Contract No:

This document was prepared in conjunction with work accomplished under Contract No. 89303321CEM000080 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

Considering Factors for Ion Concentrations in Precipitation at the Savannah River Site

Mariam Cherif, South Carolina State University

Stephen Noble, Savannah River National Laboratory

ABSTRACT

Precipitation was collected from three different areas on the Savannah River Site during 2021. The precipitation was analyzed for concentrations of 29 different ions and compared with data on factors such as wind speed, wind direction, rain drop sizes, and more. The 2021 ion concentrations were also compared to the ion concentrations from previous years at the site as well as from Santee National Wildlife Refuge which is nearby. The historical ion concentrations data was gathered from the National Atmospheric Deposition Program. Scatter plots and correlation coefficients were used to identify what factors may have the greatest impact on ion concentration in rainwater. The data generally followed the same trends with a few notable outliers. There initially seemed to be a strong correlation between the mean diameter and some ion

concentrations as both increased in July. However, ion concentrations in different areas were related to different wind directions, thus spatial variability must be considered. These factors, spatial variability of atmospheric particles and wind direction, impact concentrations of ions in precipitation.

INTRODUCTION

Atmospheric particles are microscopic particles of solid or liquid matter suspended in the atmosphere. This particulate matter can be natural (i.e., biogenic, blown dust, sea spray aerosol) or anthropogenic (i.e., from exhaust pollution, agriculture). Particulate matter can be removed through wet deposition where cloud droplets and rain drops scavenge atmospheric particles which proceed to fall to the ground. The liquid water dissolves atmospheric particles, separating positive and negative ions. This removal of particles provides cleaner air, hence why air seems fresher after rainfall. Due to this collection of particulate matter, collection and analysis of rainfall can be used to identify atmospheric particle composition.

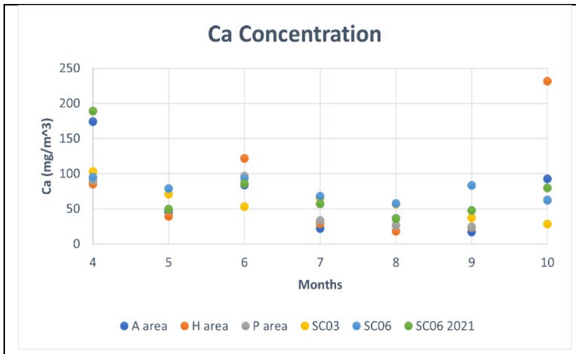
In 2021 rainfall was collected at the Savannah River Site (SRS) by Savannah River National Laboratory (SRNL), a multi-program laboratory under the U.S. Department of Energy's Office of Environmental Management. The Savannah River Site is a U.S. Department of Energy reservation that worked primarily to produce plutonium and tritium for nuclear weapons from the 1950's until the end of the Cold War in 1991. Today SRS work involves environmental cleanup, nuclear materials, and research and development activities. The 2021 data was collected by the Atmospheric Technologies Group whose scope entails renewable energy, international nuclear nonproliferation, emergency response, and climate change. Collected rainfall was analyzed for concentrations of 29 different ions. Ion concentrations were collected from different areas on site because ion concentrations differ by location (spatial variability). In addition to ion concentrations other factors such as wind speed, wind direction, droplet sizes, and historical concentrations were used to identify any relationships with the ion concentrations. These factors, along with ion concentrations, can provide a greater understanding of the sources and dispersion of particulates in the atmosphere. At the site there are areas where industrial work is conducted which may contribute to industrial pollution that impact ion concentrations present in precipitation at SRS. The site is also close to Augusta, Georgia which is a growing city that is contributing to urban pollution. Both industrial and urban pollution are similar and are responsible for high concentrations of NO_3^- in the atmosphere from combustion (vehicle traffic) and industrial processes (Keresztesi et al., 2020). In areas of agricultural activity higher amounts of K^+ from respiration and SO_4^{2-} from soil can be found (Mouli et al., 2005). At SRS there are agricultural areas surrounding the site in Aiken, Barnwell and Allendale counties, which may contribute ions from fertilizers into the atmosphere. The site is also sufficiently near the coast so that inland penetrating sea breezes (Viner et al., 2021) may contribute sea spray aerosol particles which can cause higher amounts of Na^+ in the atmosphere. In the North Atlantic Sea spray concentrations of calcium have been found and because they were found in natural and artificial seawater it suggests that Ca^{2+} is present in all natural sea spray aerosols (Salter et al., 2016). Overall, there are many different atmospheric pollutants at or surrounding the site that can contribute to ion concentrations found in precipitation.

The purpose of this paper is to identify what factors have the greatest impact on rainwater chemistry. Gaining a greater understanding of influential factors in rainwater chemistry is important because it provides information on atmospheric pollutants and their patterns. This is important because understanding the atmospheric particle composition and its contributing factors is necessary if any solutions to atmospheric pollutants will be sought.

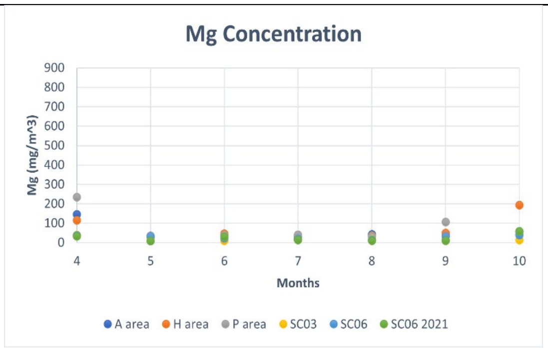
METHODS

1. *Ion Concentrations*

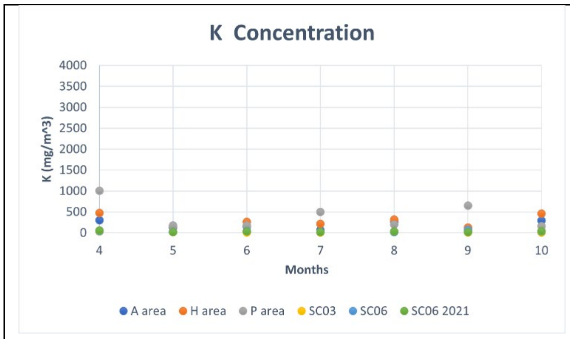
Rainfall was collected March to October in 2021. Due to Covid and the site vehicle use restrictions that had been implemented, it made collecting rainfall in March inconsistent. Therefore, the data from 2021 uses monthly averages from April to October. Data was gathered from three areas on site: A, H, and P-area. All of which follow in the same direction with roughly 20 km between A and P area which is the furthest distance. Two sites from the National Atmospheric Deposition Program (NADP) were used for comparison in this study. The National Atmospheric Deposition Program monitor precipitation chemistry for many different groups. Historical data from the same range of months was used to compare the monthly averages from 2012-2017 from the NADP site at SRS (SC03) and from a nearby region at Santee National Wildlife Refuge (SC06). Monthly averages from SC06 in 2021 and from 2011-2021 were also used to compare ion concentrations between April and October. All rainfall (our 2021 data, SC03 and SC06) used ion chromatography to determine ion concentrations. Ion chromatography uses an ion exchanger to separate ions and polar molecules which allows all ions to be measured. Ion chromatography was used to measure the concentration of 29 different ions detected in rainfall on site. The ions present at all these areas that were used to compare ion concentrations are Ca^{2+}, Mg^{2+}, K^+, Na^+, NO_3^-, Cl^-, and SO_4^{2-}. Scatter plots were used as they can show trends or a lack thereof.


Ca Concentration
250
200
150
100
50
0
Ca (mg/m^3)
4
5
6
7
8
9
10
Months
● A area ● H area ● P area ● SC03 ● SC06 ● SC06 2021

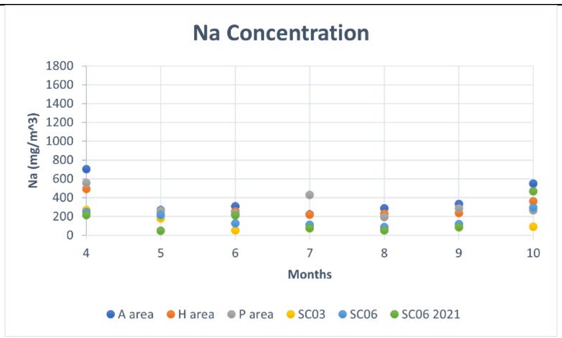
a)


Mg Concentration
900
800
700
600
500
400
300
200
100
0
Mg (mg/m^3)
4
5
6
7
8
9
10
Months
● A area ● H area ● P area ● SC03 ● SC06 ● SC06 2021

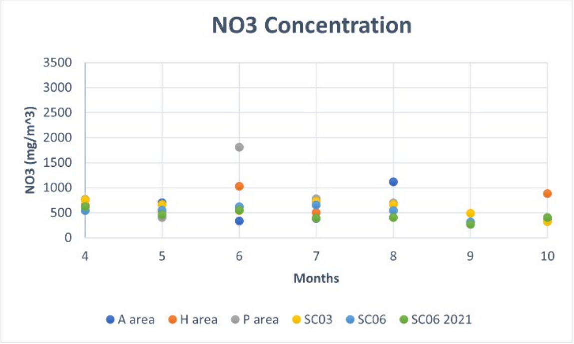
b)


K Concentration
4000
3500
3000
2500
2000
1500
1000
500
0
K (mg/m^3)
4
5
6
7
8
9
10
Months
● A area ● H area ● P area ● SC03 ● SC06 ● SC06 2021

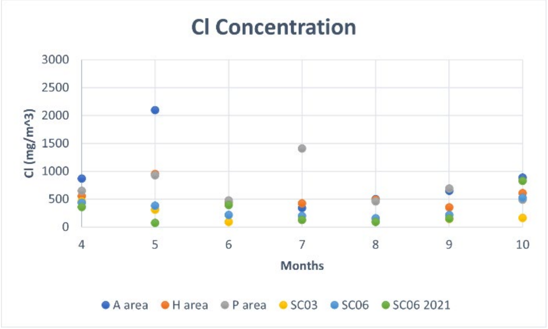
c)


Na Concentration
1800
1600
1400
1200
1000
800
600
400
200
0
Na (mg/m^3)
4
5
6
7
8
9
10
Months
● A area ● H area ● P area ● SC03 ● SC06 ● SC06 2021

d)


NO3 Concentration
3500
3000
2500
2000
1500
1000
500
0
NO3 (mg/m^3)
4
5
6
7
8
9
10
Months
● A area ● H area ● P area ● SC03 ● SC06 ● SC06 2021

e)


Cl Concentration
3000
2500
2000
1500
1000
500
0
Cl (mg/m^3)
4
5
6
7
8
9
10
Months
● A area ● H area ● P area ● SC03 ● SC06 ● SC06 2021

f)

g)

Figure 1. Ion concentrations from SC06, A, H, and P-area as well as past averages from SC03 and SC06.

2. *Droplet Sizes*

The droplet sizes were measured using a disdrometer which measures precipitation drop size distributions. The mean droplet sizes from A-area were calculated based on the given precipitation time periods. We used Pearson's correlation coefficient to identify the relationship between variables and describes them as strong or weak or as positive or negative. The monthly mean of droplet sizes was compared to ion concentrations in A-area by solving the correlation coefficient and by making a scatter plot of the monthly droplet sizes. They are also compared to ion concentrations from P-area in July.

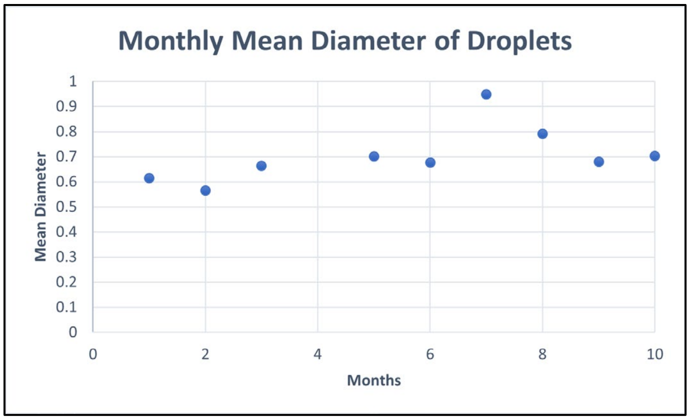


Figure 2. The mean diameter of droplets from January to October

Table 1. The correlation coefficients of the ions and the droplet diameter in A-area.

Correlation Coefficients from A-Area:		
Ca^{2+} (μg/L)	Mean Diameter	-0.15985
Mg^{2+} (μg/L)	Mean Diameter	-0.00564
K^{+} (μg/L)	Mean Diameter	0.079764
Na^{+} (μg/L)	Mean Diameter	-0.02488
NO_3^{-}(mg/L)	Mean Diameter	-0.19961
Cl^{-} (mg/L)	Mean Diameter	-0.00931
SO_4^{2-} (mg/L)	Mean Diameter	0.137302

Table 2. The correlation coefficients of the ions from P area and the droplet diameter from A-area.

Correlation Coefficients from Month 7:		
Na^{+} (μg/L)	Mean Diameter	0.908629
Cl^{-} (mg/L)	Mean Diameter	0.891824
SO_4^{2-} (mg/L)	Mean Diameter	0.925527

3. Wind Speeds and Temperatures

Wind speeds, dew point temperatures, and temperatures from A-area were also averaged based on precipitation time periods. Each factor was plotted on a scatter plot against ion concentration in A-area and the correlation coefficients were solved for.

Table 3. The correlation coefficients of the ions and the wind speeds in A-area

Correlation Coefficients of Wind Speed and Ion Concentrations:		
Ca^{2+} (µg/L)	Wind Speed (m/s)	-0.08957
Mg^{2+} (µg/L)	Wind Speed (m/s)	-0.02139
K^{+} (µg/L)	Wind Speed (m/s)	-0.27613
Na^{+} (µg/L)	Wind Speed (m/s)	-0.09736
NO$_3^-$(mg/L)	Wind Speed (m/s)	0.349438
Cl$^-$ (mg/L)	Wind Speed (m/s)	-0.02129
SO$_4^{2-}$ (mg/L)	Wind Speed (m/s)	0.108314

Table 4. The correlation coefficients of the ions and the dew point temperature in A-area

Correlation Coefficients of Dew Point Temp and Ion Concentrations:		
Ca^{2+} (µg/L)	Dew Pt Temp (C)	-0.02727
Mg^{2+} (µg/L)	Dew Pt Temp (C)	-0.00601
K^{+} (µg/L)	Dew Pt Temp (C)	0.243243
Na^{+} (µg/L)	Dew Pt Temp (C)	0.009654
NO$_3^-$(mg/L)	Dew Pt Temp (C)	0.030435
Cl$^-$ (mg/L)	Dew Pt Temp (C)	-0.16343

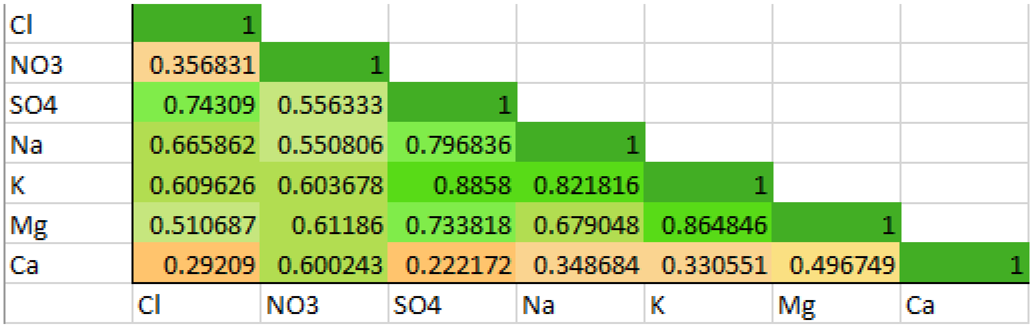
SO_4^{2-} (mg/L)	Dew Pt Temp (C)	-0.06861

Table 5. The correlation coefficients of the ions and the temperature in A-area

Correlation Coefficients of Temp and Ion Concentrations:		
Ca^{2+} (µg/L)	Temp (C)	0.051732
Mg^{2+} (µg/L)	Temp (C)	0.029845
K^+ (µg/L)	Temp (C)	0.220702
Na^+ (µg/L)	Temp (C)	0.044943
NO_3^-(mg/L)	Temp (C)	0.047492
Cl^- (mg/L)	Temp (C)	-0.21628
SO_4^{2-} (mg/L)	Temp (C)	-0.01052

4. *Comparing All Ions*

Correlation coefficient across all ions is also calculated to see if any ions have correlations such as Na^+ and Cl^-. Na^+ and Cl^- commonly form NaCl (salt) so it would be expected that these ions would be strongly correlated.



Cl	1						
NO3	0.356831	1					
SO4	0.74309	0.556333	1				
Na	0.665862	0.550806	0.796836	1			
K	0.609626	0.603678	0.8858	0.821816	1		
Mg	0.510687	0.61186	0.733818	0.679048	0.864846	1	
Ca	0.29209	0.600243	0.222172	0.348684	0.330551	0.496749	1
	Cl	NO3	SO4	Na	K	Mg	Ca

Figure 3. The correlation coefficients of Cl^-, NO^-_3, SO_4^{2-}, Na^+, K^+, Mg^{2+}, and Ca^{2+} from A, H, and P-area.

5. *Wind Direction*

Similarly, to droplet sizes, mean wind direction from A and P-area were calculated based on the given precipitation time periods. The correlation coefficient of the mean wind directions and ion concentrations from A-area were solved for. After calculating the mean wind directions of both areas, they were categorized based on their degree ranging from 0°-360° and grouping them as N, NE, E, SE, S, SW, and W. There were plots created for the wind directions of Ca^{2+}, Mg^{2+}, K^+, Na^+, NO_3^-, Cl^-, and SO_4^{2-} in both P and A-areas.

Table 6. The correlation coefficients of the ions and the wind direction in A-area

Correlation Coefficients of Wind Direction and Ion Concentrations at A-Area:		
Ca^{2+} (µg/L)	Wind Direction	-0.34548
Mg^{2+} (µg/L)	Wind Direction	-0.22455
K^+ (µg/L)	Wind Direction	-0.27706
Na^+ (µg/L)	Wind Direction	-0.22658
NO_3^-(mg/L)	Wind Direction	0.153385
Cl^- (mg/L)	Wind Direction	-0.29275
SO_4^{2-} (mg/L)	Wind Direction	-0.11544

RESULTS AND DISCUSSION

The ion concentrations generally follow the same trends across all areas and sites. There were some outliers such as higher concentrations of Ca^{2+}, Mg^{2+}, K^{+}, and NO_3^- in H-area in October (Fig. 1a, 1b, 1c, 1e). There also appeared to be a rise in P-area of Na^+, Cl^-, and SO_4^{2-} in July (Fig. 1d, 1f, 1g). As well as high concentrations of Cl in A-area during May (Fig. 1f). The cause of the outliers in October is unknown however, concentrations were exceedingly high on the last day of precipitation collection. While there was a rise in concentrations during July there was also a noticeable increase in the diameter of droplets also in July (Fig. 2). In search of what may be correlated to the increase in concentrations the correlation coefficient was solved between concentrations of Na^+, Cl^-, and SO_4^{2-} and the diameter. The R-values are all around very high and show strong correlation between the ion concentrations of Na^+, Cl^-, and SO_4^{2-} and the droplet diameter in July (Table 2).

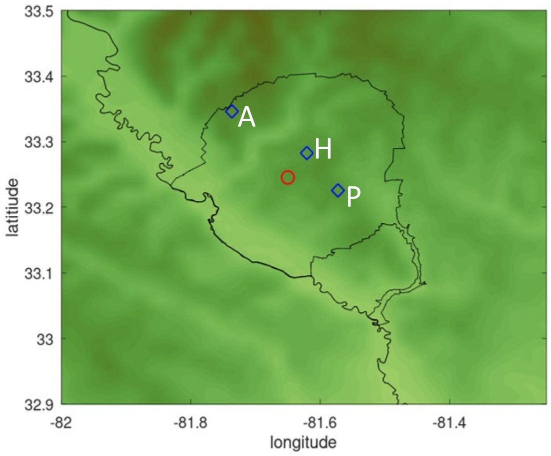
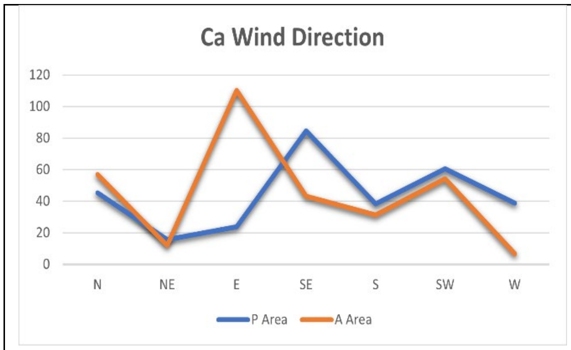
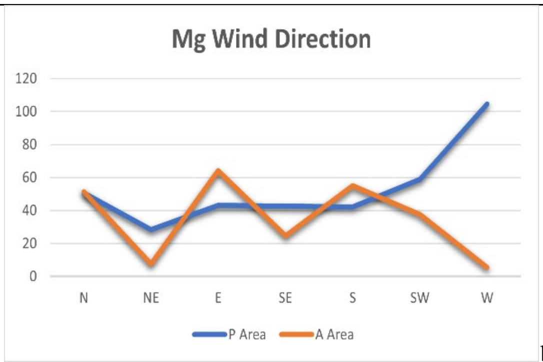


Figure 4. Map of the site that marks the areas.

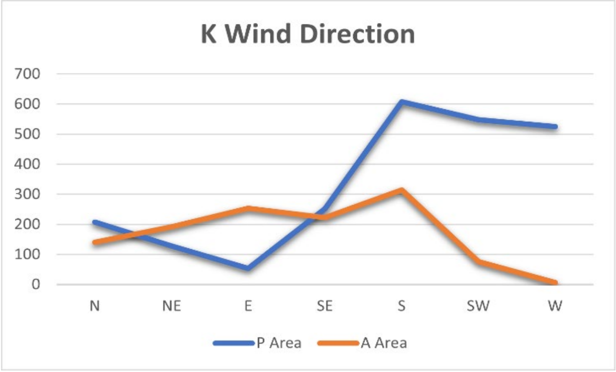
However, the increase in ion concentrations of Na^+, Cl^-, and SO_4^{2-} are at P-area and the droplet diameter measurements are from the droplets at A-area. A and P-area are roughly 20 km apart and cloud and precipitation development are likely different between the areas, therefore this spatial variability must be considered (Fig. 4). The R-values show there is little to no correlation between wind direction and ion concentrations from A-area (Table 6). Yet, the wind direction and the ion concentrations from both areas on graphs show how they vastly differ. The wind directions are different for each concentration and these differences further prove the spatial variability must be considered. Differing wind directions show different ion concentrations in different areas that thus makes the once "strong correlations" between Na^+, Cl^-, and SO_4^{2-} with the droplet diameter unreliable. This is likely because of the distance between A and P-areas and variation in wind directions that seem to impact the ionic composition. It can also be seen that wind directions and ion concentrations have a relationship so some areas may have higher concentrations of an ion due to the wind direction (Fig 5a-5g).



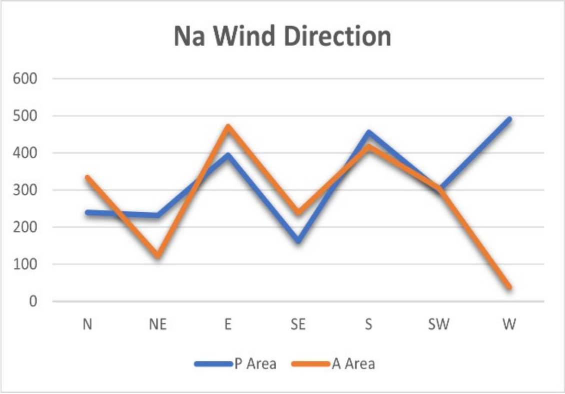
a)



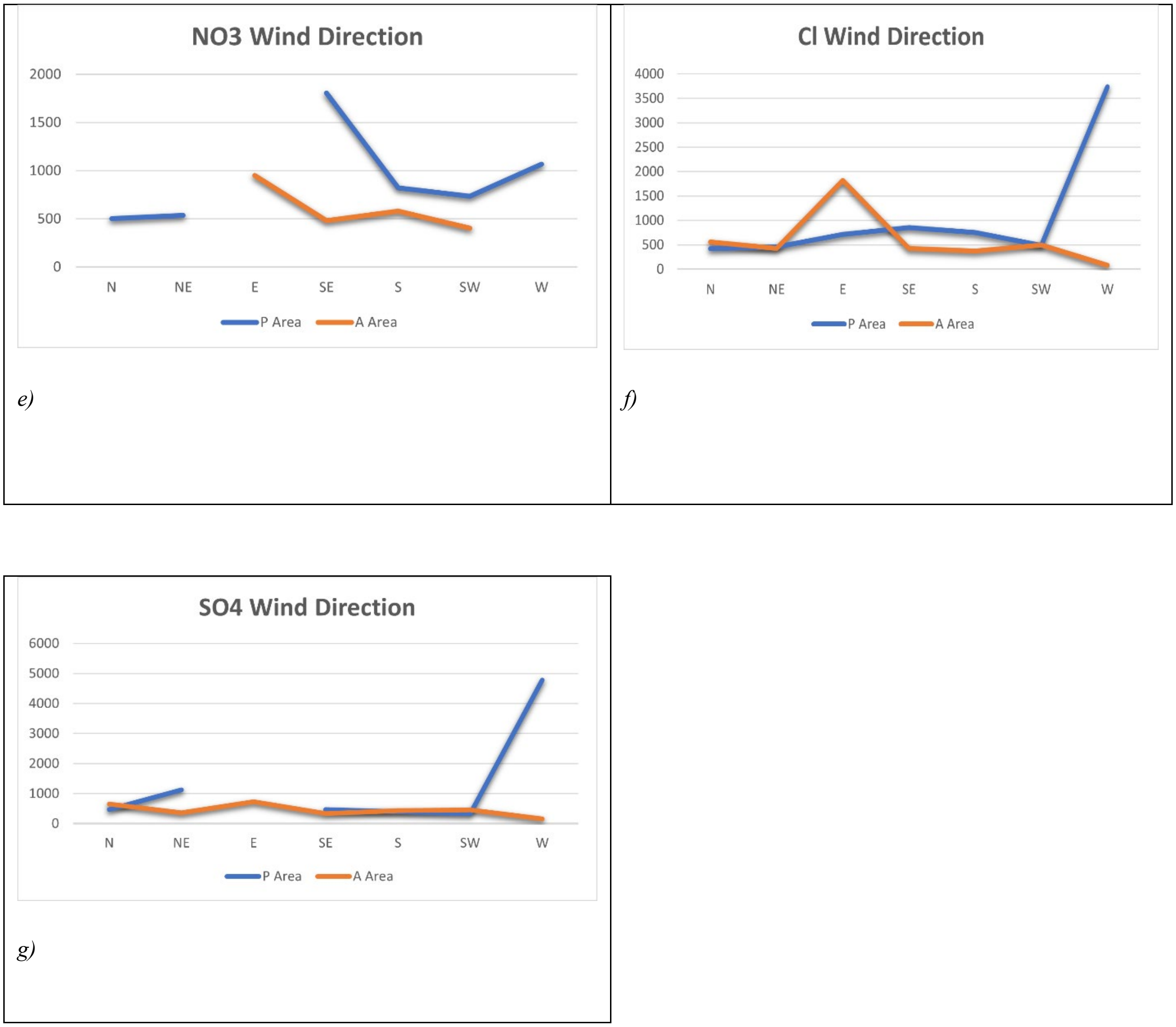
b)



c)



d)



Figures 5a-5g include wind directions from A and P area for the concentrations of Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, NO_3^{-}, Cl^{-}, and SO_4^{2-}.

Similar to the wind direction, the mean of wind speed, dew point temperature, and temperature were calculated. Each of these variables were from A-area as well as the ion concentrations which were used to calculate the R-values. None of which were significant for any of the factors, they all had little to no correlation (Tables 3, 4, 5).

The correlation coefficients across all ions in all areas was also solved and there were a few that had strong correlations (Fig. 3). The R-value of Na^{+} and Cl^{-} is 0.665862 which is generally good for atmospheric sciences but due to their tendency to bond a stronger correlation would be expected. Some pairs seem to have strong positive correlations such as: Mg^{2+} and K^+, Na^+ and K^+, and SO_4^{2-} and K^+. However, Mg^{2+} and K^+ along with Na^+ and K^+ do not have the abilities to bond because none of these ions are electron donors which is necessary to form a bond. Thus, their strong correlations are not of use or reliable because the ions do not bond and therefore, they do not truly correlate as one ion has no true effect on the other. The only pairing with a strong correlation of 0.8858 was SO_4^{2-} and K^+ which do have the ability to bond and shows they correspond with the other.

CONCLUSION

The precipitation at SRNL was collected from different areas in 2021 in the pursuit of information on the composition of atmospheric particulate matter. A plethora of ions were detected in the precipitation and the ions were compared to other possibly contributing factors. It was found that the ions had very little correlation to each other across all areas. Wind direction, wind speed, dew point temperature, and temperature were all factors that overall had little to no correlation with the ion concentrations. At a first glance it seemed that the increase of droplet sizes and ions Na^+, Cl^-, and SO_4^{2-} in July were correlated but due to the droplet sizes being from A-area and the ions increasing in P-area this correlation is suspect. There is spatial variability and such contrasting wind directions that the difference in location is the greatest factor to be considered when analyzing the ion concentrations. Overall, there was not much correlation amongst the ions and the only notable correlation was found between SO_4^{2-} and K^+. While the greatest contributing factor to ion concentration in precipitation at SRNL is unknown, through expanding analysis based on wind direction and spatial variability a greater understanding can be gained.

ACKNOWLEDGEMENTS

This work was supported in part by the U.S. Department of Energy, Office of Science, Office of Workforce Development for Teachers and Scientists (WDTS) under the Science Undergraduate Laboratory Internships Program (SULI). I would also like to thank Stephen Noble, the Atmospheric Technologies Group, and South Carolina State University.

BIBLIOGRAPHY

Gao, B., Ouyang, W., Cheng, H., Xu, Y., Lin, C., & Chen, J. M. (2019). Interactions between rainfall and fine particulate matter investigated by simultaneous chemical composition measurements in downtown Beijing. *Atmospheric Environment*, *218*, 117000. https://doi.org/10.1016/j.atmosenv.2019.117000

Grantz, D. A., Garner, J., & Johnson, D. R. (2003). Ecological effects of particulate matter. *Environment International*, *29*(2–3), 213–239. https://doi.org/10.1016/s0160-4120(02)00181-2

Keresztesi, Á., Nita, I., Boga, R., Birsan, M., Bodor, Z., & Szép, R. (2020). Spatial and long-term analysis of rainwater chemistry over the conterminous United States. *Environmental Research*, *188*, 109872. https://doi.org/10.1016/j.envres.2020.109872

Mouli, P. C., Mohan, S. V., & Reddy, S. M. (2005). Rainwater chemistry at a regional representative urban site: influence of terrestrial sources on ionic composition. *Atmospheric Environment*, *39*(6), 999–1008. https://doi.org/10.1016/j.atmosenv.2004.10.036

Salter, M., Hamacher-Barth, E., Leck, C., Werner, J., Johnson, C. M., Riipinen, I., Nilsson, E. D., & Zieger, P. (2016). Calcium enrichment in sea spray aerosol particles. *Geophysical Research Letters*, *43*(15), 8277–8285. https://doi.org/10.1002/2016gl070275

Viner, B. J., Noble, S., Qian, J., Werth, D., Gayes, P. T., Pietrafesa, L. J., & Bao, S. (2021). Frequency and Characteristics of Inland Advecting Sea Breezes in the Southeast United States. *Atmosphere*, *12*(8), 950. https://doi.org/10.3390/atmos12080950