



Assessment of spatial and temporal variations in chloride concentration in an agricultural tile-drained area in Central Illinois



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Background

- Long-term increases in chloride has been observed in numerous streams and groundwater across North America, with salinization in both urban and rural watersheds alike^{1,2}
- Implications of increased chloride concentration include
 - Intrusion of saltwater into freshwater ecosystems
 - Alteration of microbial communities
 - Acidification of streams
 - Contamination of groundwater including the release of heavy metals
- The USEPA set a chronic and ambient water threshold for chloride at 230 mg/L and 860 mg/L respectively because of the effects of elevated chloride concentration³
- Chloride sources in the environment are both anthropogenic and natural including atmospheric deposition, rainfall, deicing salts, agriculture, septic effluents and wastewater treatment plants^{4,5,6}
- In non-urban areas with little or no road salt application, agricultural sources have been positioned as contributing to the increase in chloride concentration although very few studies have explored its potential^{7,8,9,10}
- In McLean County, Central Illinois (one of the largest agricultural belts in the Midwest), agricultural fertilizers including potash (KCl) contribute a significant amount of nutrients to both surface water and groundwater systems posing a significant threat to places such as the City of Bloomington that depend on surface water reservoirs (Lake Evergreen) for their water supply

Study Area

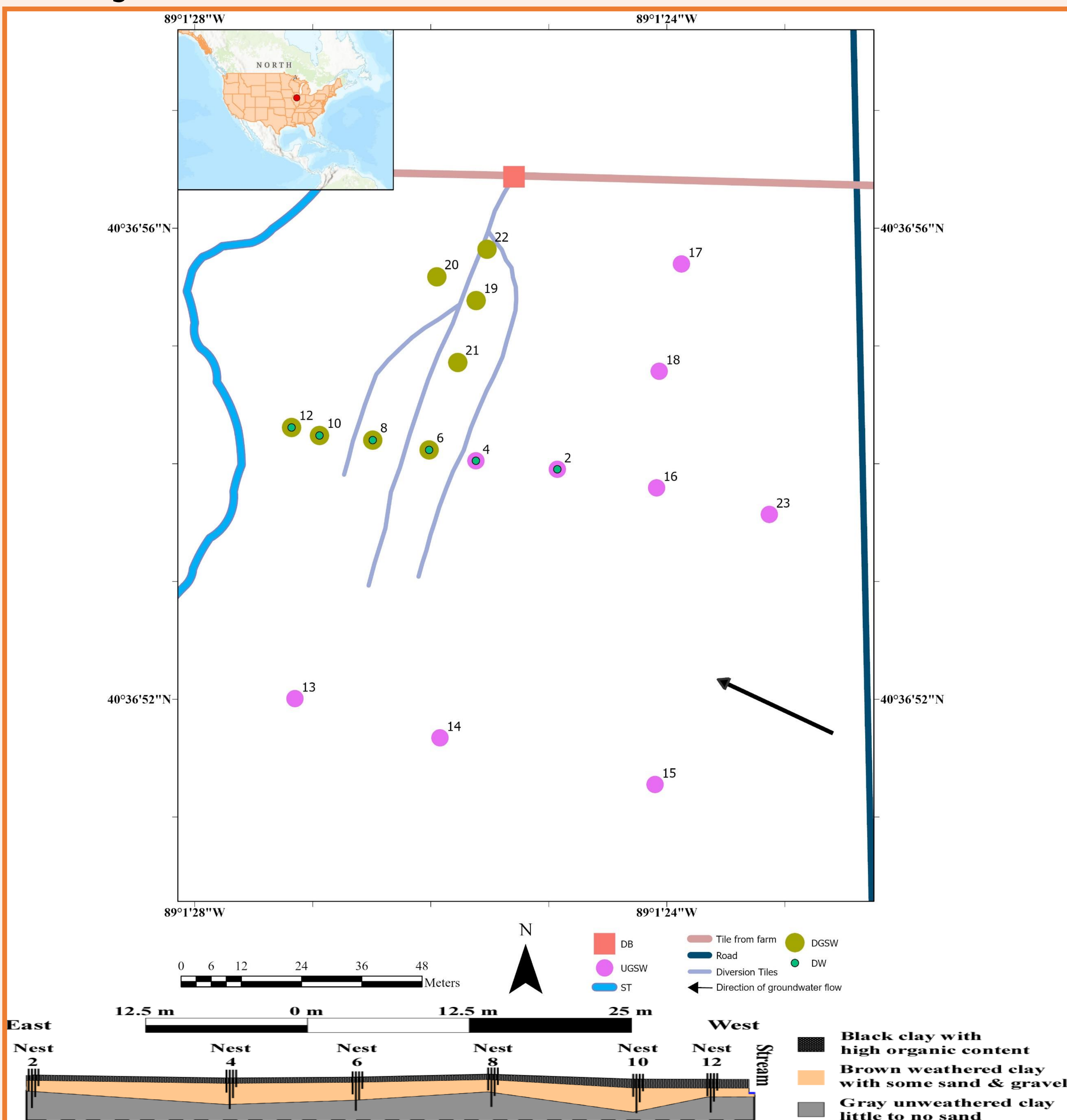


Figure 1: Saturated buffer zone (SBZ) located in central Illinois and a cross section of the nested wells. Map shows thirty-five wells, including six sets of nested wells divided into three groups namely: downgradient shallow groundwater (DGSW), upgradient shallow groundwater (UGSW), and deep groundwater (DW) in addition to the Diversion Box (DB) and the Stream (ST). The area around the study site has an agricultural land use of 84.4% and a farm is located 120m upgradient of the SBZ

Research Objectives

A saturated buffer zone (SBZ) located in Central Illinois was used to:

- Identify the number(s) of contributing populations of chloride to substantiate agricultural influence in the buffer zone
- Assess spatial and temporal variations in chloride concentration in the different groups within the buffer zone

Methodology

Field Sampling

- Over 4000 water samples collected from June 2015 - August 2022.
- In-situ measurement of temperature, dissolved oxygen, and specific conductance

Laboratory Analysis

- Major anion concentrations (F^- , Cl^- , NO_3^- , SO_4^{2-}) were measured using a Dionex ICS-1100 Ion Chromatograph at the Illinois State University LEA laboratory

Statistical Analysis

- Chemical data were analyzed using both RStudio and SigmaPlot. A two-way ANOVA ($\alpha = 0.05$) was used to determine the spatial variability (Groups) and temporal variability (Seasons). Principal Component Analysis (PCA) was done using the in-situ parameters and the major anion concentrations.

Results and Discussion

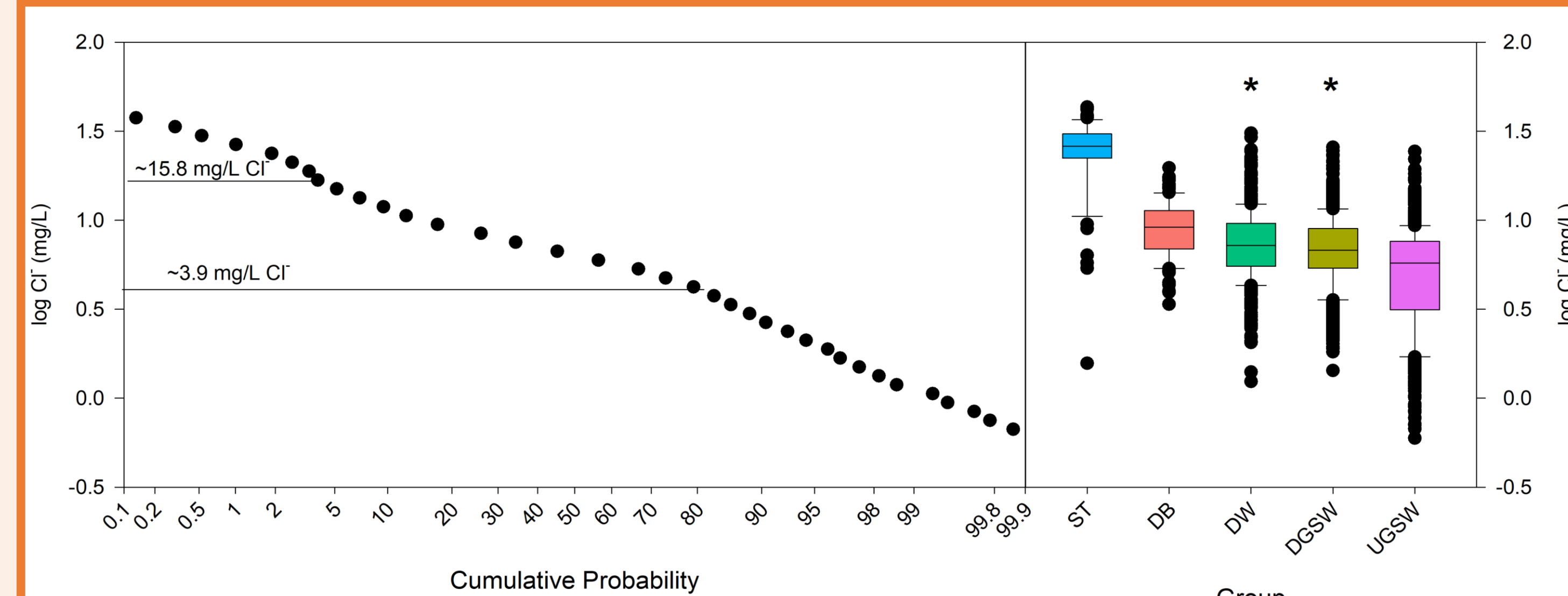


Figure 2: Cumulative probability plot and corresponding boxplots showing the different groups and the number of population of chloride in the SBZ. Note: * represents statistically similar groups

- The cumulative probability plot shows two inflection points thus indicating three populations of chloride (Fig. 2).
- The 1st population representing background concentration corresponds with the UGSW group. These are away from the diversion tiles and upgradient due to the groundwater flow direction. Hence little chance of chloride contamination (Fig 1).
- The 2nd population comprises three groups. The DB group represents the first anthropogenic signature and indicates the influence of the runoff from the farm through the diversion box (Fig. 1). The DGSW group is as a mixture of water from the DB and upgradient wells. While the third, DW group has similar concentrations as the DGSW (Fig. 2).
- The 3rd population corresponds with the ST group. Chloride (and other nutrients) are transported from the buffer zone through interflow into the stream (Fig 1). It could also be impacted upgradient by road salt or tile drainage water, which may account for the higher concentrations recorded from stream samples

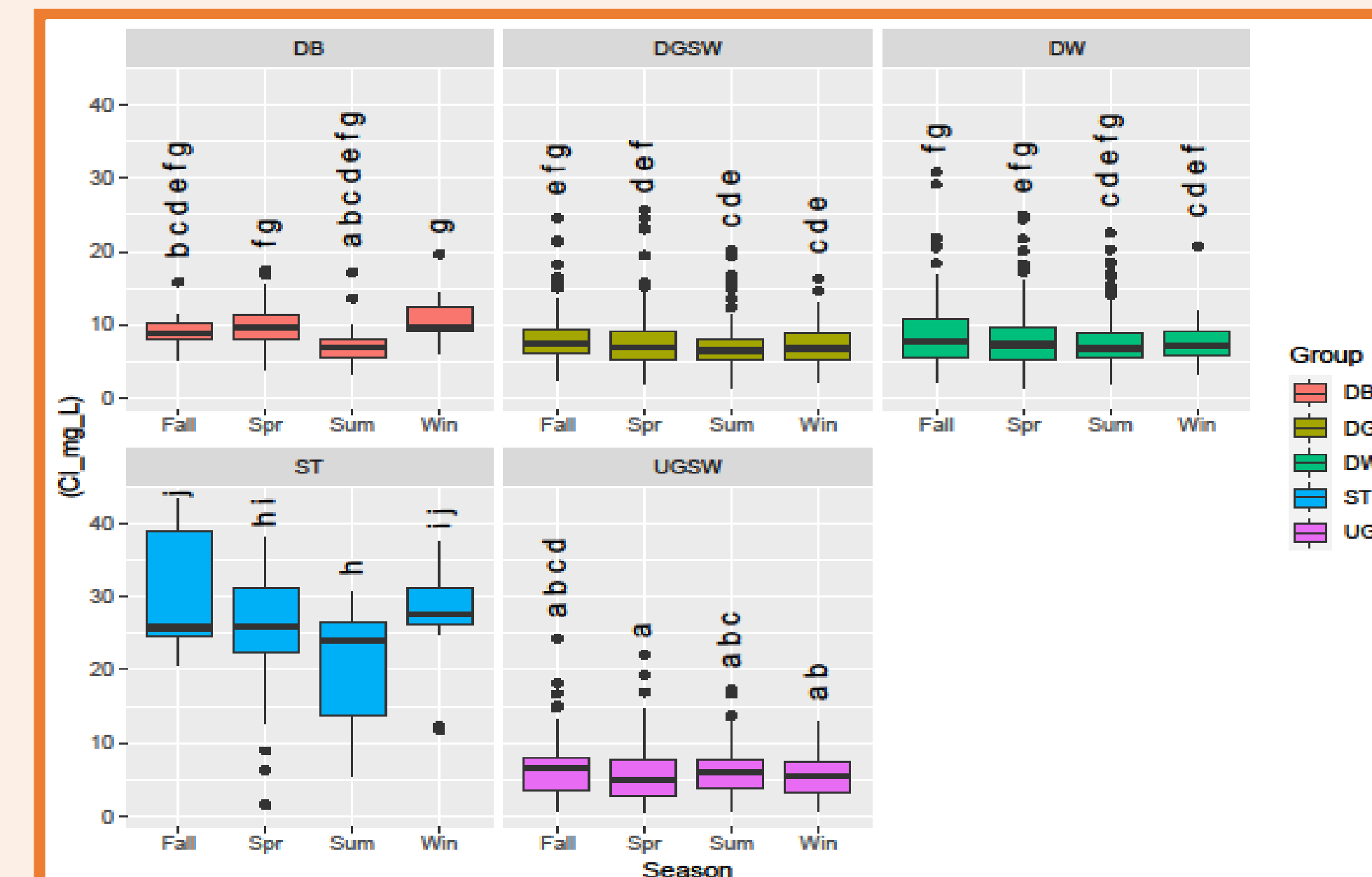


Figure 3: Boxplots showing results from the two-way ANOVA indicating seasonal variations in the different subgroups. Alphabets (gotten from Bonferroni test) indicates statistically similar groups across the different seasons

Spatial Variation

- Two-way ANOVA results also identifies three distinct populations amongst the groups namely UGSW; DB/DGSW/DW; and ST. This confirms the results gotten from the cumulative probability plots identifying three distinct chloride populations.
- The Stream and upgradient wells were also spatially different from the rest of the groups

Temporal Variation

- There were seasonal variations in both Stream (ST) and Diversion Box (DB) while Deep Groundwater (DW)/Downgradient Shallow Groundwater (DGSW)/Upgradient Shallow Groundwater (UGSW) were consistent on average across the different seasons (Fig. 3)

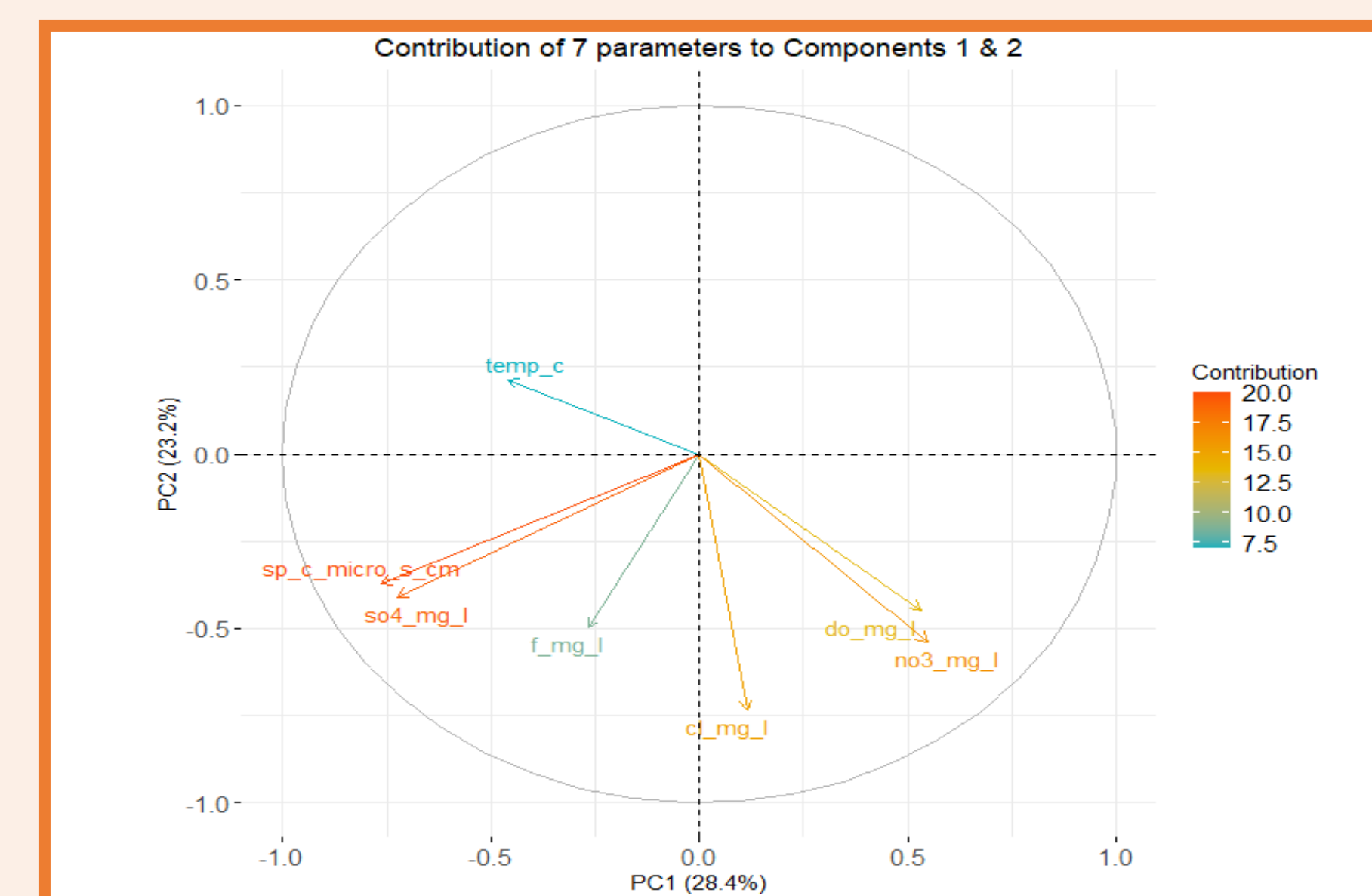


Figure 4: Principal Component Analysis (PCA) of in-situ measurements and anion concentration

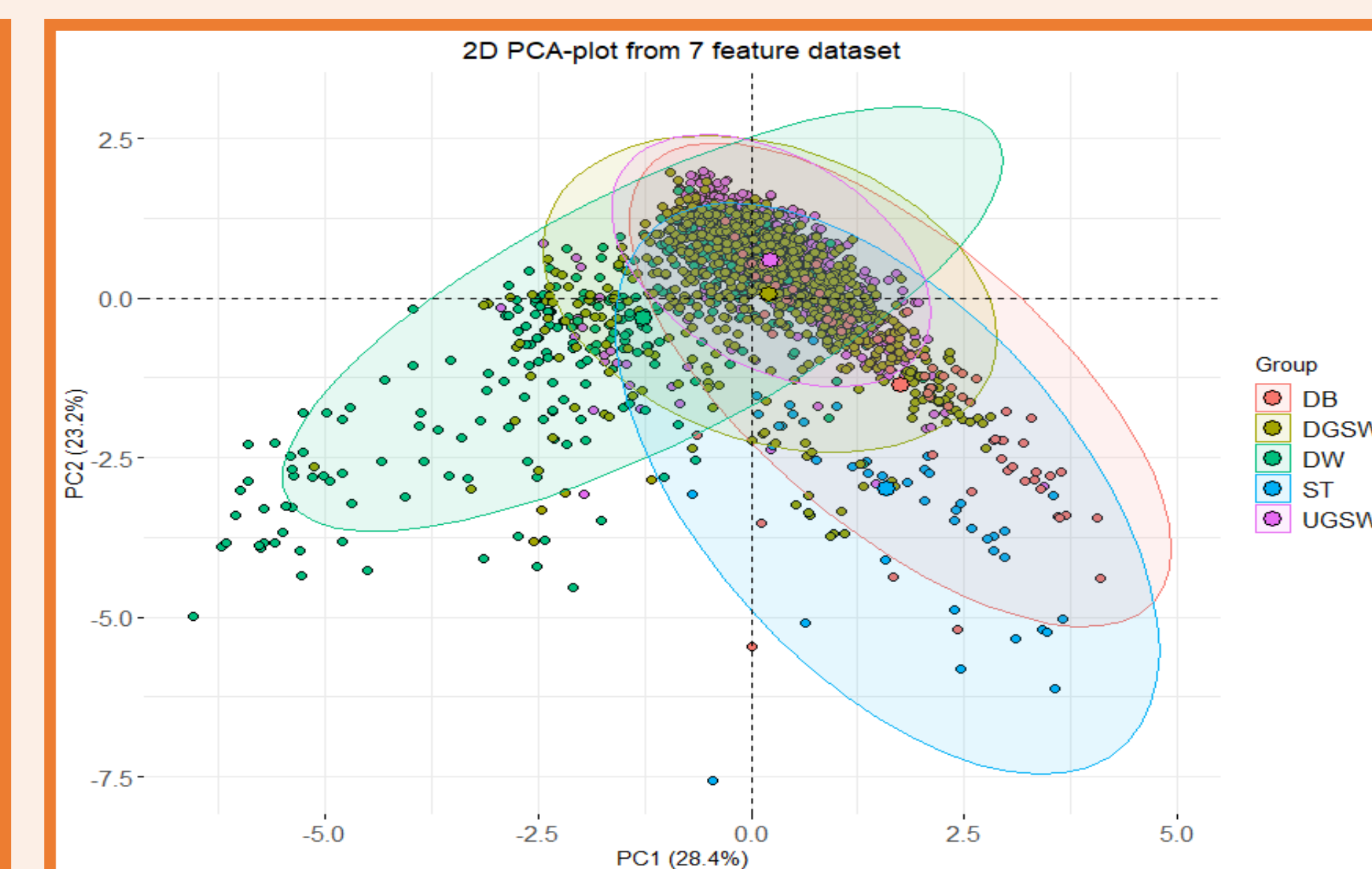


Figure 5: Principal Component Analysis (PCA) showing how the samples for the different subgroups are plotted

- The Principal Component Analysis (PCA) results indicates that water-rock interaction explained 28% of the variance (PC1), while surface processes explained 23% of the variation (PC2) (Fig. 4)
- Specific conductance, fluoride, and sulphate suggesting water-rock interactions mostly due to the deep groundwater subgroup and presence of sulphate-rich clay minerals in the subsurface
- Chloride, nitrate, and dissolved oxygen from the graph all indicate surficial processes, inferring a strong anthropogenic signature (mostly agricultural fertilizers) in the wells located on the diversion tiles in the SBZ
- Temperature aligns with surface influence but provides the lowest contribution towards the PCA score
- Classifications from the PCA show that although the DW and DGSW are similar, their sources are different (Fig. 5). It could also be seen that of the other groups, DB and ST are the most influenced by surface processes

Summary

- The results indicate that surface processes impact the SBZ as seen in the diversion box and downgradient groundwater groups.
- The farm upgradient provides the water in the DB; thus, we infer the DB water chemistry is as a result of agricultural practices. The seasons with highest average chloride concentration for the DB coincide with planting and growing seasons.
- Both the chloride concentrations of the ST and UGSW groups were spatially different from the other groups, while temporal (seasonal) differences were only seen in ST
- The ST samples are consistent with those of previous studies for tile-drain waters impacted by KCl fertilizer. Lax et al., (2017) reported above background chloride concentrations between 36 and 95 mg/L while Oberhelman and Peterson (2019) saw median chloride concentration of 49 mg/L in sampled tiles

References

- Dugan, H.A., Bartlett, S.L., Burke, S.M., Doubek, J.P., Krivak-Tetley, F.E., Skaff, N.K., Weathers, K.C. (2017). Salting our freshwater lakes. *Proceedings of the National Academy of Sciences of the United States of America*, 114, 4453-4458. <https://doi.org/10.1073/pnas.1620211114>
- Kelly, W.R. (2008). Long-term trends in chloride concentrations in shallow aquifers near Chicago. *Ground Water* 46(5):772-781. <https://doi.org/10.1111/j.1745-6584.2008.00466.x>
- EPA. (2021). Secondary Drinking Water Standards: Guidance for Nuisance Chemicals. U.S. Environmental Protection Agency, Washington, D.C. Retrieved from: <https://www.epa.gov/dwstandardsregulations/secondary-drinking-water-standards-guidance-chemicals>. (Accessed 01/20/2022).
- Kaushal, S.S., Groffman, P.M., Likens, G.E., Belt, K.T., Stack, W.P., Kelly, V.R., ... Fisher, G.T. (2005). Increased salinization of fresh water in the northeastern United States. *Proceedings of the National Academy of Sciences of the United States of America*, 102, 13517-13520. <https://doi.org/10.1073/pnas.0506414102>
- Gutches, K., Jin, L., Lautz, L., Shaw, S.B., Zhou, X. & Lu, Z. (2016). Chloride sources in urban and rural headwater catchments, Central New York. *Science of the Total Environment*, 565, 462-472. [10.1016/j.scitotenv.2016.04.181](https://doi.org/10.1016/j.scitotenv.2016.04.181)
- Mullaney, J.R., Lorenz, D. & Arntson, A.D. (2009). Chloride in groundwater and surface water in areas underlain by the glacial aquifer system, Northern United States. *Scientific Investigations Report 2009-5086*, U.S. Geological Survey. doi:10.3133/sir20095086
- Oberhelman, A., Peterson, E.W. (2020) Chloride source delineation in an urban-agricultural watershed: deicing agents versus agricultural contributions. *Hydrology Process*. <https://doi.org/10.1002/hyp.13861>
- Oberhelman, A., Peterson, E.W. (2021) Seasonal and stormflow chloride loads in an urban-agricultural watershed in central Illinois, USA. *Environ. Earth Sc.*
- Ludwikowski, J.J., Peterson, E.W. (2018) Transport and fate of chloride from road salt within a mixed urban and agricultural watershed in Illinois (USA): assessing the influence of chloride application rates. *Hydrogeology Jour* 26:1123-1135 [10.1007/s10040-018-1732-9](https://doi.org/10.1007/s10040-018-1732-9)
- Lax, S.M., Peterson, E.W. & Van der Haven, S.J. (2017). Stream chloride concentrations as a function of land use: a comparison of an agricultural watershed to an urban agricultural watershed. *Environ. Earth Sci.* 76, 708.

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