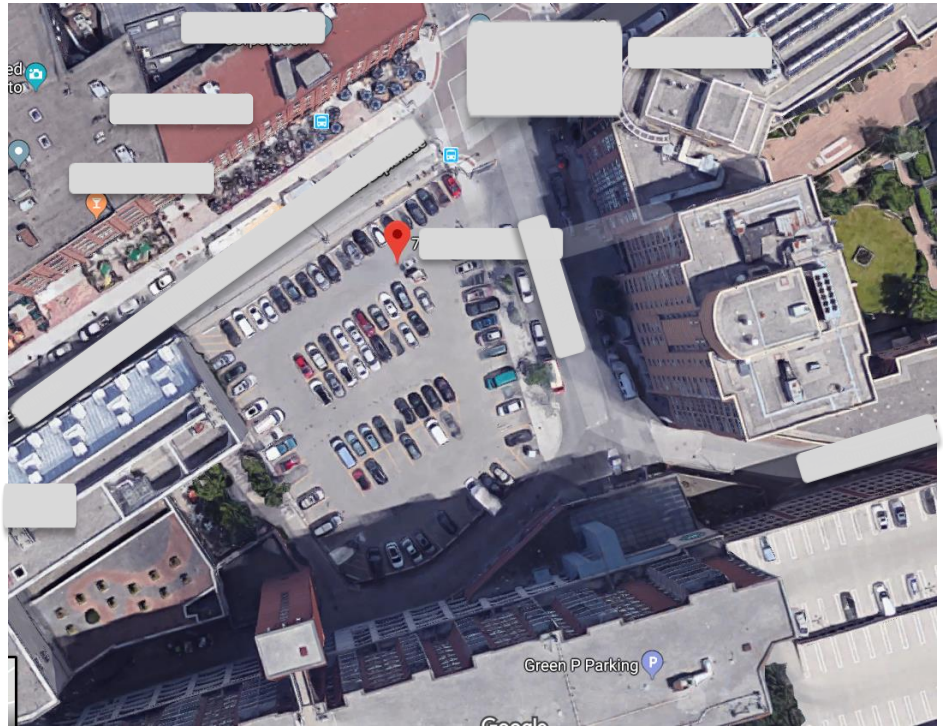
Case Study: Road Salt Forensics

- Site located in urban core of Toronto
- Parking lot since 1966
- Coal plant and fueling facility between 1912-1920
- Site to be remediated to remove soils impacted with salt, PAHs and metals
- Salt present in shallow aquifer above standards



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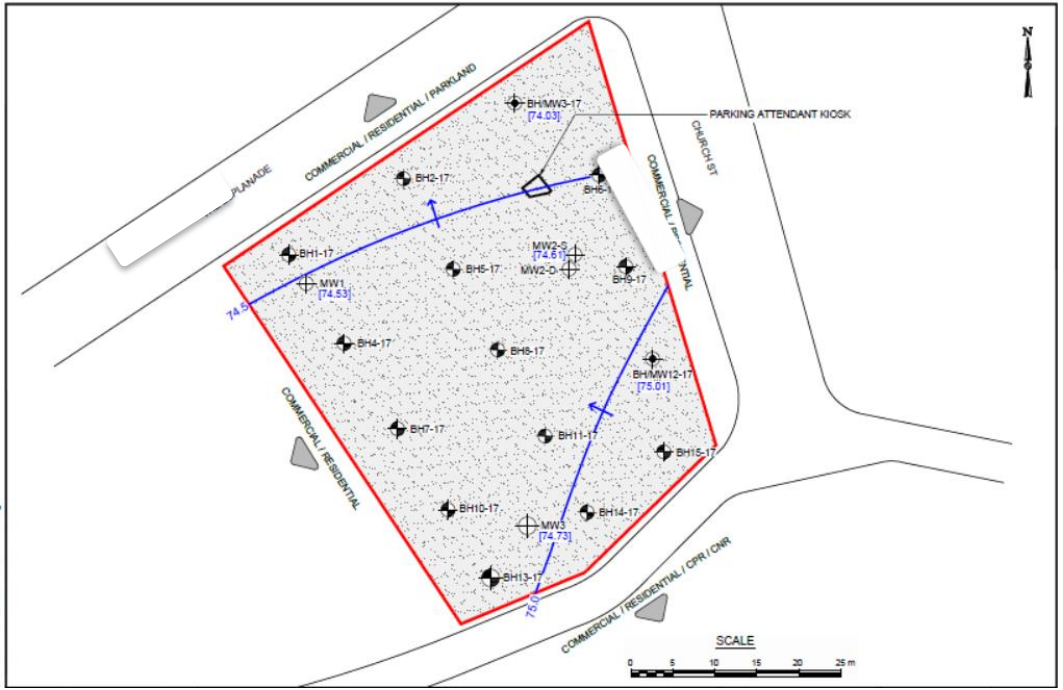
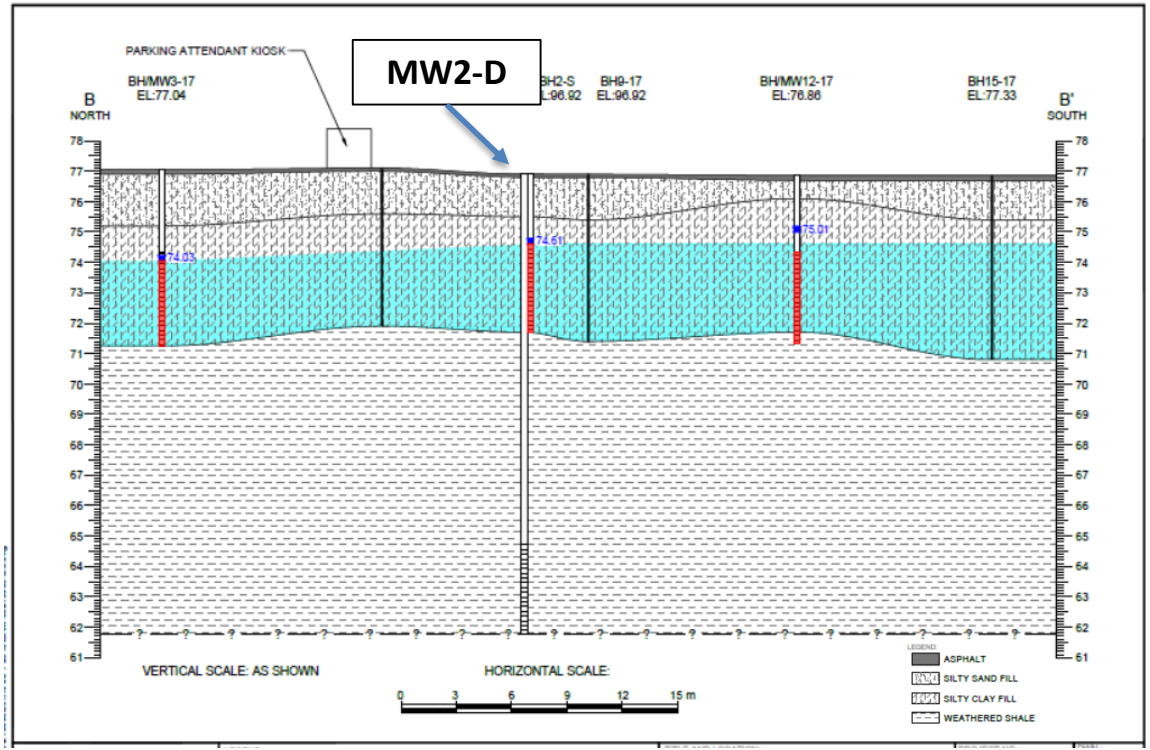
Case Study: Road Salt Forensics

- Depth to groundwater in overburden wells 1.45m
- Sodium and chloride in shallow groundwater exceed site condition standards.
- A deep monitoring well installed for vertical delineation



Case Study: Road Salt Forensics

- MW2-D installed in weathered shale
- Deep Na^+ and Cl^- > 2X shallow aquifer
- Is the deep salinity associated with road salt?



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Cl^-, Br^- and I^- in Road Salt

- Chloride, bromide and iodide are present in salt
- Chloride is generally 40-8000 times more abundant in nature than bromide
- The ratio of the ions are used distinguish pristine groundwater from wastewater sources and other anthropogenic sources including road salt
- A variety of analytical methods are available – IC, Colourimetric, NAA
- Br^-, Cl^- and I^- move conservatively in groundwater and are relatively stable – excellent markers
- Halite (road salt/rock salt) has a distinguishable very high (> 5000) ratio of Cl^-/Br^- vs natural saline water which is much lower (i.e. 150)
- Iodide also used as a ratio, however low detection limits required
- ICP/MS method now available at Maxxam

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Mass Ratio Cl^-/Br^- Concentration Plots

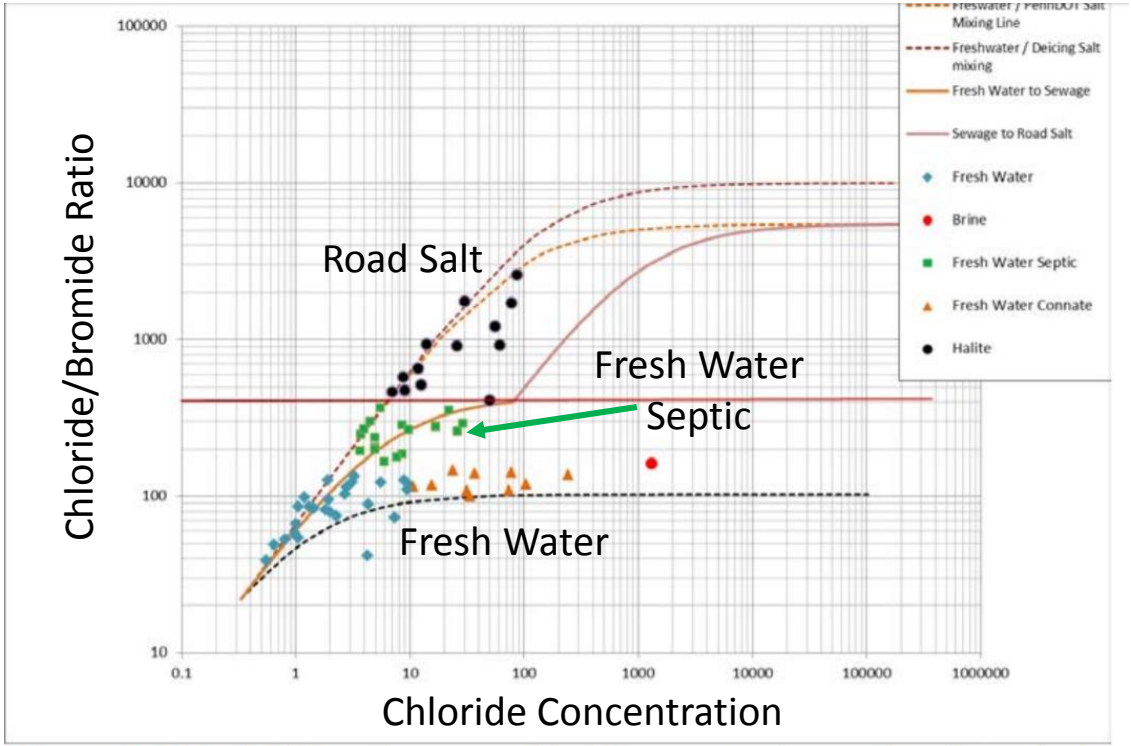

Figure 2. Plot of Cl/Br ratio versus chloride concentration used to determine 5 water types: fresh water, brine, fresh water septic, fresh water connate, and halite [3].

W Naily and Sudaryanto 2018 *IOP Conf. Ser.: Earth Environ. Sci.* **118** 012020

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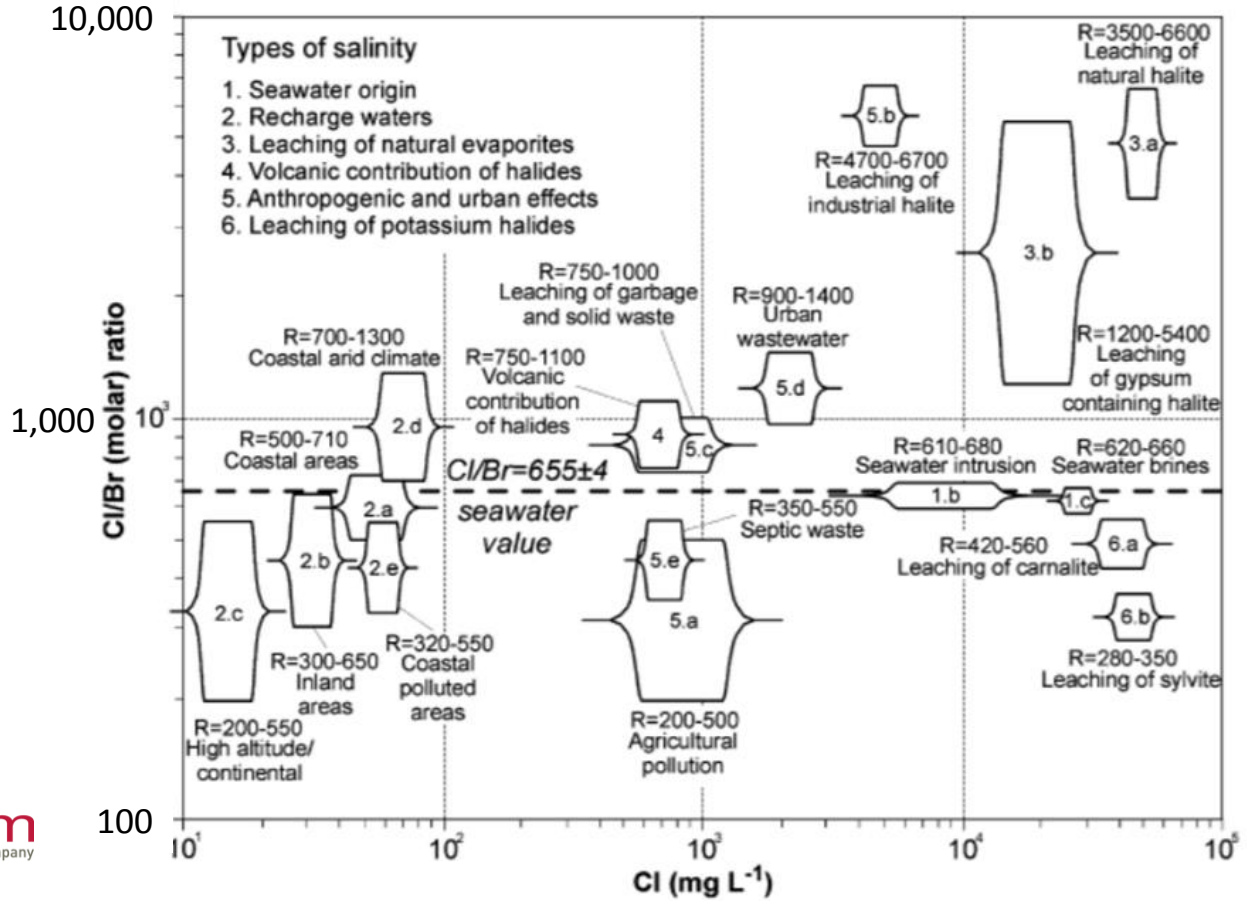
Molar Ratio Cl^-/Br^- Concentration Plots



Case Study: Road Salt Forensics

	Sample ID				
Parameter	MW1	MW3	MW12-17	MW2-S	MW2-D
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Sodium	1201	1613	1449	2511	1302
Chlorine (Cl)	1530	2150	1820	2370	2450
Bromine (Br)	< 1	< 1	< 1	< 1	20.6
Iodine (I)	< 5	< 5	< 5	< 5	< 5
Cl/Br	3060*	4300*	3640*	4740*	119
Chloride/Sodium	1.6	1.9	1.7	1.7	4.4

*bromine was not present above a reporting limit of 1 mg/L. To calculate a ratio of Br/Cl, the ½ the reporting limit was used

Report Conclusions:

- ✓ All shallow groundwater Cl/Br ratios are consistent with road salt
- ✓ Deep aquifer inconsistent with shallow groundwater and consistent with natural brine

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What's Next

- ✓ Evaluation of the tool on more road salt impacted sites
- ✓ Application in upstream Oil & Gas – differentiation of salt impacts based on formation
- ✓ Salinity packages:
  - Salinity 1 – EC, pH, SAR, Na, Cl, Br
  - Salinity 2 – EC, pH, SAR, Na, Cl, Br, I, Cl/Br, Cl/I

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