

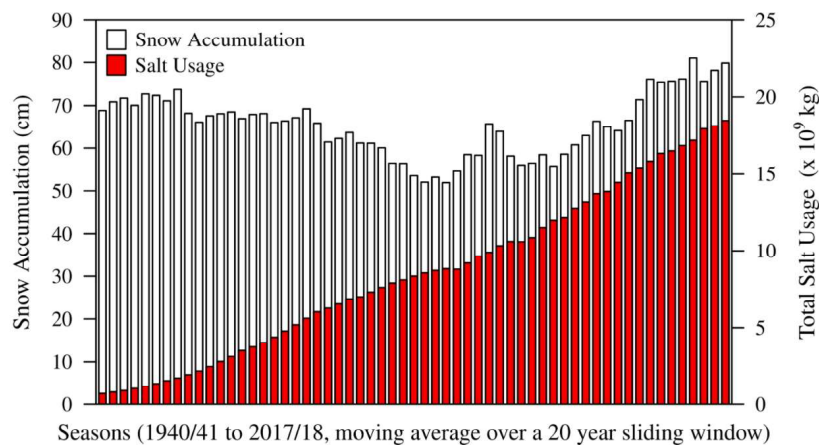
# THE EFFECT OF ROAD SALT ON TRACE METAL DETECTIONS AND CONCENTRATIONS IN A LONG ISLAND SANDY AQUIFER

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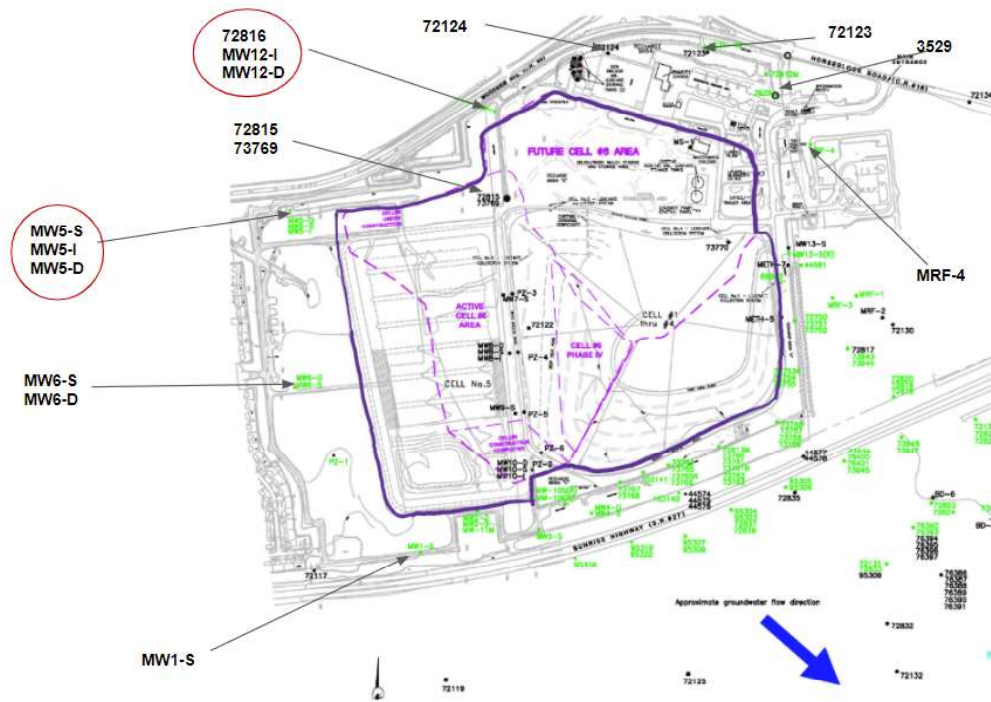
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The application of road salt (NaCl) in the U.S. for its deicing abilities has increased substantially, from an annual average of 8 million metric tons in 1975 to 18.5 million tons in 2003 (USGS, 2005). Chloride from road salting often enters groundwater systems (up to 55% of the applied salt in the Toronto urban watershed) (Howard and Hayes, 1993), resulting in concentrations in some aquifers ranging from 250 mg/L to 10,000 mg/L (Charles 2016). This can erode well infrastructures as chloride increases the corrosive potential of water and has been linked to elevated lead concentrations in drinking water facilities (Ng and Lin, 2015; Pieper et al., 2018; Stets et al, 2018). Furthermore, increases of cadmium, zinc, copper, lead, and mercury have been found to correlate with chloride ions (Norrström & Jacks, 1998; Löfgren, 2001; Backstrom et al., 2004; Sun et al, 2015). Here, we analyze long-term data (collected by USGS and Brookhaven) from monitoring wells installed in the Upper Glacial aquifer on Long Island near a landfill. We identified samples affected by road salt using a variant on Stiff diagrams (Stiff, 1951; Tonjes et al. 1995; Tonjes, 2013) and so were able to separate ambient groundwater quality from groundwater impacted by road salt. We found that Mn, Cr, B, Ni, Cd, and Hg had significantly higher detections in the salty samples, of which Cr and Ni also exhibited significantly higher median concentrations and only Cd and Hg reflected the results of past studies. No correlations were found between total dissolved solids (TDS) and each trace metal concentration, suggesting neither samples were driven by dissolution reactions. Understanding the effects of road salt on aquifer systems is critical to long-term management of drinking water quality, particularly because they are the sole source aquifers for Long Island residents.

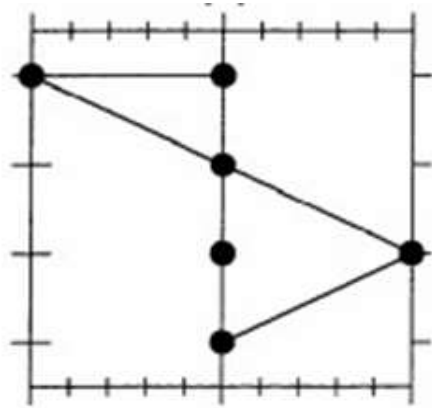


**Figure 1.0:** Average snow accumulation in Central Park, NY (from National Weather Service) versus salt usage for de-icing in the U.S. (from USGS). (Pecher et al., 2019).

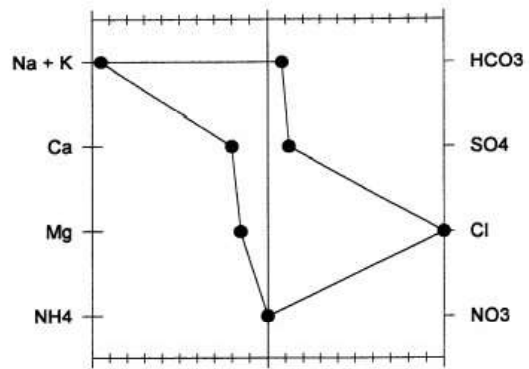


**Figure 2.0:** A total of 519 samples were drawn from 15 wells upgradient of a Brookhaven landfill. They were collected by USGS, Suffolk County (NY) Community College and Stony Brook University, and a Town consultant company (Dvirka and Bartilucci, CE). Circled in red were the wells that had the most abundant salty samples.

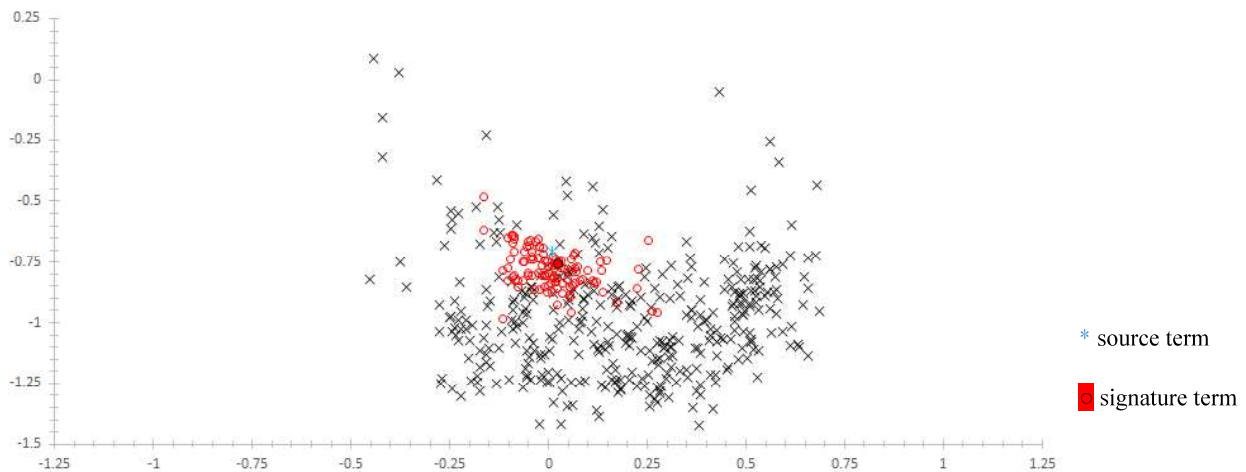
Previous studies have only correlated the increases in aqueous metals to chloride concentrations (Löfgren, 2001; Backström et al., 2004; Norrström, 2005; Kaushal et al., 2018; Stets et al., 2018), but there are many potential sources of chloride to groundwater environments, including natural sources such as weathering of rocks, minerals, atmospheric salt from the ocean, and bedded salt deposits and brine, as well as anthropogenic sources such as agriculture, mining, landfill, and wastewater treatment and septic discharge (Mullaney et al., 2009; Cañedo-Argüelles et al., 2013). This study is able to refine the impact of road salting on metals concentrations in a sandy aquifer by using a variation of Stiff diagrams (Stiff 1951; Tonjes et al., 1995; Tonjes 2013) to determine which groundwater samples had water chemistry that was dominated by road salting. The 519 samples were visually inspected and characterized by Tonjes as salty or not salty based on their correspondence with the signature road salt diagram (figure 3.1). The signature road salt diagram was created by using the source diagram (figure 3.0) as a reference, which represented the ideal shape of road salted water. This subjective analysis was verified by conducting a Principal Component Analysis (figure 3.2) of the modified Stiff diagram parameters and confirming that the samples identified as salty did create a distinct within-group cluster.



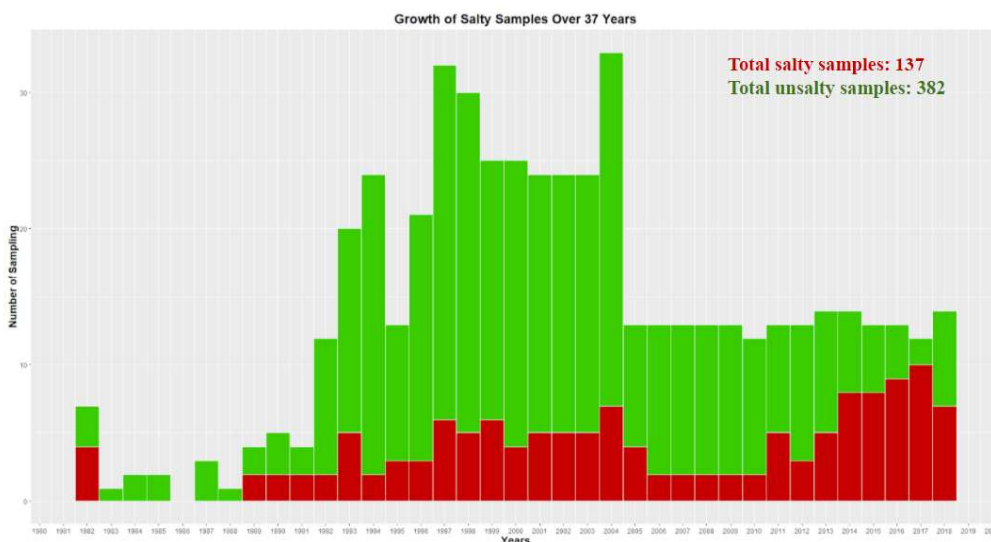
**Figure 3.0:** Source diagram - the shape for NaCl in deionized water. The x-axis represents the ionic charge of Na (right) and the Cl (left).



**Figure 3.1:** Signature road salt diagram - the ideal shape of road salt contaminated in ambient groundwater.



**Figure 3.2: Principal Component Analysis:** The x-axis and y-axis represent the first and second components of the PCA, respectively, accounting for the most variance. The PCA was conducted with eight parameters (figure 3.1).



**Figure 4.0:** Ratio of salty (in red) versus unsalty samples (in green) from 1982-2018. Starting from 2005, samples were collected twice a year from the same six wells, suggesting increased salty samples.

The percentage of detection for each metal was determined for salty vs non-salty samples (figure 5.0) where a metal was considered not detected if it had been reported as a 0 concentration or ND or below a detection limit concentration for a given sample. A t-test was performed with significance level  $p < .05$  to determine the metals that had significantly different detection between the two samples. Median concentration for detected samples was also determined for detected samples of the two sample types, and a non-parametric wilcoxon test with significance level  $p < .05$  was used.

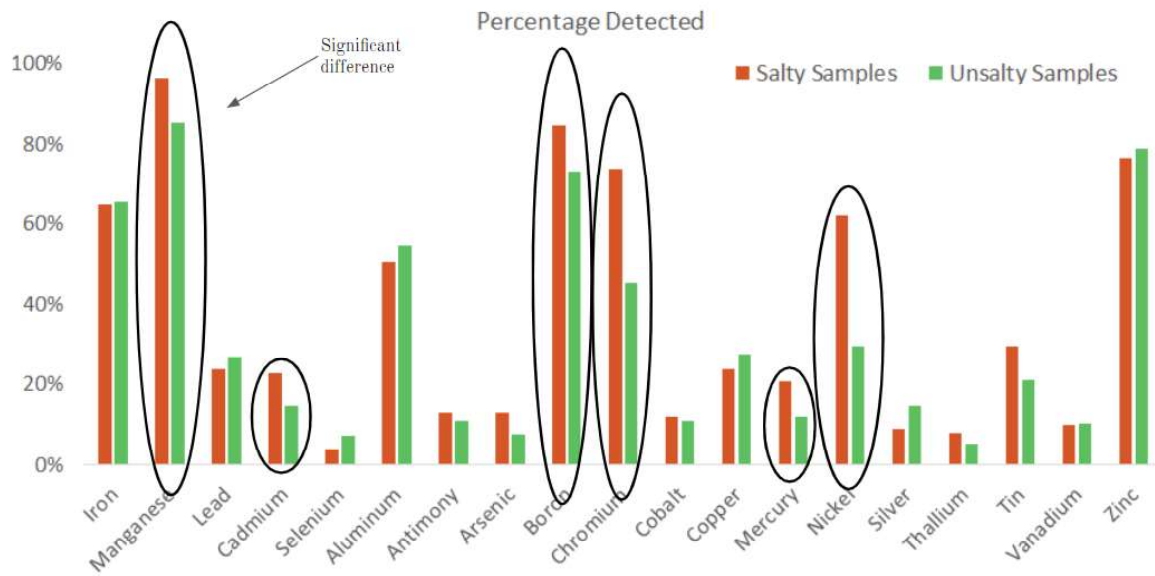
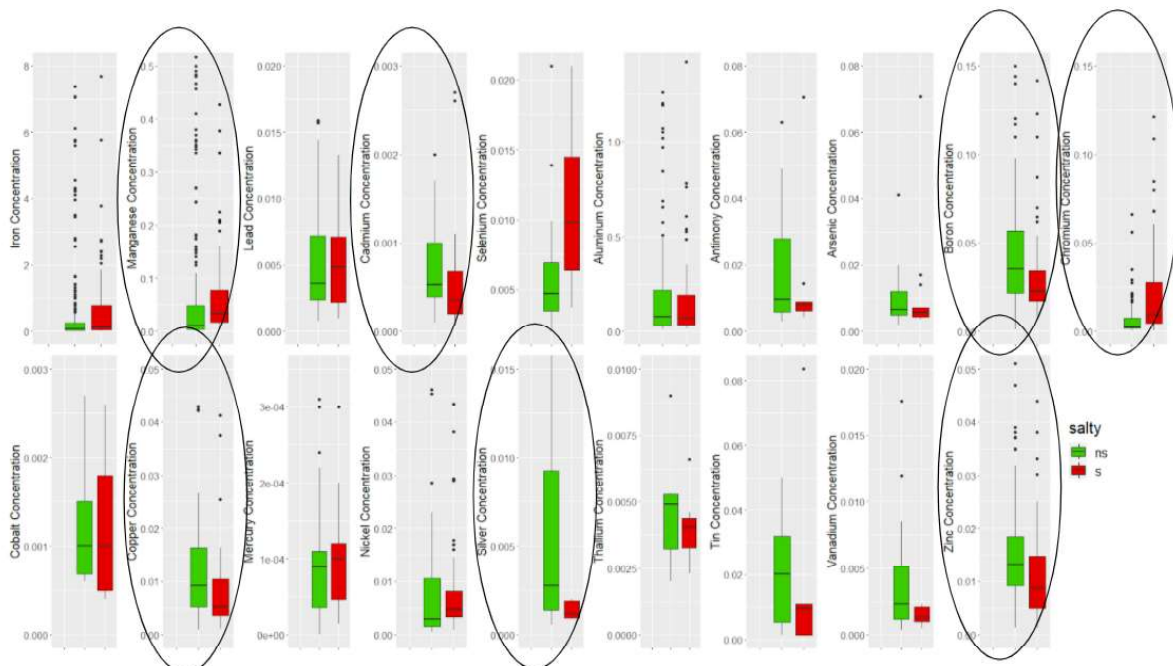
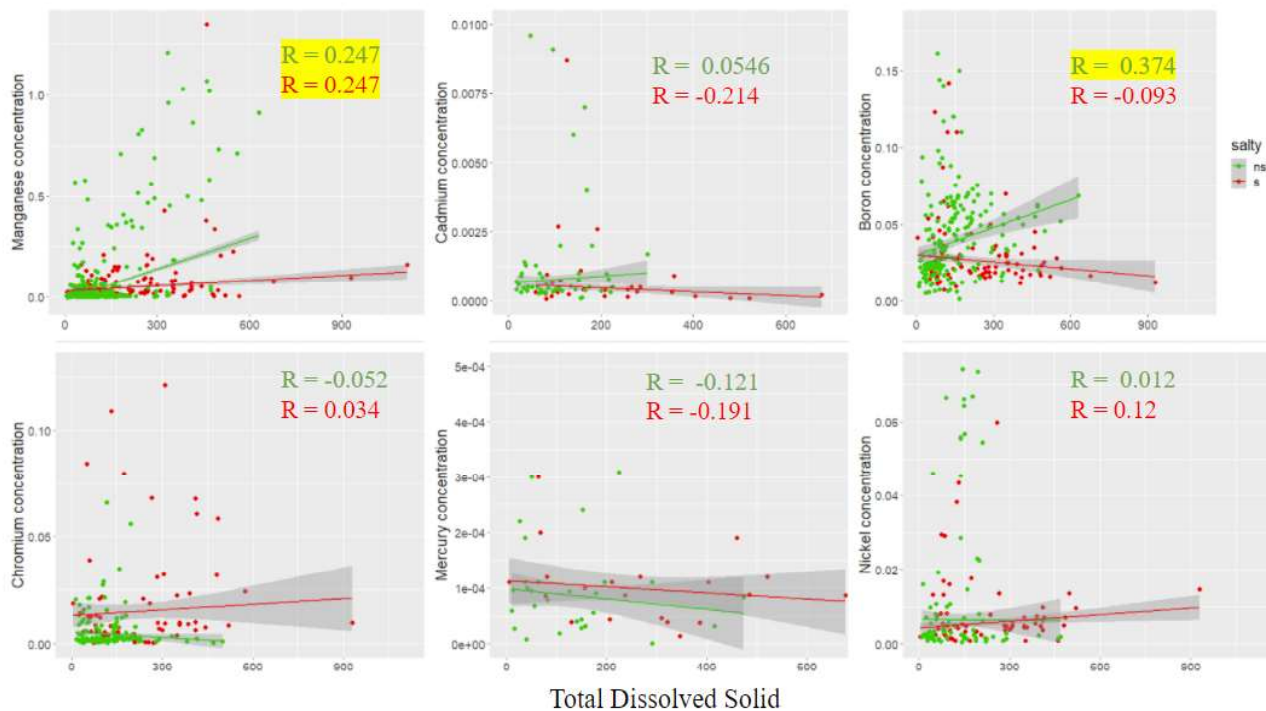


Figure 5.0: Significantly different percentages detected are circled.



**Figure 6.0:** Significantly different concentrations are circled.

Metals can form complex ions in water based on the availability of ligands such as  $[Cl^-]$ , which can increase its solubility. To maintain equilibrium, increased TDS can shift systems away from the product, dissolving metals into aqueous states. To determine if this theory holds and if there were any differences in the underlying chemistry between the two sample types, we determined the correlation between TDS and the six individual metals that were significantly elevated in detections (figure 7.0). There were generally no correlations between TDS and the metals, except Mn, which exhibited a significant correlation with TDS for both types.



**Figure 7.0:** TDS vs metal between salty (red) and non-salty (green) samples. R values that were significantly different from zero are highlighted.

## Conclusion

In using the stiff diagram to classify groundwater samples as either road salt contaminated or not, we found significantly higher detection percentages for Mn, Cr, B, Ni, Cd, and Hg in the salty samples, but only Cr and Mn had significantly higher concentrations and only Cd and Hg matched the findings of past research. However, our results strongly suggest that Cr and Mn are increased in aqueous samples because of road salting as they were found more often and at higher concentrations in samples classified as being impacted by road salting. Previous research only inferred road salt impact from elevated concentrations of  $Cl^-$  in association with roads that experience road salting. TDS concentrations did not explain the variance for any metal except Mn in either set of samples.

## Acknowledgement

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