INVESTIGATING THE ACIDITY AND LIQUID WATER CONTENT OF ATMOSPHERIC PARTICLES ON THE CHESAPEAKE BAY DURING THE OWLETS-2 CAMPAIGN

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1. INTRODUCTION

This study characterized the impact of the Chesapeake Bay on both aerosol acidity and aerosol liquid water content (LWC). Measurements were taken at the Hart-Miller Island supersite as a part of the Ozone Water-Land Environmental Transition Study (OWLETS-2). Measurements taken at the site included inorganic $PM_{2.5}$ (i.e. fine particle), gas-phase ammonia, and meteorological components. The highly time-resolved measurements were collected from June 6th, 2018 until July 6th, 2018.

The acidity of an atmospheric particle (i.e. pH) is a measure of the hydronium ion activity in the aqueous aerosol phase. Therefore, particle liquid water content has a large impact on particle acidity. Aerosol acidity cannot be measured directly. As a result, proxy methods are used, such as ammonia partitioning or thermodynamic models run with both gas-phase and particulate measurements. Aerosol acidity is an important characteristic of atmospheric particles because it can drive the partitioning of semi-volatile species, determine solubilization of trace metals in the aerosols, and overall impact the health of humans and various ecosystems.

The location on the Chesapeake Bay was important for multiple reasons. One meteorological phenomena of specific interest for this study was the bay-breeze circulations caused by the Chesapeake Bay. In coastal environments, during the day, the land heats very quickly relative to the nearby water, causing the air above the land to heat up as well and then to rise. Because the air has risen, a zone of lower pressure has been formed. The cooler air above the water then flows towards this zone. Alternatively, at night, the land cools off more quickly, causing the same effect but in reverse. As a result, polluted air is often recirculated.

Another important property of the Chesapeake Bay is the fact that it is a source of ammonia. Gas-phase ammonia concentrations from the Chesapeake Bay increase exponentially with temperature (Larsen et al. 2001). As a result, in the summer, when this study was conducted, the Bay was a significant source of gas-phase ammonia. We carried out measurements and thermodynamic modeling to determine how these processes affected aerosol pH and LWC of the particles.

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2. METHODOLOGY

2.1 PILS-IC

The Particle-Into-Liquid-Sampler (PILS) collects particulate matter in the ambient air into high purity water, which can be analyzed by a variety of liquid-based instruments (Orsini et al. 2003).

In this study, the PILS sample was continuously analyzed by a Dual Ion Chromatograph (IC). The samples travel into two different channels of the IC, one to measure the concentration of the cations and the other for the anions. The Metrohm IC used was calibrated for eight inorganic ions (Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) as well as one organic compound ($C_2O_4^{2-}$). The lower limit of detection for all species was determined to be 0.01 μg m^{-3}.

2.2 AiRRmonia

Concentrations of gas-phase ammonia were measured with an AiRRmonia Analyzer (Norman et al. 2009). Briefly, ammonia is sampled into the instrument and is absorbed through a gas-permeable membrane into an acid (i.e. stripping) solution. Next, the pH of this solution increases as sodium hydroxide is added, allowing for transfer of ammonia through a second membrane into a stream of deionized water. The concentration of ammonium is found in this stream through a conductivity measurement, which is proportional to the concentration of ammonia.
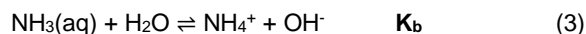
2.3 ISORROPIA II

ISORROPIA II is a thermodynamic equilibrium model for the K^+, Ca^{2+}, Mg^{2+}, NH_4^+, Na^+, SO_4^{2-}, NO_3^-, Cl^-, and H_2O aerosol system (Fountoukis and Nenes 2007). "Forward" mode calculations in the model incorporate measurements of temperature, relative humidity, and concentrations of both atmospheric gases and aerosols. "Reverse" mode calculations in the model incorporate temperature, relative humidity, and concentrations of aerosols. Previous analyses have shown that gas and aerosol measurements are required for accurate outputs for H^+ and pH values (Hennigan et al. 2015). As a result, the model was run in "forward" mode, utilizing both gas-phase ammonia measurements and inorganic fine-particle aerosol concentrations. The model does not output pH directly, but the values of LWC and H^+ concentration outputted allow for the calculation of pH:

$$pH = -\log_{10}(H_{aq}^+) = -\log_{10}(1000 H_{air}^+/W_i + W_o) \qquad (1)$$

where H_{air}^+ and W_i are outputs of ISORROPIA II (Guo et al. 2015). For this study, only the aerosol water associated with inorganic components was considered.

2.4 Phase Partitioning

Another method to estimate aerosol pH is by observing the phase partitioning of semi-volatile compounds, such as NH_3/NH_4^+. Given the system of:

$$NH_3(g) \rightleftharpoons NH_3(aq) \qquad \mathbf{K_H} \qquad (2)$$

$$NH_3(aq) + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad \mathbf{K_b} \qquad (3)$$

the activity of H^+ can be calculated through:

$$\{H^+\} = K_w\{NH_4^+\}/K_hK_bp_{NH_3} \qquad (4)$$

with $\{H^+\}$ being the activity of H^+, K_w being the water dissociation constant, K_h being the Henry's Law constant, K_b being the base dissociation constant, p_{NH_3}, and $\{NH_4^+\}$ being the activity of ammonium in the aqueous aerosol (Hennigan et al. 2015). Note that the LWC outputted from ISORROPIA II is needed for this calculation (converting the mass concentration of NH_4^+ in air to the molar concentration in water).

3. RESULTS AND DISCUSSION

Overall, the median pH predicted by ammonia partitioning (1.73 ± 0.36) was much more acidic than that predicted by ISORROPIA II (2.31 ± 0.42).
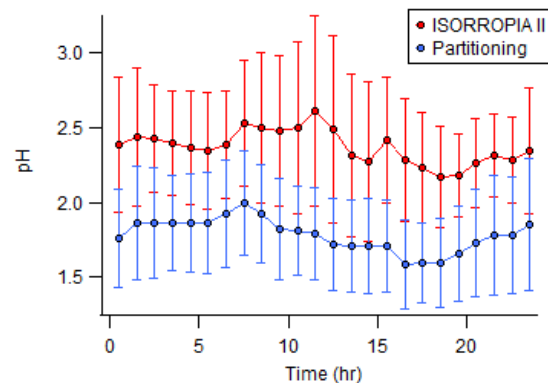

Fig. 1 shows the average diurnal profile of the pH predicted by ISORROPIA II and by ammonia partitioning (Eq. 4). Error bars represent plus/minus the standard deviation. The time given is local time for the study (EDT).

The reason for this is the location on the Chesapeake Bay. The time required for thermodynamic equilibrium to be reached between fine-mode particles and the gas phase is typically less than a few hours (Meng et al. 1995). As a result, with the Chesapeake Bay as a source of ammonia, thermodynamic equilibrium likely had not been reached when measurements were taken. ISORROPIA II predicts the pH of the atmospheric particles assuming that they are in thermodynamic equilibrium. Eventually, when the ammonia from the Bay equilibrates with the aerosols, the pH will become more basic as ammonium concentrations increase. However, when measurements are made, the system has not fully equilibrated, meaning that the ammonia partitioning is a better representation of the pH of the atmospheric particles. The average diurnal profile of the pH predicted by ammonia partitioning is more similar to that of other studies (Battaglia et al. 2017).

4. REFERENCES

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