

**A FEASIBILITY STUDY OF THE MARGA TOOL AS AN AEROSOL ANALYZER****Rufus Ty White<sup>ac</sup>, Dr. Vernon Morris<sup>abc</sup>****Department of Chemistry<sup>a</sup>, Program in Atmospheric Science<sup>b</sup>, NOAA Center for Atmospheric Science<sup>c</sup>, Howard University, Washington DC 20059**

**Abstract:** An aerosol's chemical composition is one of the key parameters defining its physical behavior, particularly with regard to the properties important for climate impact. To address this issue of gas to aerosol formation there is a need for in-situ measurements of fine aerosol and trace gases. For this study, in-situ compositional data for aerosol and trace gases were collected from June to September 2005. The aerosol microphysical measurements were obtained using a Climet Instruments CI-500. The atmospheric chemical components were measured using an instrument called the Monitoring Instrument for Aerosol and Gas (MARGA). Thermo Environmental analyzers were used to measure sulfur dioxide and nitrogen dioxide levels. In this study, daytime data with high and low RH restraints were analyzed to find consistencies with respect to accepted behavior for gas – aerosol formation. The background levels were found to be constant for both regimes under review, 3.0mg/m<sup>3</sup> for sulphate, 0.3mg/m<sup>3</sup> for nitrate and 1.3mg/m<sup>3</sup> for ammonium. We can see the nearby morning traffic which produces NO<sub>x</sub> that in turn causes an increase in nitrate from 6:00 am to 8:00 am or 9:00 am, this is seen to a much greater extent at the higher RH. We see the build up of sulphate due to photochemical production with ranges 3 – 13 mg/m<sup>3</sup>. Table 2 shows the temperature range for Figure 1 as 24.9-28.5°C and Figure 2 as 22.8-27.4°C and the average of both sets is 26°C. The daily average concentration for SO<sub>4</sub>, NO<sub>3</sub>, and NH<sub>4</sub> is higher for figure 1 for the RH > 90% atmosphere. With the most significant increase occurring in the nitrate concentration. Figure 1a shows a large increase in nitrate concentrations, this was due to the spraying of the field with insecticide and fungicide (table 2). This event was also captured by a large jump in the 0.3-0.5 micron particle count fraction. Figure 3 shows the chemistry of the aerosols for all eight days. There is a pattern in the aerosols composition and the amount SO<sub>2</sub> gas present. There is an anti-correlation between SO<sub>2</sub> and sulphate measured by MARGA. There is an anti-correlation between both particle fractions (0.3-0.5, 0.5-1.0) micron particle fraction and sulphate. Figure 3 shows early morning increase in NO<sub>2</sub> and nitrate concentrations followed by gradual decreases in both High RH and Low RH regimes. Figure 3 shows ammonium concentration increasing through the day. This may be caused by evaporation of NH<sub>3</sub> from dew-wet surfaces at sunrise and the production of NH<sub>4</sub> continues throughout the day due to the NH<sub>3</sub> deliquescence. Table 2 shows the average concentration values for the combined regimes are 6.7, 1.8, and 0.6 µg/m<sup>3</sup> for sulfate, ammonium, and nitrate respectively.

**Introduction:** Aerosols are important in atmospheric processes relating to pollution and climate change. Their hygroscopic behavior significantly influences their size distribution in the ambient atmosphere. The aerosol particle growth as a function of relative humidity (RH) has been measured in many chamber studies, each method with some constraints. Few field instruments measure aerosol chemical composition. To date there are no reliable measurements for nitrate, sulphate, and ammonium, currently these inorganic species are being sampled on filters which do not take into consideration artifacts, temperature, and relative humidity. A field study, from June 25 to September 2 2005, was carried out in Beltsville, Maryland to validate the Monitoring Instrument for Aerosol and Gas (MARGA) developed by ECN- APPLIKON as a viable atmospheric aerosol-monitoring tool. The tool was located in a field surrounded by fruit groves and cornfields. This rural environment allows MARGA to measure atmospheric aerosols in a generally urban area. The main scope of this study is to validate the MARGA's real-time measurements of the inorganic aerosol species nitrate, sulphate, and ammonium simultaneously with their gas precursors and their particle size distribution during summer days with high (RH > 90% figure 1) and low (RH < 50% figure 2) relative humidity. The daytime growths of nitrate and sulfate particles depend on photochemical pathways and RH in the gas phase with subsequent transfer into the particulate phase, which we hope to capture with this study.

**Results:**

<i>12-hour averages (6:00 am-6:00 pm)</i>												
HIGH RH >90%	0.3- 0.5	0.5-1.0	(ug/m3)	(ug/m3)	NO3 (ug/m3)	NO2	SO2	RH	Temp	SR	WD	WS
Day/Date	micron	micron	SO4	SO4	NH4	(ppb)	(ppb)	(%)	(oC)	(W/m2)	(degree)	(m/s)
1. Monday, 6/27/2005	8.3E+05	8.4E+04	2.4	0.3	1.7	7.4	2.6	99.3	24.9	287.5	52.8	1.8
2. Tuesday, 6/28/2005	1.5E+06	2.9E+05	6.2	0.8	1.4	6.3	3.5	99.1	28.5	395.8	146.6	1.5
3. Wednesday, 6/29/2005	1.2E+06	4.9E+05	7.7	0.4	1.9	6.8	4.6	98.2	25.4	292.6	214.0	1.7
4. ***Thursday, 6/30/2005	8.7E+05	9.0E+05	12.2	1.8	2.5	6.5	3.2	91.1	26.0	451.4	81.0	1.0
LOW RH < 50%	0.3- 0.5	0.5-1.0	(ug/m3)	(ug/m3)	NO3 (ug/m3)	NO2	SO2	RH	Temp	SR	WD	WS
Day/Date	micron	micron	SO4	SO4	NH4	(ppb)	(ppb)	(%)	(oC)	(W/m2)	(degree)	(m/s)
5. **Wednesday, 8/17/2005	2.4E+06	5.7E+06	5.6	0.4	1.3	6.3	5.5	47.3	27.1	599.9	197.0	1.5
6. Monday, 8/22/2005	2.1E+06	3.5E+06	6.0	0.2	2.2	7.5	9.8	43.3	27.4	527.5	232.6	2.6
7. Thursday, 8/25/2005	1.7E+06	2.6E+06	4.2	0.4	1.5	10.3	10.9	47.8	22.8	494.8	93.0	1.3
8. Friday, 9/2/2005	2.6E+06	6.4E+06	9.4	0.6	1.8	8.5	7.5	48.6	26.5	471.5	245.4	2.2
*** Field sprayed with Insecticide (Sevin SL) and Fungicide (Captan)												
** Field sprayed with Fungicide (Procure)												

**Table 1**

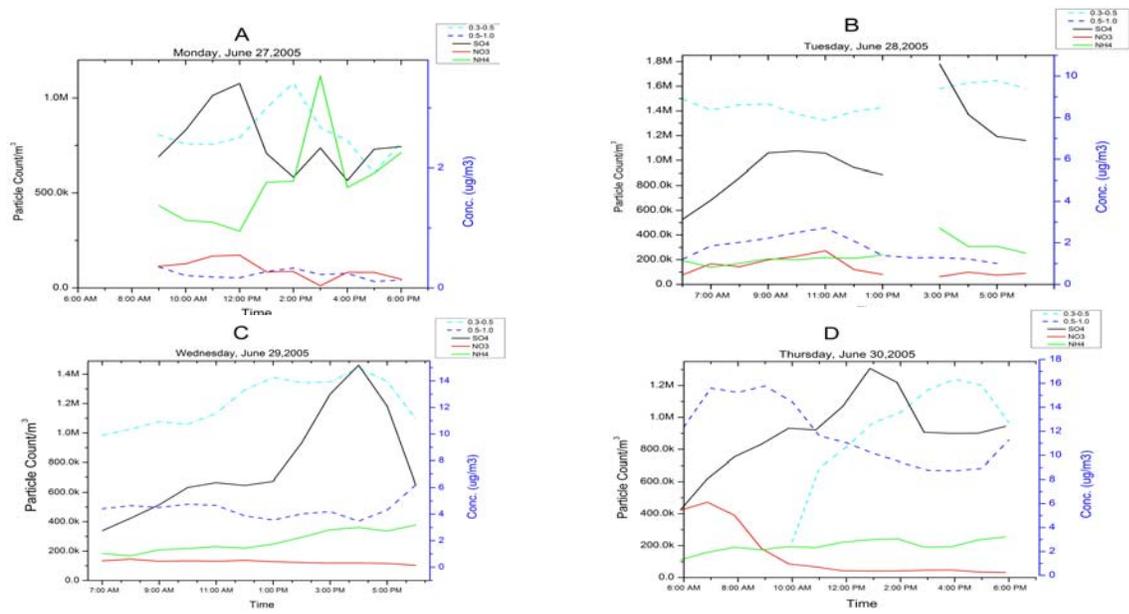


Figure 1

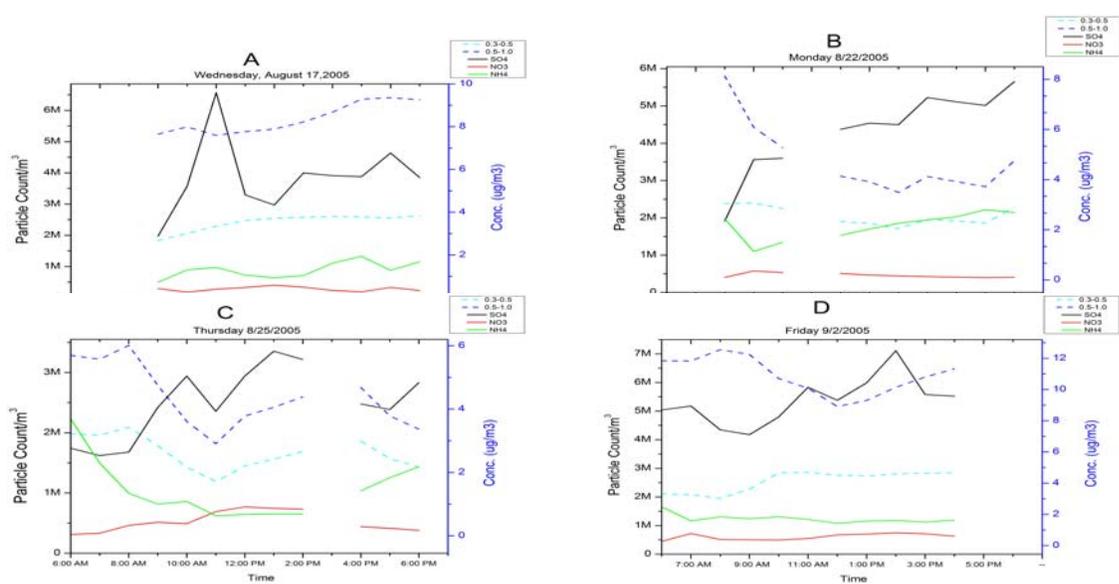
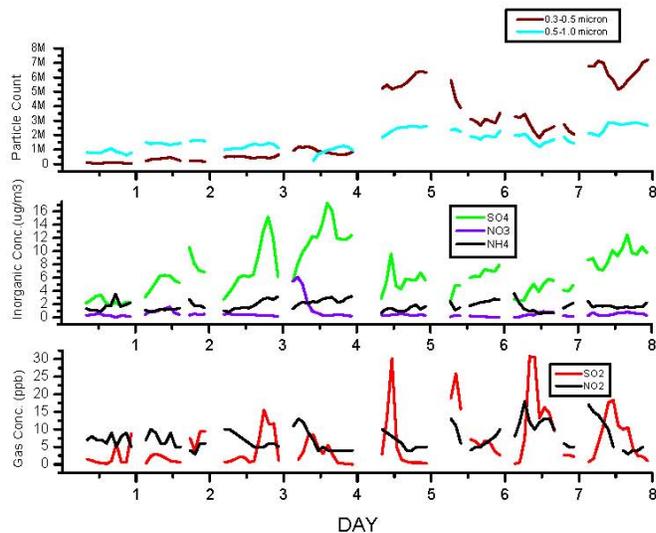


Figure 2



HIGH RH DAYS  
 1. Monday 6/27/2005  
 2. Tuesday 6/28/2005  
 3. Wednesday 6/29/2005  
 4. Thursday 6/30/2005)

LOW RH DAYS  
 5. Wednesday 8/17/2005  
 6. Monday 8/22/2005  
 7. Thursday 8/25/2005  
 8. Friday 9/2/2005

Day=starts at 6:00 am and ends 6:00 pm

**Figure 3**

**Discussion and Conclusion:** MARGA measures the concentration of inorganic species in aerosol and their related gas components in ambient air. The system is comprised of a gas denuder, a steam-jet aerosol collector, and an ion chromatographer (IC). In the instrument, steam condensation is used to grow the aerosol. The droplets formed are collected in a cyclone that drains to wet-chemical analysis (IC) systems. The aerosol components that were studied were NO<sub>3</sub>, SO<sub>4</sub>, and NH<sub>4</sub>. The MARGA detection system is continuously controlled by internal calibration performed by the addition of bromide in the case of the anion chromatograph and lithium for the cation chromatograph. Use of an internal standard tracks changes in retention time and detector response for each sample. Within specified limits, the internal program corrects the concentration results based on these readings. This assures that the correct ion species are identified and that the measured concentrations are accurate.

MARGA measurements were made in concert with a Climet LPC during summer of 2005. Both instruments were stored in a shed at a CASTNET site in Beltsville, MD. Strong daily cycles of NO<sub>2</sub> and SO<sub>2</sub> were found to correlate with traffic patterns and meteorological conditions at the site. SO<sub>2</sub> mixing ratios were very affected by meteorological and photochemical conditions. Figure 2 shows SO<sub>2</sub> increases from day to day this is due to its lifetime and low meteorological activity with a 1.5 m/s average wind speed for this four consecutive days. We used these observations together with current knowledge to assess the accuracy of the MARGA in a pseudo rural environment.

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