Measurement, analysis, and modeling of fine particulate matter in high ammonia region of Eastern North Carolina, U.S.A.

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Abstract:

An analysis of fine particulate data in eastern North Carolina is conducted in order to investigate the impact of hog industry and its emissions of ammonia into the atmosphere. The fine particulate data are simulated using ISORROPIA, an equilibrium thermodynamic model that simulates the gas and aerosol equilibrium of inorganic atmospheric species. The observational data analyses show that the major constituents of fine particulate matter (PM2.5) are organic carbon, elemental carbon, sulfate, nitrate, and ammonium. The observed PM2.5 concentration is positively correlated with temperature but anti-correlated with wind speed. The correlation between PM2.5 and wind direction at some locations suggests an impact of ammonia emissions from hog facilities on PM2.5 formation. The modeled results are in good agreement with observations, with slightly better agreement at urban sites than at rural sites. The predicted total inorganic PM concentrations are within 5 % of the observed values under conditions with median initial total PM species concentrations, median relative humidity (RH), and median temperature. Ambient conditions with high PM precursor concentrations, low temperature, and high relative humidity appear to favor the formation of the secondary PM.

Keywords: PM2.5; ammonia; hog industry; ISORROPIA; inorganic aerosols

Introduction

Particulate matter has become a relatively recent concern in the overall air quality of our environment. In 1997, the Environmental Protection Agency modified the National Ambient Air Quality Standards for particulate matter by dividing the total suspended particulate standard into two separate modes of particulates, fine (PM2.5) and coarse (PM10-2.5) particles, with the standards for fine particulates being 65 µg m^{-3} daily and 15 µg m^{-3} annually. The US EPA has recently tightened the daily-average standard for PM2.5 to be 35 µg m^{-3} The fine mode of PM is known to contribute to human respiratory problems, dry and wet acidic deposition, reduced visibility, and radiative forcing (US EPA, Office of Air & Radiation, 2005). PM2.5 is composed of primary and secondary pollutants; primary PM2.5 species may include organic carbon, elemental carbon, soil dust, ash, and sulfate. Secondary PM2.5 may include sulfate, nitrate, ammonium, and organic carbon, which are formed through the oxidation of their gas-phase precursors such as sulfur dioxide, nitrogen dioxide, ammonia, and volatile organic compounds.

In particular areas of the United States, ammonia and ammonium have become a significant contributor to total PM2.5 concentration. Ammonia can react with acidic compounds to form various aerosols such as ammonium nitrate (NH_4NO_3), ammonium chloride (NH_4Cl), ammonium sulfate ($(NH_4)_2SO_4$), and ammonium bisulfate (NH_4HSO_4). Globally, it is estimated that a total of 49.3 Tg of NH_3 is emitted into the atmosphere with 56 % of this total being anthropogenic. The largest contributor to these ammonia emissions is domestic animal waste decomposition, which accounts for 22 Tg NH_3 (Warneck P. 1988, Schlessinger W. H. et al. 1992, Crutzen P. J. et al. 1990, Duce R. et al. 1991). In the state of North Carolina alone, the largest source of ammonia emission is domestic animal waste (Aneja V. P. et al. 2001).

In recent years, the hog industry of North Carolina has experienced rapid growth. Between 1986 and 2005, the hog population expanded from 2.4 million up to 9.7 million, which makes it rank the second in terms of pig production by state nationwide (NCDA & CS, 2005). The swine in North Carolina are estimated to emit 68,540 tons of ammonia per year, which makes swine the largest contributor among all domesticated animals in North Carolina

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(Aneja V. P. et al. 1998). These swine are concentrated in the coastal plain region of the state or the southeast corner covering Bladen, Duplin, Greene, Lenoir, Sampson, and Wayne counties (Walker J. T. 1998).

A number of aerosol modules have been developed to simulate fine particulate matter. A particular area of focus has been studying the inorganic aerosols of fine particulate matter, which make up 25-50 % of total fine particulate matter (Grey H. A. et al. 1986). Some examples of these aerosol modules are MARS-A, SEQULIB, SCAPE2, EQUISOLV II, and AIM2, which have been thoroughly reviewed for their similarities and differences (Zhang Y. et al. 2000). ISORROPIA is a thermodynamic equilibrium model used for predicting the partitioning of major inorganic species between the gas phase and aerosol phase. This model was selected due to its efficiency in computation and its overall satisfactory performance against more comprehensive aerosol thermodynamic models. With an input of temperature, relative humidity, and the total (gas + aerosol) concentrations of sodium, ammonium, nitrate, chloride, and sulfate, ISORROPIA predicts how much the total amount will be in the gas and aerosol phases (Nenes A. et al. 1998 1999).

The primary objective of this study is to investigate the effect of increased ammonia emissions on the PM2.5 concentrations throughout eastern North Carolina. The source of these increased ammonia emissions is the presence of the hog industry. The work conducted here includes analysis of the constituents of PM2.5, their correlations with meteorological variables, and the impact of the hog facilities on PM2.5 concentrations. Another objective is to test how well ISORROPIA can predict the PM2.5 concentrations and under what ambient conditions the model has its best performance in reproducing PM2.5 concentrations.

Measurement and Modeling Methods

PM2.5 observational data was obtained from the North Carolina Division of Air Quality (http://daq.state.nc.us/). This data consists of average daily values for seven sites in Eastern North Carolina between 2001 and early 2004. The exact specifications of the particulate data are listed in Table 1. Fayetteville and Raleigh are the urban sites, which are situated to the west of the majority of the hog facilities. Goldsboro, Kenansville, and Kinston are the rural sites, with Kenansville being both the smallest city and the most enclosed by the hog facilities. Jacksonville and Wilmington are two coastal sites with the hog facilities to the north and west of their positions. Figure 1 shows the locations of the seven sites in North Carolina and their relative positions to hog facilities (Blunden J. 2003). For all these sites, when the average daily value consists of less than 90 % of the individual hours reporting, the average daily data point is considered inaccurate and is discarded. Meteorological data was obtained for each site from the North Carolina State Climate Office (http://www.nc-climate.ncsu.edu). While PM2.5 data is available for all seven sites, speciated PM2.5 data is only available for two urban sites, Fayetteville and Raleigh, and one rural site, Kinston.

Table 1:
The PM2.5 Sampling Sites in North Carolina.

Site Names	Time Period of Sampling	# of Points	Site Type	Kind of Sample
Fayetteville	Jan 2002 - Jan 2004	124	Urban	Speciated Fine PM Conc.
Goldsboro	Jan 2001 - Dec 2003	362	Rural	Fine PM Concentrations
Jacksonville	Jan 2001 - Dec 2003	354	Coastal	Fine PM Concentrations
Kenansville	Jan 2001 - Dec 2003	361	Rural	Fine PM Concentrations
Kinston	Jan 2002 - Jan 2004	123	Rural	Speciated Fine PM Conc.
Kinston	Jan 2001 - Dec 2003	360	Rural	Fine PM Concentrations
Raleigh	Jan 2002 - Jan 2004	146	Urban	Speciated Fine PM Conc.
Raleigh	Jan 2001 - Dec 2003	1084	Urban	Fine PM Concentrations
Wilmington	Jan 2001 - Dec 2003	348	Coastal	Fine PM Concentrations

The model is set for a forward problem, in which the total (both gas and aerosol) concentrations of ammonium, sulfate, sodium, chloride, and nitrate concentrations in addition to relative humidity (RH) and temperature (T) are used to calculate the total aerosol mass. Also, the model is set to run in the thermodynamically-stable state (i.e., solids can be formed when RH decreases below its deliquescence relative humidity (DRH)) instead of the metastable state (i.e., aerosols are in liquid even when RH < DRH). The initial conditions for the ISORROPIA model simulations are listed in Table 2. These conditions were selected based on available observational data in North Carolina and literature values when observational data was not available.

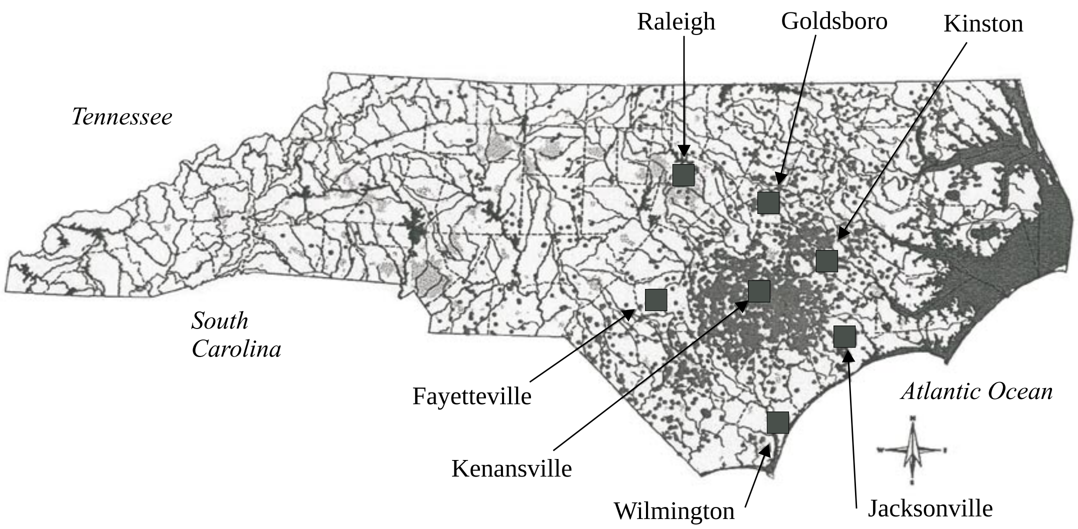

Figure 1:
Map of Hog Facilities in North Carolina and Fine Particulate Sampling Sites

Table 2:
The initial species concentrations and meteorological conditions for ISORROPIA simulations

Input Variables[a]		Kinston	Fayetteville	Raleigh
Sodium		0.22	0.19	0.17
Sulfate	Median	3.43	3.53	3.36
	Minimum	0.58	0.75	0.72
	Maximum	14.30	12.9	13.8
Ammonium	Median	3.13[b]	3.19[c]	5.10[c]
	Minimum	0.32	0.07	0.83
	Maximum	11.50	11.4	16.4
Nitrate	Median	1.07[b]	1.41[c]	1.60[c]
	Minimum	0.26	0.18	0.19
	Maximum	5.24	12.3	19.4
Chloride	Median	0.14[b]	0.33[c]	0.34[c]
	Minimum	0.10	0.02	0.02
	Maximum	0.97	3.20	4.75
Relative Humidity	Median	77	74	74
	Minimum	46	38	36
	Maximum	97	100	98
Temperature	Median	291.00	291.39	289.86
	Minimum	269.61	271.22	268.72
	Maximum	302.44	304.39	301.94

[a] All concentrations are given in µg m^{-3}

[b] (Walker J. T. et al. 2004)

[c] (Bari A. et al. 2003)

For each modeled site (i.e., Kinston, Fayetteville, and Raleigh), three levels of initial total PM species were used: median, minimum and maximum, representing the median, lower and upper limits of the 2002 observations respectively. For each concentration level, the model was run under three meteorological conditions: median RH/median T, minimum RH/maximum T, and maximum RH/minimum T. The output variables include concentrations of gaseous species (i.e., ammonia, hydrochloric acid, and nitric acid) and aerosol species (i.e., sulfate, ammonium, nitrate, sodium, chloride, and water), as well as the pH value.

Observed PM2.5 and its Correlations with Meteorological Variables

The particulate data was first analyzed for its main constituents at the three sites with detailed speciated PM2.5 data over the entirety of the sampling period, as shown in Figure 2. The plot shows the major constituents of PM2.5 to be organic carbon (OC), sulfate, and ammonium consistent with the results by Harrison R. M. et al. (2004), and Tanner R. L. et al. (2004). The additional components of PM2.5 include nitrate, elemental carbon (EC), and over fifty trace elemental species. The PM2.5 OC concentrations were higher in the urban areas, due to large local emissions of primary OC and volatile organic compounds (VOCs). The sulfate and ammonium emissions were found to be larger in the rural site, due to the influence of the hog farming facilities in the rural area.

Figure 3 shows the scatter plots of PM2.5 concentration vs. RH at Raleigh, Kinston, and Wilmington that represent urban, rural, and coastal areas. High PM2.5 concentrations (> 20 µg/m^3) occur with the range of RH between 60 and 90 %, and this effect is more prominent in the urban areas. This trend supports the fact that the overall RH increases the film of water formed on the surface of the particles favors the formation of PM2.5.

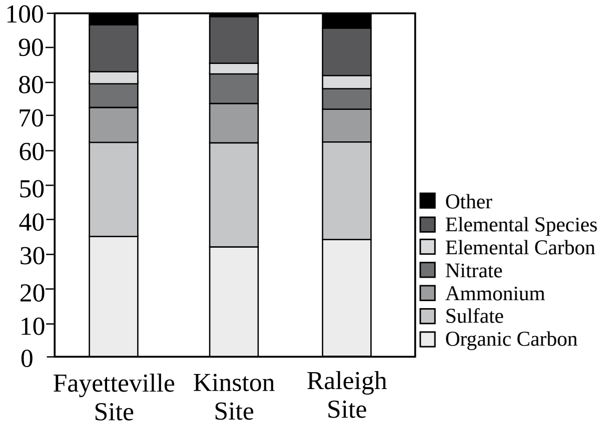

Figure 2:

PM2.5 Composition at Three Speciated Sites (Kinston, Fayetteville, Raleigh) over entire sampling period

Figure 4 shows the correlation between PM2.5 concentrations and wind speeds at three sites. The observed anti-correlation between PM concentration and wind speed is consistent with that of Chu S.-H. et al. (2004) and de Hartog J. J. et al. (2005). The PM2.5-temperature plots for Raleigh, Kenansville, and Wilmington are shown in Figure 5 to represent urban, rural, and coastal areas respectively. Many high PM2.5 concentrations occurred at high temperatures. The slopes range from 0.08 to 0.18 at the urban and the rural sites and 0.01 to 0.02 at the coastal site. To investigate the impact of ammonia on PM2.5 concentrations, the ammonium concentrations were plotted against the total fine particulate concentrations (figure not shown). The values for the slope, intercept, and the coefficient of determination are shown in table 3. There are significant correlations in the two urban sites (i.e., Raleigh and Fayetteville), but no correlation at the rural site (i.e., Kinston). The very low R^2 value in the Kinston correlation plot is due to the local variability of local primary OC PM2.5 emissions (i.e., local biomass burning from farming practices).

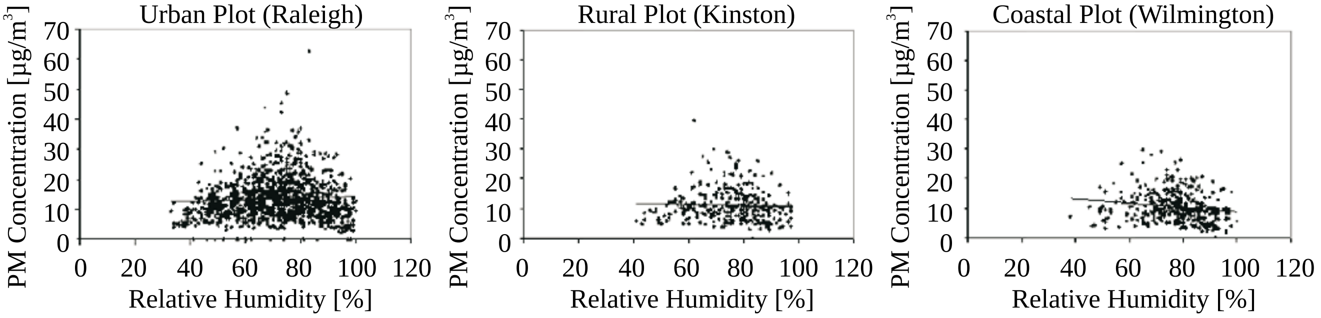

Figure 3:

(a) Urban (Raleigh) Relative Humidity vs. PM2.5 Concentration

(b) Rural (Kinston) Relative Humidity vs. PM2.5 Concentration

(c) Coastal (Wilmington) Relative Humidity vs. PM2.5 Concentration

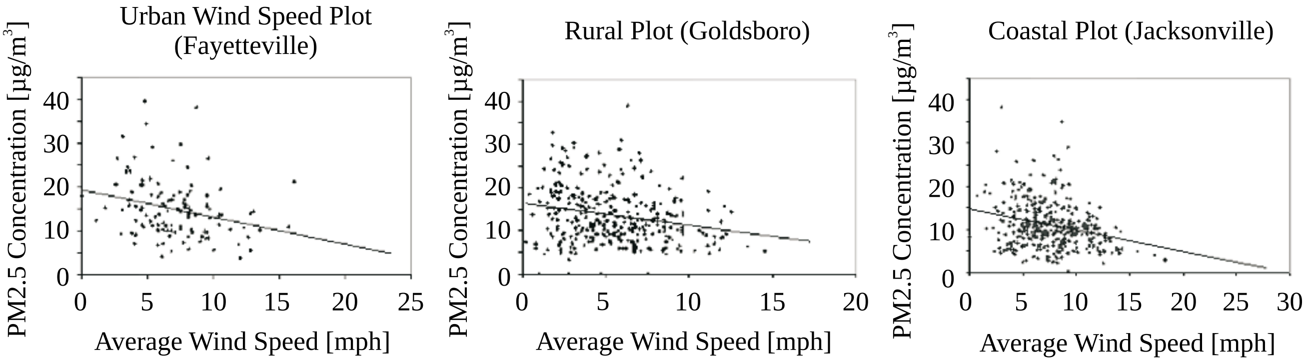

Figure 4:

(a) Urban (Fayetteville) Wind Speed vs. PM2.5 Concentration

(b) Rural (Goldsboro) Wind Speed vs. PM2.5 Concentration

(c) Coastal (Jacksonville) Wind Speed vs. PM2.5 Concentration

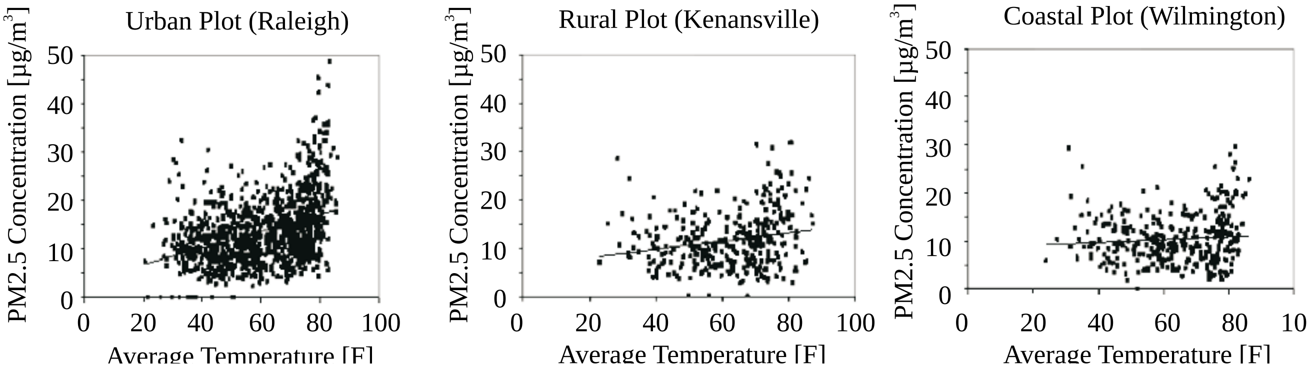

Figure 5:

(a) Urban (Raleigh) Temperature vs. PM2.5 Concentration

(b) Rural (Kenansville) Temperature vs. PM2.5 Concentration

(c) Coastal (Wilmington) Temperature vs. PM2.5 Concentration

Table 3:

The slope, y-intercept, and linear fit R^2 value from the Total PM2.5 vs. Ammonium PM2.5 Plots for Kinston, Fayetteville, and Raleigh

	Slope	Intercept	R^2
Fayetteville	0.0841	0.1758	0.591
Kinston	0.0168	1.21	0.011
Raleigh	0.0995	-0.05	0.712

To investigate the correlation between wind direction and PM distributions, a box whisker plot is made for all seven sites with respect to the eight cardinal directions, as shown in Figure 6. The minimum, 25th percentile, average, 75th percentile, and the maximum of each distribution are plotted. The impact of the hog facilities on PM2.5 concentrations can be seen at some sites. For example, higher PM2.5 average concentrations were found from a southeast flow at Raleigh (urban), which corresponds to Raleigh's orientation to the hog facilities. High PM2.5 concentrations at Kinston (rural) were from the southwest and west directions, which correspond exactly to Kinston's orientation to the majority of hog facilities. The highest average concentrations at Fayetteville were found from the southeast direction, rather than the east from which the emissions of hog facilities come. The weak correlation between the PM2.5 concentrations and the east wind direction at Fayetteville is likely due to the fact that fewer measurements were available at this site and the easterlies were not the prevailing winds during those days with observations. At the other two rural sites (i.e., Goldsboro and Kenansville), relatively homogeneous correlation between PM2.5 concentrations and cardinal directions was found. High PM2.5 average concentrations at Goldsboro were from the southeast, southwest, west, and north directions with the peak concentrations coming from the southeast. The PM2.5 concentrations range from 2.7 to 31.4 with an average of 10.8 µg m^{-3} at Kenansville , which are very high for a small rural town. This indicates the impact of the hog facilities. The two coastal sites (i.e., Jacksonville and Wilmington) have higher concentrations from the southwest and west directions, indicating the impact of emissions from the state of South Carolina. High correlation was also found for the east direction at Jacksonville and the northwest direction at Wilmington.

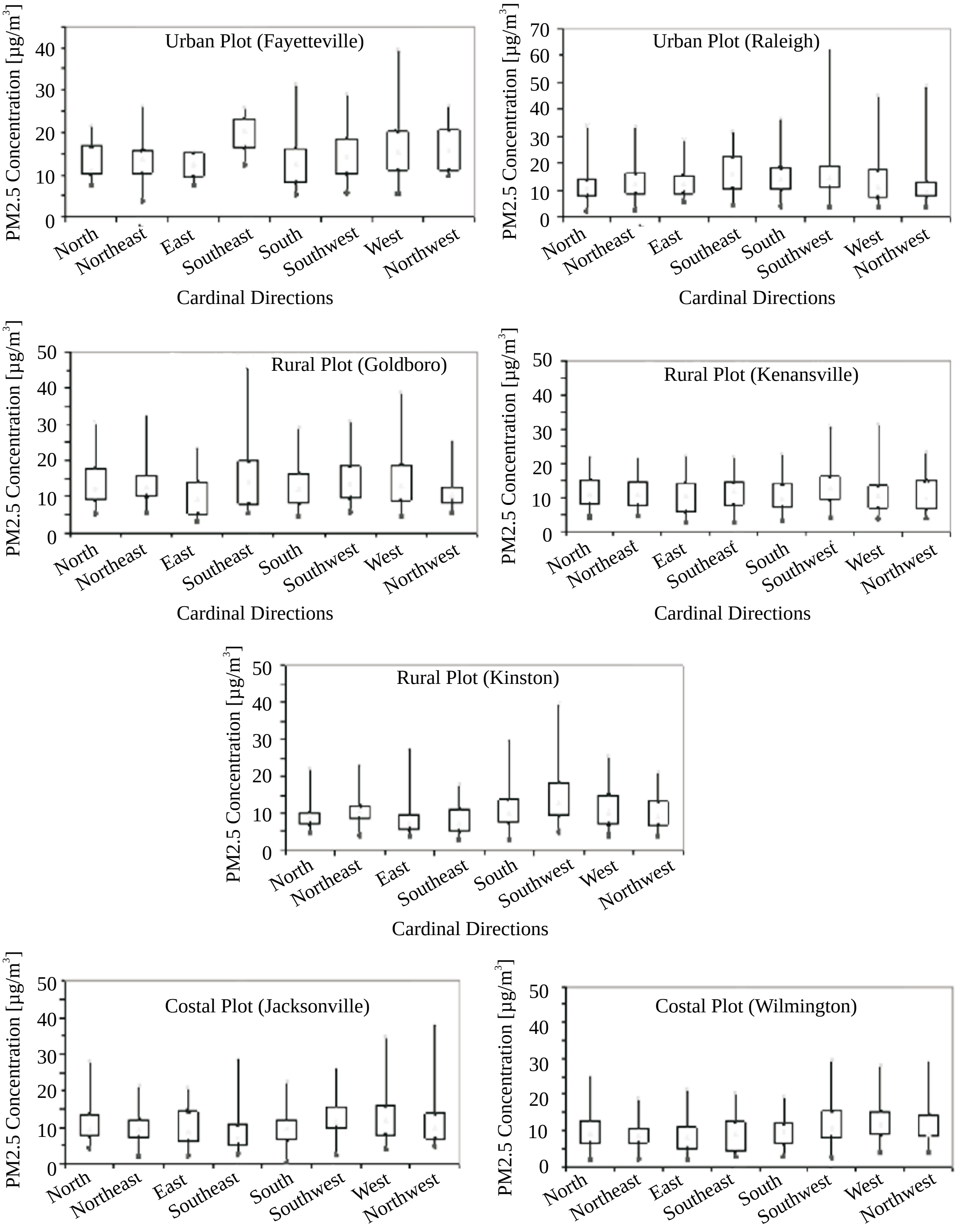

Figure 6:

(a) Urban (Fayetteville) Wind Direction Box-Whisker Plot

(b) Urban (Raleigh) Wind Direction Box-Whisker Plot

(c) Rural (Goldsboro) Wind Direction Box-Whisker Plot

(d) Rural (Kenansville) Wind Direction Box-Whisker Plot

(e) Rural (Kinston) Wind Direction Box-Whisker Plot

(f) Coastal (Jacksonville) Wind Direction Box-Whisker Plot

(g) Coastal (Wilmington) Wind Direction Box-Whisker Plot

Fine Particulate Modeling Results

Figure 7 shows the observed and predicted average total inorganic $PM_{2.5}$ concentrations and its composition at three sites: Fayetteville, Kinston, and Raleigh ("total inorganic PM2.5 or total inorganic PM" is defined as the sum of the four major inorganic constituents: ammonium, chloride, nitrate, and sulfate).

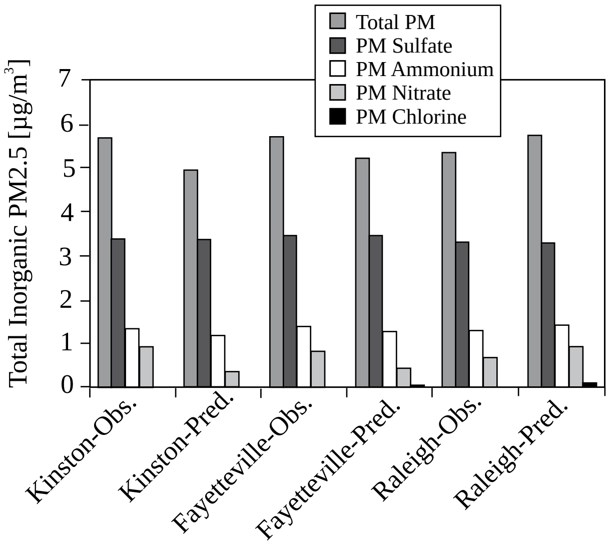

Figure 7:
Observed and Predicted Total Inorganic PM2.5 Concentrations at Kinston, Fayetteville, and Raleigh, NC under median RH and temperature conditions

The predicted values were obtained under the conditions with median initial total PM species concentration, median RH and median T, as shown in Table 2. The observations at all three sites show that sulfate has the largest contribution (approximately 2/3 of the total observed inorganic aerosol), followed respectively by ammonium, nitrate, and chloride. The simulation results from ISORROPIA generally agree well with observed PM2.5 in terms of both magnitude and composition. Compared with observed total inorganic PM2.5 concentration, ISORROPIA underestimates by 0.50-0.75 µg m^{-3} (8.7-12.5 %) at Fayetteville and Kinston, and overestimates the observed values by 0.37 µg m^{-3} (6.9 %) at Raleigh. At all three sites, sulfate has the largest contribution followed respectively by ammonium, nitrate, and chloride. The ammonium concentration at Kinston and Fayetteville is underpredicted by ~0.1 µg m^{-3} (~7.4 %) and that at Raleigh is overpredicted by the same value (7.7 %). The largest differences between observed and predicted values are in the nitrate concentration. It is underpredicted by 0.39 µg m^{-3} at Fayetteville and 0.54 µg m^{-3} at Kinston (48 % and 59 % respectively). The nitrate concentration predicted at Raleigh is 0.25 µg m^{-3} (37 %) greater than the observed nitrate concentrations. The observed chlorine concentrations are nearly zero while the predicted chlorine concentrations at the three sites are < 0.1 µg m^{-3}. At each site, the predicted pH and aerosol water concentrations are in the range of 7.53-7.56, and 5 µg m^{-3} respectively. The model gives the best agreement against observations at Raleigh among the three sites.

Figure 8 shows the predicted total inorganic PM2.5 concentration at the maximum initial pollutant concentrations at each site under the three different meteorological settings.

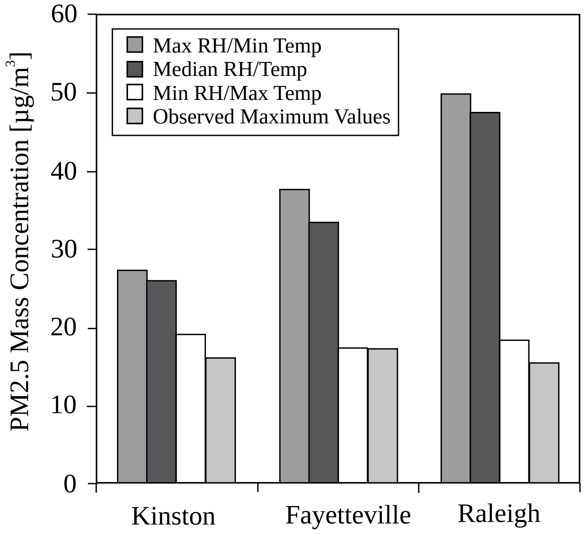

Figure 8:
Predicted Total Inorganic PM2.5 Concentrations under three meteorological conditions and maximum observed Total Inorganic PM2.5 Concentrations at Kinston, Fayetteville, and Raleigh, NC

The maximum observed values are also plotted for comparison. For the median RH/median T and the maximum RH/minimum T conditions, the predicted total PM2.5 inorganic aerosol concentrations range from 26 to 50 µg m^{-3} at the three sites, which consistently overpredicts the observed maximum concentrations (15-18 µg m^{-3}) at all sites**.** The predicted total inorganic PM2.5 concentration increases as the urban development of the area increases (Kinston (rural), Fayetteville (small city), Raleigh (large city)). These differences are due to differences in the predicted particulate nitrate concentration, which is factors 2 and 3 higher at Fayetteville and Raleigh, respectively, than that at Kinston. The predicted particulate ammonium concentration is higher by 32 % and 80 % at Fayetteville and Raleigh, respectively, due to formation of ammonium nitrate. With the higher sulfate concentrations at Kinston and Raleigh, the aerosol is much more acidic at these sites (with pH values of 4.5-4.8), whereas that at Fayetteville is more neutral (6.8). The predicted total inorganic aerosol concentrations range from 17.23 to 19.09 µg m^{-3} at the three sites under the minimum RH/maximum T condition. Such a condition favors evaporation of nitrate and water, resulting in zero nitrate and water concentration in the aerosol phase. The aerosol consists of primarily ammonium sulfate salt. The differences in predicted total inorganic aerosol concentrations among these sites are thus much smaller.

A similar plot is shown at the minimum pollutant concentrations at each site in Figure 9.

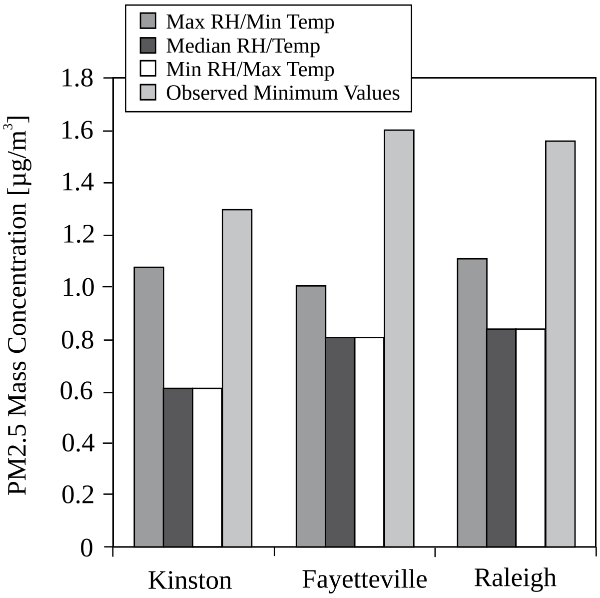

Figure 9:
Predicted Total Inorganic PM2.5 Concentrations under three meteorological conditions and minimum observed Total Inorganic PM2.5 Concentrations at Kinston, Fayetteville, and Raleigh, NC

The model underestimates the observed minimum concentrations by less than 1 µg m^{-3} at each site. Under the median RH/median temperature and the minimum RH/maximum T conditions, the total inorganic PM2.5 concentrations are the same and they consist of sulfate salts only. The nitrate concentrations are either zero or negligible. Under the maximum RH/minimum T conditions, some nitrate forms. The total PM species concentrations predicted at the three sites range from 1.01 to 1.11 µg m^{-3}. Under this condition, the urban areas are characterized by 20 % more sulfate than the rural site, but the rural site (i.e. Kinston) had slightly more nitrate, ammonium, and chloride resulting in total PM2.5 concentration that is slightly higher than that at Fayetteville but lower than that at Raleigh.

Conclusion

The concentrations and trends of PM2.5 in eastern North Carolina are studied with data analysis and an aerosol thermodynamic box model that predicts the gas/particle partitioning of PM. The unique emission fluxes of pollutants (e.g. ammonia) from the hog industry and their impacts on PM concentrations make this region a unique environment to understand the role of these emissions in PM formation. The major constituents of fine PM2.5 from the greatest to the least are OC, sulfate, ammonium, nitrate, and EC. Higher PM2.5 concentrations tend to occur between 60 and 90 % RH with this effect being more pronounced in urban areas. There is a positive relationship between temperature and PM2.5 concentrations, and a negative relationship between wind speed and PM2.5 concentrations. The box-whisker plots of wind direction demonstrate that there is a connection between hog facility density and fine particulate concentration, but with the limited data, these concentrations could not be attributed to any specific pollutant.

ISORROPIA is used to simulate the gas/particle partitioning and the total inorganic aerosol concentration at three sites in eastern North Carolina. The model predictions show that the major predicted constituents of inorganic aerosols are sulfate, ammonium, and nitrate, which agrees with the overall measurements. The predicted average total inorganic concentrations are slightly (< 1 µg m^{-3}) lower than the observations. While the model predicts the concentrations of sulfate and ammonium that are in good agreement with observations, it tends to underpredict the observed particulate nitrate concentrations by 0.22 µg m^{-3} (27.5 %) at all three sites. The simulation results are sensitive to initial total PM concentrations and meteorological conditions, with the highest secondary PM formation occurring under the condition with maximum initial total PM concentrations, maximum RH, and minimum temperature.

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