The Effects of Local Weather Patterns on Nitrate and Sulfate Rainwater Concentrations in Wilmington, North Carolina

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Analysis of weather patterns on a synoptic or regional scale is the common direction of study in air pollution meteorology with few studies analyzing weather conditions proximal to collection sites. A study that focuses on local weather conditions may lead to better understanding and more accurate forecasting of rain water chemistry than synoptic or regional scale studies. The objective of this project is to determine the relationship between local weather patterns and rain water chemistry in Wilmington, NC. Daily and hourly meteorological data (average temperature, relative humidity, wind speed and direction, and maximum and minimum temperatures) were collected for the 48 hour period prior to each rain event. In addition, the nitrate and sulfate concentrations were obtained from the Marine and Atmospheric Chemistry Research Laboratory (MACRL) at UNCW. Data analysis of local weather conditions 48 hours prior to 24 storm events, including review of descriptive statistics, graphical and linear regression analysis, *t*-tests, and synoptic weather map analysis, was completed to determine any relationship between variables. The overall conclusion of the study is that there are no obvious or significant relationships between nitrate and sulfate concentrations and local meteorological variables. However, wind direction frequency and statistical tests suggest that trajectory, whether terrestrial or marine, is the most important factor influencing rain water chemistry.

Introduction

Rainwater chemistry is important because pollutants such as nitrate, sulfate and ammonium (of which, nitrogen and ammonium are nitrogen analytes) can be carried in water released from the atmosphere. NO and NO_2 typically enter the atmosphere through anthropogenic sources such as automobiles and fossil fuel combustion in power plants (Long, 2003; Botkin *et al.*, 1995). The oxidation of NO and NO_2 forms atmospheric nitrate. Sulfate emissions from power plants are oxidized to form sulfuric acid which in turn becomes sulfate. Burning coal in power plants is the major anthropogenic source of sulfate. However, petroleum refining, the production of paper, cement and aluminum also contribute sulfate (Long, 2003; Botkin *et al.*, 1995).

Large amounts of sulfuric and nitric acid deposition can lead to negative impacts on acid-sensitive ecosystems due to their respective contribution to acidic deposition (Lehmann *et al.*, 2005). In addition, excess nitrogen is one of the most harmful nutrients to plant algal and microbial production, and atmospheric deposition is responsible for 35% to 60% of nitrogen analytes entering coastal waters of the Atlantic (Kieber *et al.,* 2005). The nitrogen is harmful to these organisms because phytoplankton requires nitrogen to bloom, however, when the concentration of the nutrient is too large, the blooms become too numerous. As a result, the overabundance of phytoplankton is not completely consumed by the organisms that feed on them and are left to die or be decomposed by bacteria. The bacteria consume large amounts of oxygen during decomposition and deplete the surrounding waters of much needed oxygen. Decreased amounts of oxygen lead to hypoxia (reduced amounts of oxygen) and anoxia (a complete absence of oxygen). These conditions can potentially lead to toxic algal blooms, changes in types of phytoplankton populations and higher occurrences of fish and shell-fish disease (Russell *et al.*, 1998).

Research has linked the occurrence of pollutants in rainwater with specific weather patterns in order to gain a better understanding of how weather may diminish or exacerbate pollution levels (Russell *et al.*, 1998 ;Walker *et al.* 2000; Dayan & Lamb, 2003; Hewitt *et al.*, 2003). Such research explores how storm path and trajectory, storm type, circulation around a storm, geographic location, seasonality, and precipitation amount affect pollutants found in rainwater. One example of this research , which focused on the Chesapeake Bay region, classified storm trajectories and their associated pollutants into five different groups: westerly, easterly, northwesterly, southwesterly and southerly (Russell *et al.,* 1998). Analysis indicated that easterly trajectories were characterized by the lowest amount of nitrogen because these air masses traveled over the Atlantic Ocean. The southerly trajectory was associated with high concentrations of nitrate. Further, this study indicated that source region information can be used to determine how much nitrogen is deposited through the atmosphere, what processes produce the nitrogen, and also where the nitrogen originated. Air masses that travel over heavily populated (and therefore, heavily traveled) areas may pick up nitrogen analytes from anthropogenic emissions. The Chesapeake Bay study also showed that NO_x (the collective term for NO and NO_2) emissions from combustion sources are the main source of nitrate in atmospheric deposition. This is the reason that storms that originate over land tend to have higher concentrations of analytes than the storms that originate over water.

It is common in suxh research (Dayan and Lamb, 2003; Russell *et al.*, 1998; and Walker *et al.,* 2000) to consider a seasonal aspect of the atmospheric chemistry. Results from seasonal analysis indicate that high nitrate and ammonium concentrations occur during the spring, early summer and winter months. The spring/early summer high concentrations can be attributed to the increase in soil fertilizers and animal waste emissions associated with planting in the spring while the winter highs can be attributed to increased fuel emissions (Russell *et al.*, 1998). Seasonality is also a factor in synoptic scale meteorology. Changes in mean seasonal patterns in upper air flow can cause fluctuations in the ammonium concentrations (Walker *et al.*, 2000).

These studies (Dayan and Lamb, 2003; Russell *et al.*, 1998; and Walker *et al.,* 2000) also indicate that the amount of precipitation is a factor that affects concentrations of nitrogen analytes in atmospheric deposition. The term "washout" is used in many studies to explain why there seems to be smaller concentrations of analytes when precipitation amounts are larger. High amounts of water dilute the concentration of the pollutant.

The overall conclusion of these studies is that rainwater chemistry is highly variable and more research needs to be completed in order to better understand what the future may bring concerning the impact of rainwater pollution on animal, aquatic and possibly human populations. Identification of pollution sources, transport characteristics and predicted concentrations may lead to physical or chemical controls used for the development of sound environmental management policies to prevent future damage to sensitive aquatic and terrestrial ecosystem (Walker *et al.*, 2000).

While such results are helpful, a more in depth analysis of local weather conditions associated with the local rain water chemistry is needed. Previous studies have found regional variation in trends of atmospheric chemistry across the United States. For instance, Lehmann *et al.* (2005) found in the west central United States there were significant nitrate increases while in the northeastern United States there were significant decreases. Further, significant dissolved inorganic nitrogen decreases were observed in the northeastern United States while elsewhere there were significant increases. Such spatial variability underscores the need to combine knowledge of regional meteorology with knowledge of atmospheric chemistry to better understand air pollution dynamics. The majority of previous research has completed analysis of weather patterns on a synoptic scale with few studies analyzing weather conditions proximal to collection sites. A study that focuses on local weather conditions may lead to better understanding and more accurate forecasting of rain water chemistry. Such information may prove to be very important given the potential for error in synoptic scale trajectory analysis and when pollution sources are near the collection sites. Therefore, the study described here is of particular importance because it will further research local scale processes in air pollution dynamics. Accordingly, the purpose of this study is to determine the relationship between local weather patterns and nitrate and sulfate rain water chemistry in Wilmington, NC.

Wilmington, North Carolina is characterized by frequent and ample rainfall throughout the year; however, summer usually has higher amounts of rainfall. Thunderstorms are the main source for summer rainfall. These thunderstorms are usually short in duration but rainfall is heavy and unevenly distributed across the area. Slow, steady rain is common in the winter months and is associated with slow-moving, low-pressure systems, usually staying in the area one or two days (Garoogian, 2000)

In a study of rainfall chemistry in Wilmington, the Marine and Atmospheric Chemistry Research Laboratory (MACRL) at UNCW has monitored the rainwater chemistry of 129 precipitation events between February 2002 and August 2003. This research includes chemical analysis for ammonium, nitrate, organic nitrogen and free amino acids concentrations in rain water and correlates these concentrations with atmospheric trajectories of the storms producing rain (Long, 2003; Kieber *et al.*, 2005). The trajectories of the storms were classified as terrestrial, oceanic or mixed. Their analysis indicates that terrestrial storms are associated with significant values of all chemicals except organic nitrogen. Oceanic storms were associated with low concentrations of all chemicals, especially ammonium. The results suggest that for the Wilmington, NC area, storms that have a terrestrial origin have high concentrations of nitrogen analytes, suggesting the influence of swine production, while storms of oceanic origin are characterized by low concentrations of nitrogen analytes. In addition, the Wilmington, NC area also has highs of ammonium in the spring and summer and high nitrate amounts in the winter months. This analysis did not examine the local weather conditions associated with rainfall events.

The overall objective of this project is to determine the relationship between local weather patterns and rain water chemistry in Wilmington, NC. Specific objectives to be completed in this study include:

1. Compare local weather conditions for 12 winter and 12 summer rain events identified in the MACRL database by trajectory, season, storm type and nitrate and sulfate concentration.
2. Determine if a relationship exists between local weather conditions and nitrate and sulfate concentration in precipitation.
3. Determine if a statistical difference exists in local weather conditions and nitrate and sulfate concentration by season and trajectory.
4. Determine the type of storm systems preceding rain events and compare nitrate and sulfate concentration by storm type.

Methodology

Daily and hourly meteorological data were collected from the Wilmington, North Carolina National Weather Service (NWS) Office web page (http://www.erh.noaa.gov/er/ilm/) and the Plymouth State Weather Center 24 HR Surface Station Summary Generator web page (http://vortex.plymouth.edu/statlog-u.html) for the Wilmington, NC weather station (Figure 1). This data consisted of average temperature, relative humidity, wind speed and direction, and maximum and

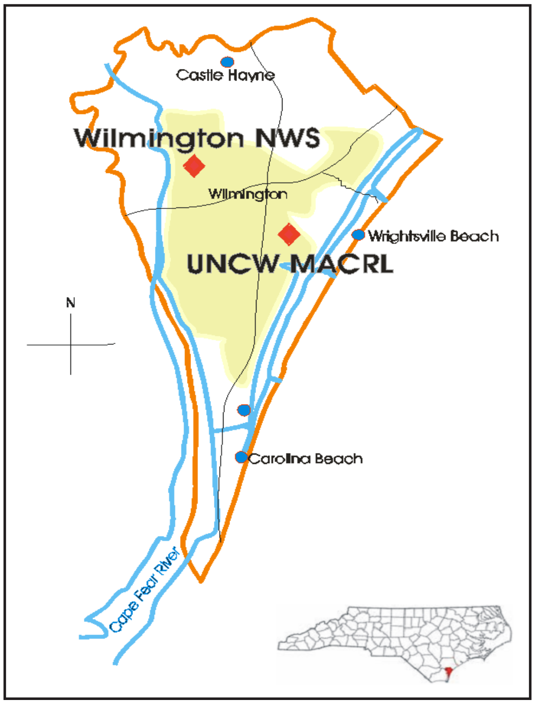

Figure 1. Map of New Hanover County indicating location of the two collection sites referenced in this study.

minimum temperatures for the 48 hour period prior to each rain event. This data, along with the nitrate and sulfate concentrations obtained from the MACRL Lab at UNCW (Figure 1), were entered into an Excel spreadsheet. Descriptive statistics, specifically mean and standard deviation, were calculated for each variable in order to determine difference and similarities in atmospheric conditions before a rain event by season, trajectory, and chemical concentration. Three histograms were constructed illustrating wind direction, one with all storms included, another showing only marine trajectory storms and the third, illustrating terrestrial storms only. Scatter plots were constructed, plotting each variable against nitrate and sulfate amounts. Trend lines were fit to the scatter plot through linear regression to describe the relationship between variables. The trend lines are intended to describe relationships as opposed to predictive models. Tables listing the maximum, minimum and 48 hour average of each local meteorological variable and chemical by marine vs. terrestrial trajectory and summer vs. winter were constructed. Statistical *t*-tests (two-sample, two-tailed tests assuming equal variance) were completed for each variable and chemical concentration comparing the mean values of two seasonal and trajectory samples (summer vs. winter and marine vs. terrestrial trajectory). The *t*-test was used to determine if a statistically significant difference in variables existed before a rain event by season and trajectory. Finally, NOAA daily weather maps were used to determine synoptic scale weather conditions 48 hours before rain events. Chemical concentration was then compared by storm type. Statistical tests to determine statistically significant difference could not be performed on data by storm type given the small sample size for each storm type.

Results and Discussion

A review of histograms reveals that the most frequent wind direction preceding storm events is from the East-Northeast (Figure 2). The most frequent wind direction preceding a storm associated with marine trajectory storms was East-Northeast (Figure 3). The most common wind direction preceding a terrestrial trajectory storm was South-Southwest (Figure 4). All trend lines fitted to scatter plots indicate a positive relationship between local meteorological values and nitrate and sulfate concentrations except for the scatter plots plotting the chemicals nitrate and sulfate against precipitation (Table 1). Such a relationship suggests that as temperature, relative humidity, and wind speed increase so does sulfate and nitrate concentrations. The scatter plots between precipitation amount and both nitrate and sulfate indicate a negative relationship. Trend lines fitted to scatter plots indicate a negative relationship between precipitation amount and nitrate and sulfate concentration. All of the linear regressions are poor models with all r^2 values for all models below 0.1 (Table 1), indicating that meteorological variables explain a low amount of variance in sulfate and nitrate concentrations. The precipitation models are the only models with a slope significantly different from zero, suggesting a "washout" effect may be present in Wilmington.

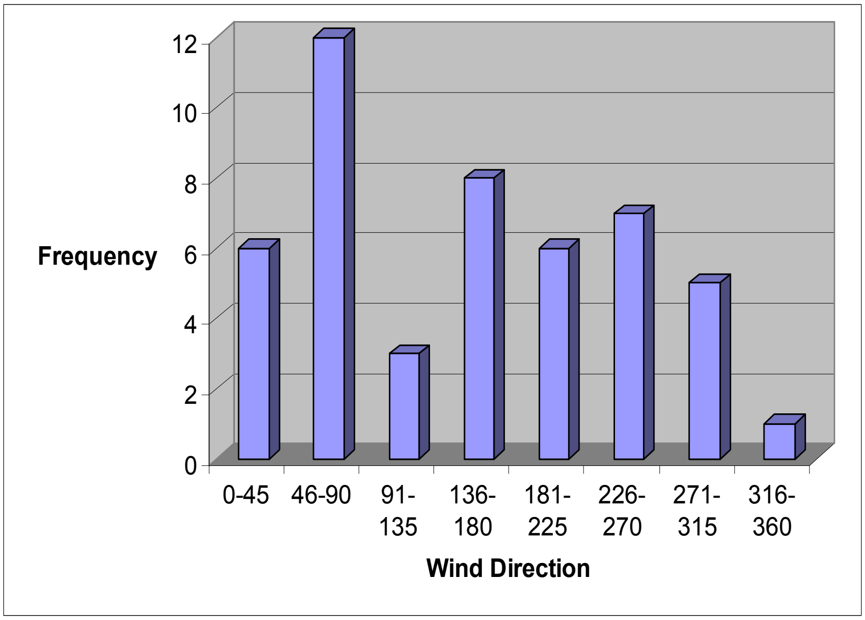

Figure 2. Wind direction histogram displaying frequency of wind direction for all 24 storm events from August 25, 2003 to June 29, 2005 in Wilmington, NC.

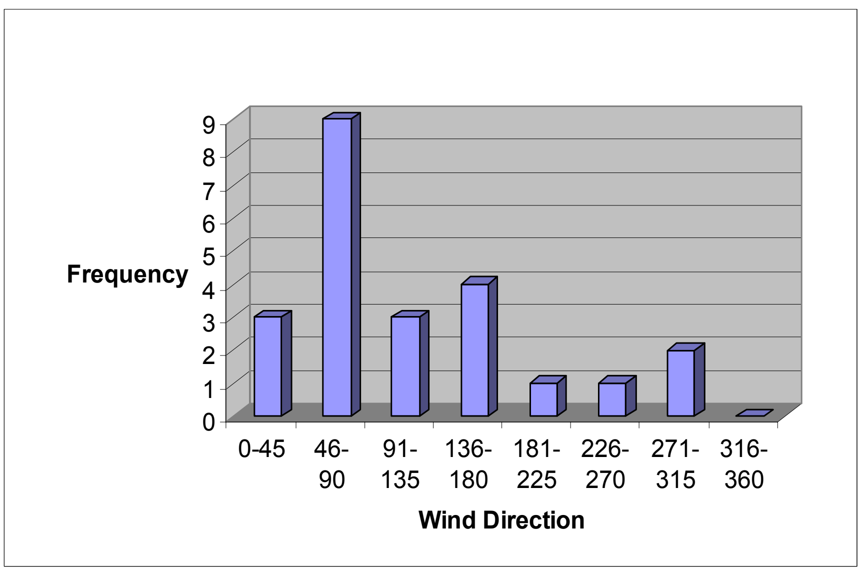

Figure 3. Wind direction histogram displaying frequency of wind direction for marine trajectory storms from August 25, 2002 to June 29, 2005 in Wilmington, NC.

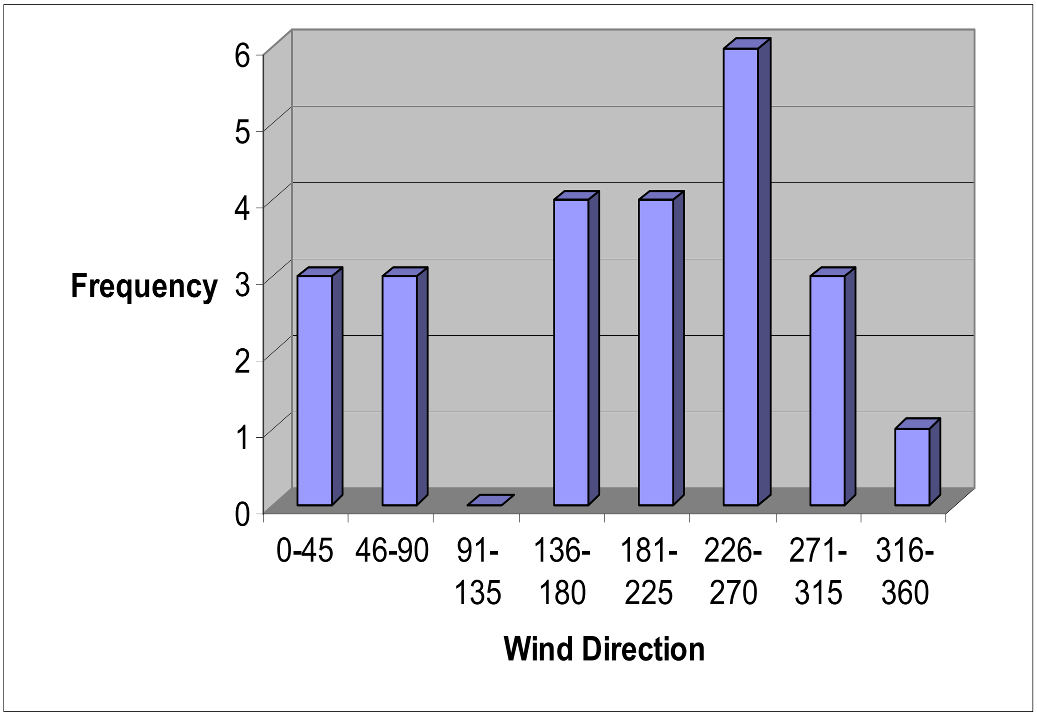

Figure 4. Wind direction histogram displaying frequency of wind direction from terrestrial trajectory storms from August 25, 2002 to June 29, 2005 in Wilmington, NC.

Table 1. Summary of scatter plot trend line slopes and r^2 for 24 rain events from August 25, 2002 to June 29, 2005 in Wilmington, NC.

Scatter Plot	*Slope*	*r^2 Value*	*p Value*
Nitrate and Average Temperature	0.3132	0.0579	0.85
Nitrate and Average Wind Speed	0.9565	0.0214	0.39
Nitrate and Relative Humidity	22.3370	0.0761	0.78
Nitrate and Precipitation	-0.4017	0.2136	0.02
Sulfate and Average Temperature	0.0792	0.0072	0.39
Sulfate and Average Wind Speed	0.8241	0.0311	0.19
Sulfate and Relative Humidity	6.5988	0.0133	0.12
Sulfate and Precipitation	-0.3000	0.2330	0.02

Based on this analysis, the most striking result is the frequency of local surface wind direction associated with marine and terrestrial trajectories. It is clear that different wind directions dominate each of the trajectory types. The most frequent directions are consistent with trajectory descriptions in that local surface winds associated with a terrestrial trajectory will come from the SSW across the southeastern United States land surface, and that local winds associated with a marine trajectory are ENE, originating and traveling across open water. Unfortunately, it is difficult to compare chemical concentrations by wind direction through a box plot or statistical tests due to the high variability in wind directions and low number of observations for specific wind directions. Beyond wind direction, scatter plots and regression analysis do not indicate any obvious relationships between local meteorological variables and nitrate and sulfate concentrations.

The hypothesis tested in each *t*-test represents an attempt to detect a significant difference in the mean of two populations by season and trajectory, two factors identified in previous research as significant in the relationship between weather conditions and precipitation chemistry. Specifically, the *t*-tests compare the meteorological variables temperature, wind speed, relative humidity and precipitation by season and trajectory (Table 2). The *t*-tests indicate no significant difference in variable by season or trajectory except for a significant differences in temperature and precipitation (precipitation terrestrial mean 15 mm, precipitation marine mean 25 mm; precipitation summer mean 24mm, precipitation winter mean 15 mm) between summer and winter (summer mean temperature 77.3°F, winter mean temperature 53.1°F) (Table 2). Such a result is expected and not surprising given the annual temperature range of Wilmington, NC and the different air masses that dominate the region during these two seasons and by trajectory.

In terms of concentrations of nitrates and sulfates by precipitation amount, there was no significant difference in either nitrate or sulfate concentrations when comparing levels between winter and summer (Table 2). In terms of comparison of nitrate and sulfate concentrations by trajectory type, nitrate levels are not significantly different for marine or terrestrial storms (Table 2). However, there is a significant difference in sulfate concentrations between marine (11.7ìM) and terrestrial trajectories (22.0ìM) with terrestrial concentrations double marine concentrations. This statistically significant difference between marine and terrestrial sulfate concentrations may be directly associated with point source industrial pollution only existing over land. The high amounts of precipitation in marine storms may dilute sulfate concentrations.

Analysis of NOAA daily weather maps revealed that the most common storm system occurring during the 48 hours prior to the storm event was equally divided between Cold Fronts and Stationary Fronts (Table 3). Review of the direction that these frontal storms travel indicates that the systems travel most frequently from the west to east (7) or northwest to southeast (3) (Table 3). In addition to these directions, systems occasionally travel from north to south, south to north, or northwest to southeast (Table 3). A comparison of nitrate concentrations levels across storm types indicates that Cold Front storms have the highest mean nitrate concentration (27.91uM). However, this high mean value may be due to one anomalous storm on 6/17/2003, 67.9 micromolar concentration. When this value is removed from the sample, the mean value drops to 21.2 uM, a value closer to the range of the other storm types. Using this adjusted mean value, Cold Front nitrate concentrations are still greater than other storm types. Backside Flow of High Pressure is the lowest concentration of the other storm types (Table 3). In terms of sulfate concentration, Cold Fronts have the greatest mean concentration and Backside Flow of High Pressure has the lowest mean concentration (Table 3). Given the small sample size of storm types, statistical tests cannot be completed to determine if these differences are statistically significant. Since, a west to east track dominates Cold Front storms, and a Northeasterly track dominates the Backside Flow around a High, it appears that the difference in nitrate and sulfate concentrations is again linked to air mass travel over land-based point-sources and high precipitation amounts for marine storms. A separation of storm events into marine

Table 2. Summary of *t*-test statistic hypothesis testing of local meteorological variables and sulfate and nitrate variables.

Test	*t-value*	*p-value*	*df*	*Significant?*
Marine vs. Terrestrial Sulfate	2.070	0.049	22	yes
Marine vs. Terrestrial Temperature	0.060	>0.623	22	no
Marine vs. Terrestrial Nitrate	1.020	0.329	22	no
Marine vs. Terrestrial Wind Direction	2.600	0.017	22	no
Marine vs. Terrestrial Relative Humidity	0.034	>0.623	22	no
Marine vs. Terrestrial Wind Speed	0.370	>0.623	22	no
Marine vs. Terrestrial Precipitation	4.110	0.001	22	yes
Summer vs. Winter Sulfate	0.060	>0.623	22	no
Summer vs. Winter Temperature	8.060	<0.000	22	yes
Summer vs. Winter Nitrate	0.250	>0.623	22	no
Summer vs. Winter Wind Direction	0.720	0.492	22	no
Summer vs. Winter Relative Humidity	0.330	.0.623	22	no
Summer vs. Winter Wind Speed	0.500	0.623	22	no
Summer vs. Winter Precipitation	4.200	0.001	22	yes

and terrestrial trajectory types indicates that Cold Front and Stationary Front storms dominate terrestrial trajectories, and Backside High Pressure Flow and Stationary Front storms dominate the marine trajectory. These frequencies further support the hypothesis that high chemical concentration exist for trajectories over land and low concentrations for trajectories over water (Table 3).

Conclusions

The purpose of this study was to determine the relationship between local weather patterns and nitrate and sulfate concentrations in rain water at Wilmington, North Carolina. Data analysis of local weather conditions 48 hours prior to 24 storm events, including review of descriptive statistics, graphical and linear regression analysis, *t*-tests, and synoptic weather map analysis, was completed to determine any relationship between variables. The overall conclusion of the study is that there are no obvious relationships between nitrate and sulfate concentrations and local meteorological variables. Instead, wind direction frequency and statistical tests suggest that trajectory, whether terrestrial or marine, is the most important factor influencing rain water chemistry. Further, weather map analysis indicated terrestrial storms, such as Cold Fronts, have higher amounts of nitrate and sulfate while marine storms are characterized by lower concentrations of the chemicals. In conclusion, this study indicates that storm track is the most important factor influencing nitrate and sulfate concentration in the Wilmington, NC area while local weather conditions may not add significant additional information to existing knowledge based upon trajectory analysis.

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Table 3. Summary of synoptic storm type data for the 24 rain events included in this analysis. Chemical concentrations provided in micromolars.

Dates	*Storm Type*	*Rain (mm)*	NO_3^-	SO_4^{2-}
1/14/05 marine	Backside H, NE	24	0.5	5.5
11/10/02 marine	Backside H, NE	2	0.2	6.2
6/29/205 marine	Backside H, NE	39	1.3	3.0
7/14/03 marine	Backside H, NE	2	3.4	2.8
Aggregate		17	1.4	4.4
6/17/03 marine	Cold Front, N-S	3	67.8	38.2
12/4/02 terrestrial	Cold Front, NW-SE	10	41.0	42.9
2/11/03 terrestrial	Cold Front, NW-SE	13	11.8	16.4
12/14/02 terrestrial	Cold Front,W-E	31	10.4	10.8
5/24/05 terrestrial	Cold Front,W-E	13	20.5	41.0
7/12/03 terrestrial	Cold Front,W-E	5	42.9	28.4
12/11/03 marine	Cold Front,W-E	11.4	1.0	6.6
Aggregate		12	27.9	26.3
2/14/04 terrestrial	Frontside H	18	5.3	7.7
2/27/04 marine	Low	30	4.7	9.7
8/8/03 terrestrial	Stationary Front, NW-SE	22	4.1	4.2
10/11/02 marine	Stationary Front, SW-NE	4	40.4	27.7
12/9/04 terrestrial	Stationary Front, W-E	4	44.3	36.9
7/17/04 terrestrial	Stationary Front, W-E	9	22.7	18.3
8/31/02 marine	Stationary Front, W-E	102	2.5	2.2
6/2/055 marine	Stationary Front,S-N	51	4.3	8.2
Aggregate		31.9	19.7	16.2
5/25/05 terrestrial	Trough, L N	14	11.9	16.3
8/25/02 terrestrial	Trough, L N	12	31.3	31.9
6/26/05marine	Trough, L S	28	1.5	6.1
Aggregate		18	14.9	18.1
12/10/2003 terrestrial	Warm Front, SE-NW	29	1.9	9.5
2/22/2003 marine	Warm Front, SE-NW	8	30.0	24.6
Aggregate		19	15.9	17.0

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