

## 1.8 ANALYSIS OF PARTICLE FORMATION PROCESSES THROUGH THE EFFECT OF METEOROLOGICAL CONDITIONS ON ORGANIC AND INORGANIC NITROGEN CONCENTRATIONS IN ATMOSPHERIC AEROSOLS

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### 1. INTRODUCTION

Atmospheric deposition of nitrogen species represents an additional nutrient source to natural environments, and can unbalance the nitrogen cycle by increasing nutrient levels beyond the requirements. Nitrogen saturation has negative consequences such as eutrophication, a phenomenon associated with high phytoplankton concentrations, decrease in sea grass coverage, reduction in light penetration, decrease of oxygen levels, poor water quality and fish kills (Paerl, H. W. 1988). In the late 1970s eutrophication affected coastal areas of USA, especially Tampa Bay, FL where high nitrogen levels were linked to a 46% loss of the sea grass coverage between 1950 and 1982 (Tomasko, D. A. et al. 2005). For 1992-1994 it was estimated that 29% of the total nitrogen loading was caused by atmospheric deposition of dissolved inorganic nitrogen species (DIN), mostly deposited as ammonia/ammonium from fertilizer industries and agricultural emissions or as nitric acid/nitrate after transformation of  $\text{NO}_x$  from power plants and vehicle emissions (TBNEP 1996). For 1996-1999 this number slightly decreased to 22%, equivalent to 760 metric tons-N  $\text{yr}^{-1}$ , 58% of this value as ammonia/ammonium and 42% as nitric acid/nitrate with a larger flux coming from wet deposition (56% of the total-N flux) (Poor et al. 2001). Corrective actions have focused on the reduction of anthropogenic nitrogen loadings to the bay and include improvement in the treatment of wastewater effluents and re-powering power plants from coal to natural gas. In recent years, overall water quality on the bay has increased and the sea grass coverage is 20 % higher than in 1982 but still 65% of the 1950 coverage (Tomasko et al. 2005).

Organic nitrogen species, however, have not been included in these estimates and many nitrogen sources could be missing from current inventories. Dissolved organic nitrogen (DON) species have shown to be present in rainwater and aerosol samples collected on

the bay and represent ~10% of the total dissolved nitrogen, represented by the sum of dissolved inorganic nitrogen (DIN) and DON. (TDN = DIN + DON) flux (Calderón et al. 2005b). DON species are found in the form of aliphatic amines (e.g. methylamine, dimethylamine (Calderón et al. 2005b), (Gibb et al. 1999), (Mace et al. 2003b), amino acids (e.g. glycine, arginine (Zhang and Anastasio 2003), (Mace et al. 2003c) and urea (Mace et al. 2003a), (Cornell et al. 1998).

Aerosols collected at Tampa Bay contain DIN species ( $\text{NH}_4^+$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ) and DON in fine ( $\text{PM}_{2.5}$ ) and coarse particles ( $\text{PM}_{10-2.5}$ ) under 10  $\mu\text{m}$  of aerodynamic diameter. As in other aerosols collected around urban areas, DIN in fine particles is  $97 \pm 3$  %  $\text{NH}_4^+$ , and it is very likely to be in the form of ammonium sulfate. On the other hand, DON is  $13 \pm 3$  % dimethylamine (DMA), most likely due to oceanic emissions from biological processes of living organisms. DIN in coarse particles is  $80 \pm 11$  % nitrate assumed to be in the form of sodium nitrate, and DON represents  $13 \pm 13$  % of the TDN concentration. DMA is under detection levels. Approximately ~80% of the total DON in  $\text{PM}_{10}$  is in the fine particles (Calderón et al. 2005b). The dominance of sodium nitrate on coarse particles is typical of Tampa Bay and other estuarine and coastal environments, where sea salt reacts with nitric acid and depletes chloride by production of hydrochloric acid (HCl) (Evans, et al. 2004).

In Tampa Bay, concentrations of DON in fine and coarse particles are  $5.3 \pm 2.6$  and  $2.1 \pm 1.6$   $\text{nmol m}^{-3}$  ( $n=55$ ) respectively, and DON concentrations in rainwater samples are  $3.3 \pm 3.1$   $\mu\text{M-N}$  ( $n=13$ ). We estimated that gas scavenging should be responsible for 99% of the DON concentrations in rainwater. This estimation is mainly based on the assumption that DON-enriched particles follow the same log-normal size distribution found for ammonium-enriched particles. This assumption is supported by the strong correlation between measurements of ammonium and DON

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concentrations in fine particles at different meteorological conditions (Pearson Correlation Coefficient  $r = 0.83$   $n=45$ ) (Calderón et al. 2005b).

Although the complete chemical composition, particle size distribution and gas phase concentrations of DON species are still unknown, the information obtained so far revealed their importance for the correct estimation of nitrogen loadings to the Tampa Bay, and therefore highlights the need for better inventories of nitrogen sources.

Our research goal in this study is to improve our knowledge about DON species by revealing how they integrate into atmospheric particles. Particle formation processes are driven by mass transfer and chemical reactions and therefore should show correlations with meteorological data. Meteorological parameters, such as relative humidity, temperature, wind speed and direction, drive the formation, interaction, size and deposition of particles as well as gas absorption rates into droplets on the atmosphere. Temperature, for example, is a driving force for chemical reactions, as well as for mass-transfer during evaporation, absorption and desorption processes.

To evaluate this idea, 24-hr integrated DIN and DON concentrations in  $PM_{10}$  samples and average meteorological conditions for two different periods (dry and wet) were analyzed using multilinear regression techniques. Results were compared to identify seasonal effects and normal background conditions that define the air quality and the nitrogen atmospheric deposition flux over Tampa Bay.

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## 2. DESCRIPTION OF THE SITE

Aerosol samples were collected at a monitoring site on the eastern end of the Gandy Bridge in Tampa, Florida ( $27.78^{\circ}N$ ,  $82.54^{\circ}W$ ). The urban monitoring site is  $\sim 20$  km from the Gulf of Mexico, and  $\sim 50$  m from Old Tampa Bay. The monitoring site and the main  $NO_x$  and  $NH_3$  sources can be seen in Figure 1 (Strayer, H. 2005).

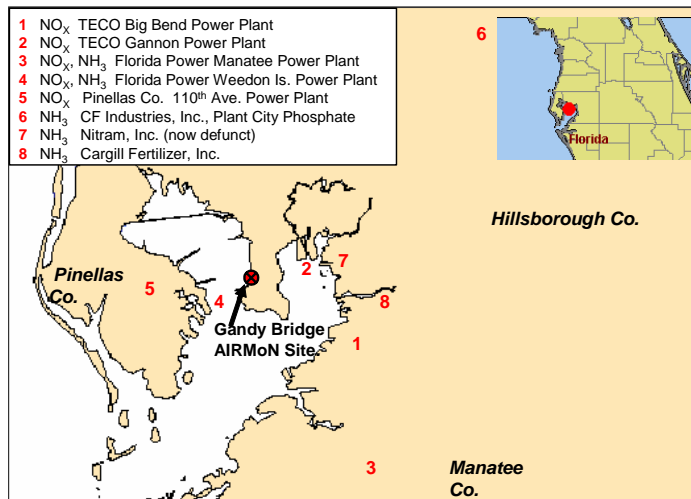


Figure 1. Map of the Tampa Bay area and the Gandy Bridge AIRMoN site, identifying the locations of the largest local  $NO_x$  and  $NH_3$  emissions sources (Strayer, H. 2005).

## 3. EXPERIMENTAL TECHNIQUES

Particulate matter (PM) was collected using a Rupprecht and Patashnick (R&P) dichotomous Partisol-Plus model 2025 sequential air sampler with an inlet cut-point that is 50% for particles with an  $10 \mu m$ . Collected particles are subsequently separated in a virtual impactor with a  $2.5 \mu m$  cut-point. The fine ( $PM_{2.5}$ ) and coarse ( $PM_{10-2.5}$ ) fractions were collected at flow rates of  $15 L min^{-1}$  and  $1.7 L min^{-1}$ , respectively, over 24 hr. (Poor et al. 2002) provides details about the operation and field performance of the dichotomous sampler.

Particles were collected onto PTFE<sup>®</sup>  $2 \mu m$  pore size,  $46.2$  mm diameter filters (Whatman, Inc.). Field blanks (unexposed filters to the air flow taken to the site) were used to account for contamination from filter storage, handling and transport. Sample, field blanks and lab blanks were extracted for one hour under sonication in an isothermal bath at  $45^{\circ}C$  with  $\sim 20$  ml of double deionized water (DDW) into amber glass bottles without headspace. All extracts were acidified to pH 2 with concentrated sulfuric acid and separated in two aliquots for DIN and DON analyses.

DIN sample concentration was measured by ion chromatographic analyses of  $NH_4^+$ ,  $NO_2^-$ ,  $NO_3^-$  using a Dionex 600 ion chromatograph equipped with a CD25A conductivity detector and an AS50 autosampler. Anions were separated by an AS14 analytical column ( $4 \times 250$

mm) and ASRS-Ultra 4-mm suppressor in an isocratic regime with a sodium carbonate/bicarbonate solution. Cations were separated in a CS16 analytical column (4 x 250 mm) kept at 40 °C and a CSRS-Ultra II 4-mm suppressor using an isocratic and gradient regime with a methanesulfonic acid (MSA) solution. Check standards were run after every ten samples and were within 5% of their prepared concentrations (within 10% for concentrations near the detection limit).

DON sample concentration was determined as the difference between nitrite, nitrate and ammonium concentrations in irradiated and non-irradiated aliquots using the UV-photolysis method. Organic nitrogen is decomposed to inorganic forms using UV-light (253.7 nm, 35 W) at pH 2 and 24-hr exposure periods in a Rayonet Photochemical Chamber Reactor Model RPR-100 (Southern New England Co, Inc.). Details about the method performance and its applicability to atmospheric samples can be found elsewhere (Calderón et al. 2005a). Solutions with known DON concentrations much higher than those in samples (e.g. urea, dimethylamine, methylamine, diethanolamine) were irradiated with the samples and their conversion varied between 92 and 120 %.

#### 4. STATISTICAL ANALYSES

For each sampling day, values of relative humidity, dry bulb temperature, wind speed and wind direction were obtained as hourly surface weather observations from the Tampa International Airport (8 km north from the site) available at the National Climatic Data Center website ([www.ncdc.noaa.gov/servlets/ULCD](http://www.ncdc.noaa.gov/servlets/ULCD)).

Simple averaging of the hourly data per sampling day was used for relative humidity (RH, %), dry bulb temperature (DBT, °C), inverse of dry bulb temperature (INVDBT, °C<sup>-1</sup>), wind speed (WS, knots).

Wind direction (WD, deg) and its standard deviation (WDirSTD, deg), the east-west and the north south wind components (knots) were calculated using vector computation with measurements of the horizontal component and the azimuth angle of the wind vector using the equations presented by the (U.S. Environmental Protection Agency 2000). The standard deviation of the wind direction was used as a measure of mixing in the atmosphere; and it was determined using the Yamartino method with hourly wind direction

values (U.S. Environmental Protection Agency 2000). Equations 1, 2 and 3 define the average wind direction and its standard deviation; values of the  $\phi$  variable are chosen between (0, 1, 3/2) to place the resultant wind vector in the right quadrant indicated by the signs of its components. n is the number of hourly data points included to describe the variable variation of the sampling period.

$$WDAve = \arctg \left( \frac{-\sum_{i=1}^n WS_i * \sin\left(\frac{WD_i * 2\pi}{360}\right)}{-\sum_{i=1}^n WS_i * \cos\left(\frac{WD_i * 2\pi}{360}\right)} \right) + \phi * \pi \quad (1)$$

$$WDirSTD = \arcsin(\varepsilon) * (1 + 0.1547 * \varepsilon^3) * \frac{360}{2\pi} \quad (2)$$

$$\varepsilon = \sqrt{1 - \left( \left( \frac{\sum_{i=1}^n \sin\left(\frac{WD_i * 2\pi}{360}\right)}{n} \right)^2 + \left( \frac{\sum_{i=1}^n \cos\left(\frac{WD_i * 2\pi}{360}\right)}{n} \right)^2 \right)} \quad (3)$$

The persistence, or the ratio between the module of the average wind vector and the simple average wind speed per day, was calculated to evaluate the effect of sustained winds in a certain direction on daily measurements and its relation with possible fixed sources. However it was impossible to find significant correlations between this variable and the DIN and DON concentrations using Pearson Correlation Coefficients and Multi-linear Regression Analyses.

DIN and DON concentrations were measured in two different seasons, the dry period with samples taken between November-2004 and April-2005 and the wet period between July and September-2005. The latitude of Tampa Bay is near enough to the Equator not to shown strong seasonal tendencies in temperature for example. There are significant variations in daily precipitation rates during the hurricane season (wet period) and the rest of the year (dry period). During our sampling period, just two rainstorms were associated with Hurricane Katrina but no aerosol samples were collected during those events.

Average values for meteorological conditions are reported on Table 1 and were individually compared by a t-test (two-tailed), after comparison of the data variances by an F-test. When the variances were different from each other, a new number of degrees of

freedom was calculated. The p-values indicated significant differences (at 95% confidence level) between the DBT, RH, WS and precipitation means for both periods.

The dry period was characterized by lower temperature, humidity and daily precipitation (few and short rain events) with higher wind speeds. The wet period can be considered as isothermal due to the small standard deviations of the dry bulb temperature. Another important characteristic of this period is the constantly high water content of the air.

Table 2 shows the average values of DIN concentrations as well as DON concentrations. Using the same comparison procedure applied to the meteorological values, it was determined that both periods have just significant differences (at 95% confidence level) in the  $\text{NO}_3^-$  content of particles.

Because coarse particles contain high nitrate concentrations, their DIN concentrations showed also significant differences between the periods. A possible explanation for these differences can be found if we consider that nitrate particle contents were lower during the wet period because sodium-enriched coarse particles are efficiently removed by rain droplets and then do not remain suspended in air during sampling periods with rain events.

Nitrate-enriched particles are formed after the nitric acid removal via reaction with sea salt (NaCl). Even if nitric acid concentrations are high, nitrate-particles are removed by rain as soon as they are formed. This makes impossible to maintain the same  $\text{DIN-NO}_3^-$  particle concentrations seen in the atmosphere on the dry period.

A very different tendency is observed for  $\text{NH}_4^+$  particle contents. They do not show significant difference even when temperature and relative humidity are different for each period. Because it was already shown that DON and  $\text{NH}_4^+$  are strongly correlated and mainly present in fine particles, we expected to have non-significant differences in DON particles contents from both periods.

Before the application of multi-linear regression techniques to the data, we looked for possible deviations from the normal distribution using the Shapiro-Wilk test provided by the UNIVARIATE command on SAS (SAS Institute, Inc.). Data for DBT, RH and WDirSTD from both periods and WS of the wet period had non significant deviations from the normal

distributions; deviations were seen also for WD and WS of the dry period,  $\text{NH}_4^+$  particle concentrations for both periods, and nitrate and DON concentrations on the wet and dry periods, respectively. A natural logarithmic transformation was applied to all concentration values to correct these deviations.

The log transformation was also intended to correct wedge patterns in residual vs. fitted plots seen in the first regressions caused by heteroscedasticity or unequal variance of the data. Improvements in the normality of data and residuals from regressions, as well on the correlation coefficient  $r$ , were found for all variables after the log transformation in almost all cases. The log-transformation keeps does not alter any distribution moments.

Similar transformations have been found in literature and pretended to reach the same goal: improve fit and achieve constant variance in the models (Robarge et al. 2002).

Table 1. Average Meteorological Conditions at the Gandy Bridge monitoring site

<b>Average <math>\pm \sigma</math></b>	<b>Dry Period: Nov, 2004 – Apr, 2005 (n=30)</b>	<b>Wet Period: Jul-Sep, 2005 (n=25)</b>	<b>p-value (<math>\alpha=0.05</math> )</b>
Dry Bulb Temperature ( $^{\circ}\text{C}$ )	19.9 $\pm$ 3.1	28.2 $\pm$ 0.9	<b>0</b>
Relative Humidity (%)	63.5 $\pm$ 10.5	76.8 $\pm$ 3.7	<b>0</b>
Wind Speed (knots)	7.1 $\pm$ 2.1	4.9 $\pm$ 1.9	<b>0</b>
Wind Direction (deg)	194.4 $\pm$ 113.1	131.4 $\pm$ 106.8	0.06
Standard Deviation of Wind Direction (deg)	47.9 $\pm$ 24.8	59.3 $\pm$ 25.7	0.13
Persistence (%)	70.5 $\pm$ 25.3	57.9 $\pm$ 28.4	0.06
East-West Wind Component (knots)	0.9 $\pm$ 3.6	-0.1 $\pm$ 3.4	<b>0.24</b>
North-South Wind Component (knots)	-0.9 $\pm$ 4.4	0.2 $\pm$ 2.4	0.35
Precipitation (mm/day)	0.4 $\pm$ 1.8	7 $\pm$ 11	<b>0.002</b>

Table 2. Average DIN and DON concentrations at the Gandy Bridge Monitoring Site

Average $\pm \sigma$ (nmol/m <sup>3</sup> )	Dry Period: Nov, 2004 – Apr, 2005 (n=30)	Wet Period: Jul-Sep, 2005 (n=25)	p-value ( $\alpha=0.05$ )
PM <sub>2.5</sub> DIN-NH <sub>4</sub> <sup>+</sup>	49.1 $\pm$ 27.0	70.5 $\pm$ 57.3	0.17
PM <sub>2.5</sub> DIN-NO <sub>3</sub> <sup>-</sup>	6.3 $\pm$ 3.7	2.4 $\pm$ 1.6	0
PM <sub>2.5</sub> DIN	55.4 $\pm$ 26.1	72.9 $\pm$ 56.2	0.28
PM <sub>2.5</sub> DON	6.1 $\pm$ 2.6	4.9 $\pm$ 2.7	0.05
PM <sub>10-2.5</sub> DIN-NH <sub>4</sub> <sup>+</sup>	1.6 $\pm$ 1.2	1.5 $\pm$ 1.0	0.48
PM <sub>10-2.5</sub> DIN-NO <sub>3</sub> <sup>-</sup>	22.3 $\pm$ 10.8	11.4 $\pm$ 6.0	0
PM <sub>10-2.5</sub> DIN	23.9 $\pm$ 11.5	13.0 $\pm$ 6.2	0
PM <sub>10-2.5</sub> DON	1.7 $\pm$ 1.7	2.4 $\pm$ 1.6	0.08

Because NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> are at very different particle sizes respectively concentrated in fine and coarse modes and appear to be formed by different processes, we added their concentrations in the fine and coarse mode and studied them as single data distributions. To evaluate individual effects of meteorological variables on DIN and DON concentrations, we calculated the Pearson correlation coefficients for all possible binary combinations between variables.

Figures 2, 3, 5 and 6 show the r values. They are significantly different from zero (at 90% confidence level) when p-values are lower than or equal to 0.1.

During the dry period, DIN-NH<sub>4</sub><sup>+</sup> concentrations were correlated with almost all meteorological conditions except with wind direction. The strongest positive correlation is seen with the relative humidity. At high water contents the gaseous precursors of ammonium sulfate, ammonia and sulfuric acid, have more absorptive media and are effectively removed from the atmosphere. Particles covered by water films and/or water droplets more effectively scavenge inorganic nitrogen gases, such as ammonium and nitric acid, at higher relative humidity values. For example, the higher the ammonium and sulfate contents in liquid phase, the

higher the rate formation of their salt. As is also expected, ammonium particle contents are positively correlated with temperature. The higher the temperature, the higher are the gas absorption rates the reagents concentrations and the rate of chemical reactions leading to the formation of ammonium salts.

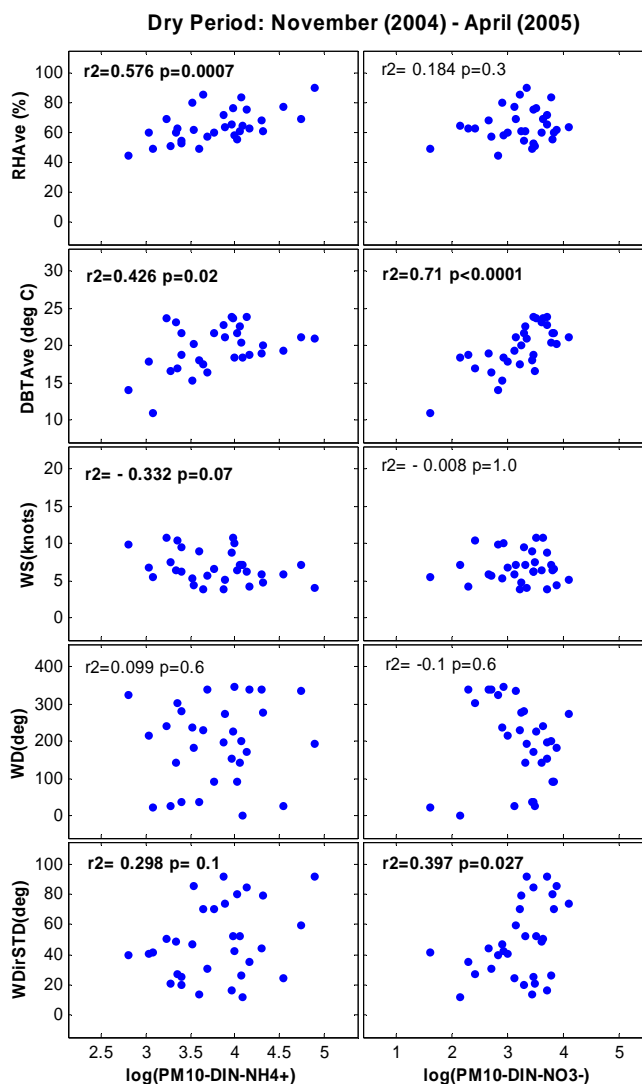


Figure 2. Correlations between meteorological data and DIN-NH<sub>4</sub><sup>+</sup> and DIN-NO<sub>3</sub><sup>-</sup> concentrations during the dry period 2005.

There is a negative correlation with wind speed, which means that the higher the wind speed the lower the DIN-NH<sub>4</sub><sup>+</sup> concentration. High wind speeds are related to higher mass fluxes of air. If the whole mass of air blowing over the site was homogeneous in composition, then it would be expected to have higher DIN concentrations at higher wind speeds. But for

cleaner air masses blowing at the higher wind speeds, it is expected to have lower concentration of inorganic nitrogen gases and therefore lower absorption to particles due to the dilution effect. In conclusion, this suggests that ammonium is diluted not delivered but stronger winds. We might expect the opposite for  $\text{NO}_3^-$  as higher winds deliver more sea salt and with this more reactive surface area.

$\text{DIN-NO}_3^-$  concentrations do not show the same behavior seen for ammonium in the dry period. Nitrate particle concentrations do not have significant correlation with relative humidity. Instead they showed a very strong positive correlation with temperature. Nitrate in particles is mainly present as sodium nitrate, and the equilibrium constant for its chemical formation goes down ~9% with an increment of 5 °C from 20 °C. A decrease of ~39% in the nitric acid dissociation constant is also associated with a temperature increase from 20 °C to 25 °C (Seinfeld, J. H. and Pandis, S. N. 1998). Those tendencies intimately related with the particle formation of sodium nitrate do not match what was seen during the dry period. The temperature effect must be related then with the increase in the rate of chemical reactions leading to the nitric acid production from  $\text{NO}_x$  in the atmosphere.

In addition,  $\text{DIN-NO}_3^-$  concentrations show a moderate correlation with the standard deviation of the wind direction. This variable is a measure of mixing in the atmosphere, and it showed to be negatively correlated with wind speed ( $r=-0.51$   $p=0.0032$ ). The higher the standard deviation of the wind direction, the lower is the wind speed. This could indicate more stable conditions in the atmosphere, better mixing and more contact time between pollutants. Also, variations in the wind direction could benefit the sea spray formation and with this increase, NaCl concentrations available to form sodium nitrate. Although atmospheric stability do not depend exclusive on wind conditions, it has been associated with them (Raberge et al. 2002)

Figure 3 shows the correlations for DON particle concentrations with meteorological data. As for DIN concentrations, DON contents increase when relative humidity and temperature increase; and they decrease when wind speed increases. This behavior could indicate that DON concentrations in particles depend also on the quantity of water available to absorb organic nitrogen gases or to serve as a media for aqueous

phase reactions leading to DON formation, as was seen for ammonium sulfate and sodium nitrate formation.

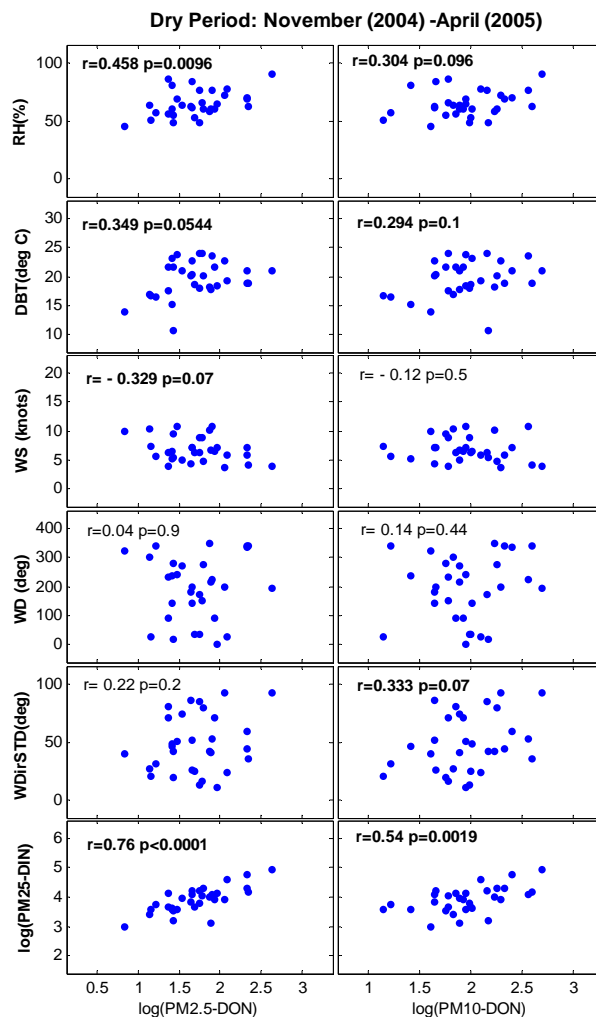


Figure 3. Correlations between meteorological data and DON concentrations during the dry period 2005.

Evidence suggesting that DON in particles could come from such gas-to-particle conversion processes was already found from samples collected at the same site. DON is concentrated on fine particles and their DON-fraction is 14% dimethylamine (DMA). DMA is a very volatile substance (Vapor pressure at 20 °C= 1.2 atm) and its presence in particles could indicate two things, first very high gaseous DMA concentrations and second high retention of the DMA contents of air by the acidic particles. DMA when diluted in water shows a basic character and is efficiently retained after protonation when the solution is acidic (Calderón et al. 2005b). However, DON showed a stronger correlation with the DIN concentrations in fine particles (~90 %

ammonium). This could suggest that the same processes leading to ammonium sulfate production drive the DON formation or transference to the particles. This tendency was also observed for the wet period, where DON and DIN contents in fine particles were correlated with a moderate coefficient. The variation of temperature and relative humidity during the wet period is almost negligible when it is compared to conditions on the dry period. This explain why no significant correlations were seen between these variables and all DIN and DON concentrations. Whatever is the influence of those variables on the concentrations; it remained constant during the whole sampling period and does not help to explain the variance in the concentrations.

DIN-NH<sub>4</sub><sup>+</sup> concentrations in the wet period showed negative correlations with the speed and the direction of the wind. Both variables are positively correlated with wind speed ( $r=0.42$ ,  $p=0.04$ ) as it can be seen in Figure 4. Stronger winds were registered when the winds came from north and south west directions. On the other hand, DIN-NO<sub>3</sub><sup>-</sup> concentrations correlated significantly with only one meteorological variable, a negative correlation with the standard deviation of the wind direction, as was seen in the dry period (Figure 5). The same possible explanations are applicable in this case.

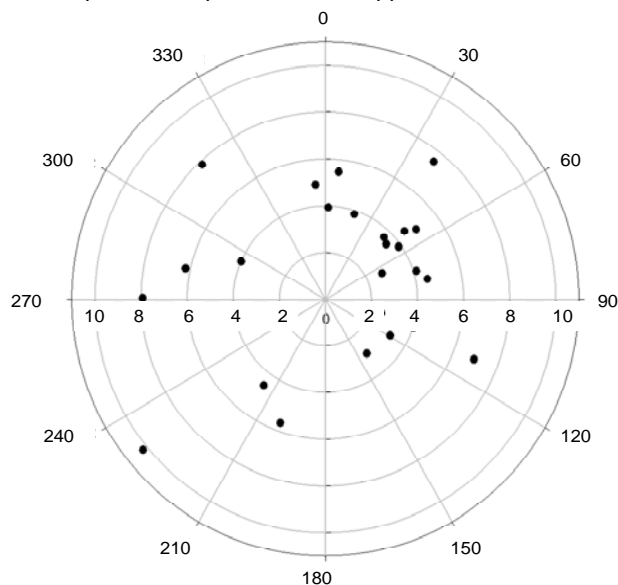


Figure 4. Variation of the Wind Speed and Direction on the wet period.

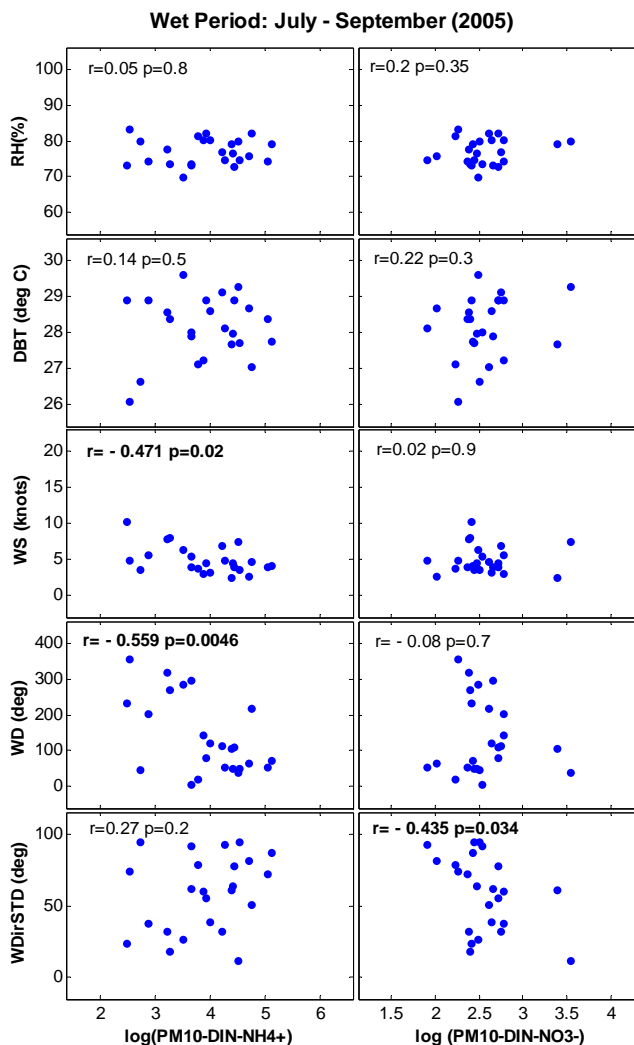


Figure 5. Correlations between meteorological data and DIN-NH<sub>4</sub><sup>+</sup> and DIN-NO<sub>3</sub><sup>-</sup> concentrations during the wet Period 2005.

As was seen in the first period, DON in fine particles correlates positively with their DIN content; and therefore increases in wind speed and wind direction should produce a decrease in DON concentrations. This is confirmed by the negative correlations coefficients reported for those variables in Figure 6.

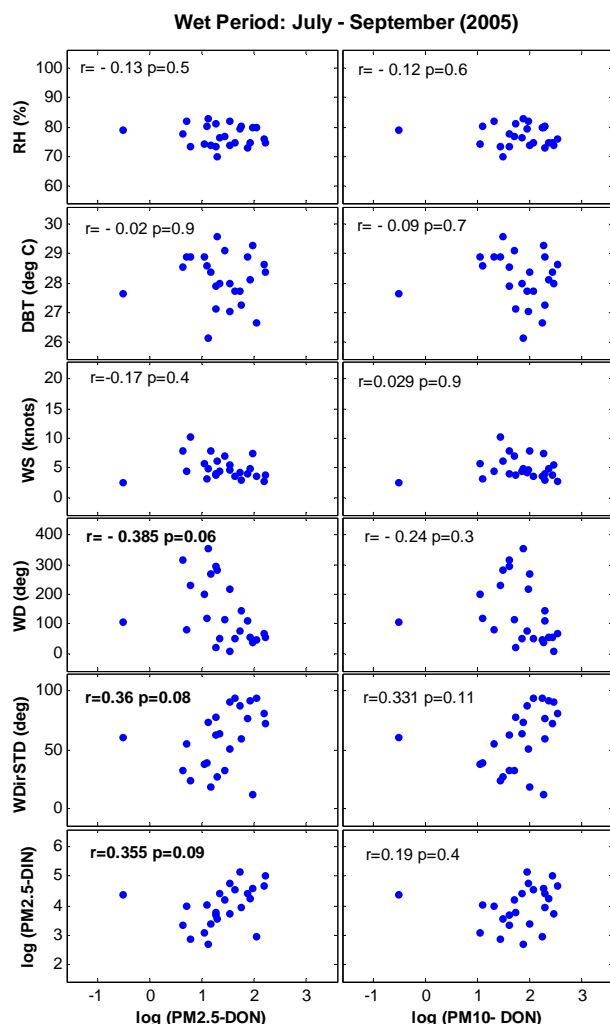


Figure 6. Correlations between meteorological data and DON concentrations during the wet period 2005.

## 5. Multi-Linear Regressions

All regressions were done using the stepwise method with significance levels for variable addition and retention in the model of 0.5 and 0.1 respectively. The method adds progressively to the model those independent variables that make significant contributions to the description of the dependent variable variance according to the confidence level for addition. Once a new variable is added, the significance test is done for the remaining of the variables and those which do not offer significant contribution according to the retention confidence level are discarded until all the non-included variables are tested at the addition level or have been already discarded (SAS Institute Inc 2004).

Outliers were identified and extracted from the data set when they had higher values than critical values for at least two of these variables: studentized residuals, h-ratio, DFFITS and DFBETAS statistics, and second, if their presence decreased the multivariable correlation.

Probability-probability plots were used to check normality of the model residuals. Collinearity diagnostics were also performed on each data set to avoid unstable estimates and high standard errors due to linear dependence between predictor variables. All conditions indices for all variables were under 25. Collinearities are expected to exist when condition indices are higher than 200 (SAS Institute Inc 2004).

The final chosen set of independent variables could explain a large fraction of the variance for the dependent variable. All regression models showed strong multiple correlation coefficients ( $r > 0.6$ ) for the optimal weighted linear combination of the predictor variables included in this study.

Before presenting the regression results, it is necessary to say that even when statistical analyses could reveal very important variable dependencies, the information obtained from them is not conclusive. They do not substitute experimental or modeled data. Tendencies in variable dependences were used here as indicators for possible processes.

The goodness of the fitting for  $\text{DIN-NH}_4^+$  concentrations in the dry and wet periods can be seen on Figure 7. Equations 4 and 5 showed that higher temperatures and lower wind speeds (more stable atmosphere) lead to higher particle contents of  $\text{DIN-NH}_4^+$ . The variation of those variables helped to explain an important fraction of the variance of the ammonium concentrations in both periods. Additional influences of relative humidity and wind direction were caught by the model.

The relationship between temperature and the log-transformed ammonia concentrations was also observed by Raberge et al. 2002. In this study, wind speed also showed a negative correlation with log-transformed concentrations and helped to explain 7% of their variance. Authors claimed that low wind speeds can help to accumulate trace gases close to boundary layer increasing their concentrations in the vicinity of sources. On the other hand, wind direction helped to explain ~15 % of the variance and together, temperature, wind direction and wind speed explained 76% of the variance in the log-transformed ammonium



concentrations (Raberge et al. 2002). Because ammonia is one of the main precursors of ammonium in particles, those conclusions could be extended to ours.

$$\log(DIN - NH_4^+) = 3.72 - 0.07 * WS + 0.019 * RH - \frac{12.88}{DBT} \quad (4)$$

$$R = 0.76 \quad Adj - R = 0.72 \quad n = 28$$

$$\log(DIN - NH_4^+) = 15.01 - 0.2 * WS + 0.003 * WD - \frac{275.4}{DBT} \quad (5)$$

$$R = 0.89 \quad Adj - R = 0.86 \quad n = 20$$

In the case of nitrate particle concentrations, even when Figure 8 shows two distinctive groups of points with lower concentrations during the wet period, both regressions showed a negative effect of the wind direction. Winds blowing from north and south west were associated with decreases in the nitrate particle contents. As was expected according to the binary correlation coefficient, temperature showed a positive effect on DIN-NO<sub>3</sub><sup>-</sup> concentrations. This effect could not be caught for the wet period because DBT variance was very small.

$$\log(DIN - NO_3^-) = 5.7 - 0.002 * WD + 0.002 * WDirSTD - \frac{41.5}{DBT} \quad (6)$$

$$R = 0.89 \quad Adj - R = 0.88 \quad n = 27$$

$$\log(DIN - NO_3^-) = 3.21 - 0.06 * WS - 0.0006 * WD - 0.005 * WDirSTD \quad (7)$$

(7)

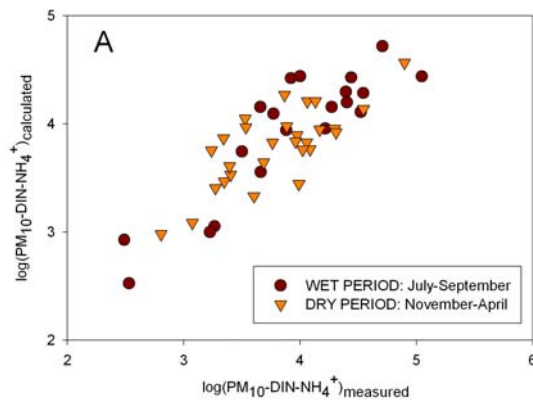


Figure 7. Predicted versus measured DIN-NH<sub>4</sub><sup>+</sup> concentrations in PM<sub>10</sub>.

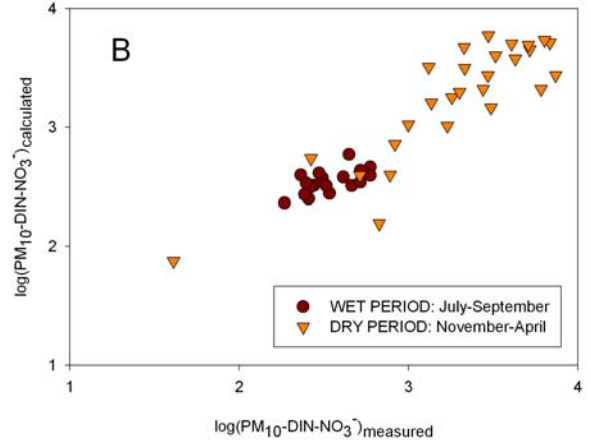


Figure 8. Predicted versus measured DIN-NO<sub>3</sub><sup>-</sup> concentrations in PM<sub>10</sub>.

So far, the effect of the meteorological conditions on the main two inorganic nitrogen species is as expected. However, a more interesting behavior is seen for organic nitrogen in fine particles. The optimal multiple regressions are shown in equations 8 and 9, and the goodness of the fitting in Figure 9.

The variance in DON concentrations for both periods can be well explained using only their DIN contents. As was suggested before, two situations are likely to occur. First, it is possible that DIN and DON are fed into particles by the same processes, or second, they come from similar sources; therefore the higher the DIN the higher the DON.

The DIN behavior in fine particles led to assumption of absorption of gases as the main process involved in particle formation; then DON could come from absorption of organic nitrogen gases in the atmosphere. This is the most likely process that can explain the DMA levels seen on fine particles. On the other hand, it is possible that inorganic nitrogen species and water present in particles could develop a film with a high chemical affinity for organic nitrogen species. With a high fine particle concentration, more surface area for the DON-absorption became available and DON concentration increases.

$$\log(PM_{2.5} - DON) = -1.38 + 0.8 * \log(PM_{2.5} DIN) \quad (8)$$

$$R = 0.89 \quad Adj - R = 0.88 \quad n = 27$$

$$\log(PM_{2.5} - DON) = -0.6 + 0.5 * \log(PM_{2.5} DIN) \quad (9)$$

$R = 0.80 \quad Adj - R = 0.79 \quad n = 21$

For DON in coarse particles the optimal linear combinations of the predictor variables could not catch as much data variance as the other models (Figure 10). It is important to say that after including DON concentration in coarse particles, the good correlation with meteorological conditions for the fine particles was lost. This could indicate that DON sources for coarse particles are different from the ones for fine particles. External effects, not related with the chosen meteorological set, such as vegetation abundance or pollen concentrations could be responsible for this.

$$\log(PM_{10} - DON) = 0.8 + 0.3 * \log(PM_{10} - DIN - NH_4^+) \quad (10)$$

$R = 0.56 \quad Adj - R = 0.54 \quad n = 28$

$$\log(PM_{10} - DON) = 4.02 - 0.002 * WD - 0.8 * \log(PM_{10} - DIN - NO_3^-) \quad (11)$$

$R = 0.65 \quad Adj - R = 0.60 \quad n = 20$

The variables included in the regression of DON concentrations from the wet period do not match those from the dry period, and therefore No additional information can be found from comparing seasonal effects.

## 6. CONCLUSIONS

Results from multi-linear regression of DON and DIN concentrations with meteorological data suggested as expected that gas-to-particle conversions are the main source of nitrogen in particles collected over Tampa Bay. This agrees with results from previous studies, and highlights the need for gas measurements that can offer more information about a possible and very important role of the gas phase on dry and wet deposition fluxes of organic nitrogen. As gases, they can be very well distributed in the atmosphere, can be removed by rainwater scavenging and/or direct mass transfer from the air to the water surface, offering a more global and continuous effect. If they had longer life times they could represent a very important source of  $NO_x$  after degradation by sunlight. In regard to DON, regression models showed a secondary source or formation process for DON in coarse particles, possibly

related to external factors such as vegetation debris or suspended pollen.

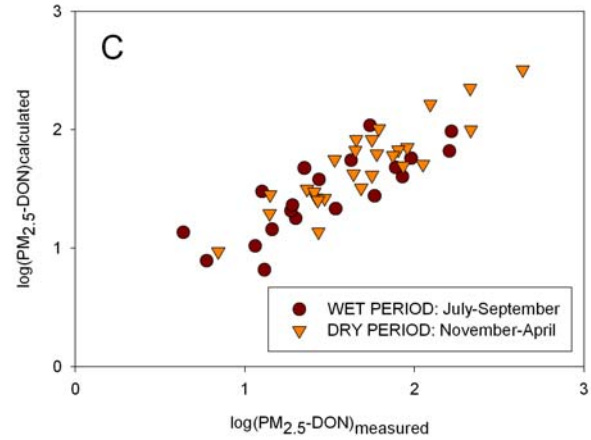


Figure 4. Predicted versus measured DON concentrations in  $PM_{2.5}$ .

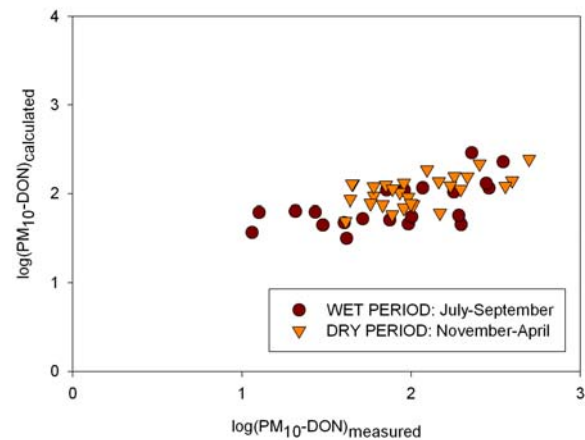


Figure 5. Predicted versus measured DON concentrations in  $PM_{10}$ .

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