

**Atmospheric ammonia measurements and implications for
particulate matter formation in Houston, TX**

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Abstract

Simultaneous measurements of atmospheric NH_3 , HNO_3 , soluble gas-phase chloride, and aerosol species were made in Houston, TX, from August 5, 2010 to August 9, 2010. Gaseous NH_3 was measured using a 10.4- μm external cavity quantum cascade laser-based sensor employing conventional photo-acoustic spectroscopy, while gaseous HNO_3 and HCl were sampled using a mist chamber-ion chromatograph (IC) system. Particle chemical composition was determined using a particle-into-liquid-sampler-IC system. There was a large amount of variability in the mixing ratios of NH_3 (3.0 ± 2.5 ppb), HNO_3 (287.4 ± 291.6 ppt), and HCl (221.3 ± 260.7 ppt). Elevated NH_3 levels occurred around mid-day when NH_4^+ (0.5 ± 1.0 $\mu\text{g}/\text{m}^3$) and SO_4^{2-} (4.5 ± 4.3 $\mu\text{g}/\text{m}^3$) also increased considerably, indicating that NH_3 had a strong impact on aerosol particle mass. By contrast, the formation of NH_4NO_3 and NH_4Cl was not observed during the campaign. Power plant plumes were found to be potential contributors to the enhancements in NH_3 under favorable meteorological conditions. Increased particle number concentrations were predicted by the SAM-TOMAS model downwind of a large coal-fired power plant when NH_3 emissions based on these measurements were included. This study shows that NH_3 mixing ratios in the polluted Houston atmosphere occasionally exceeded previous modeling predictions, suggesting the influence of both local and regional sources while also highlighting the potential importance of NH_3 with respect to particle number concentration.

Key words: ammonia, particulate matter, gas-particle partitioning, aerosol nucleation.

1 Introduction

2 Ammonia (NH_3) is widely present in the atmosphere due to many anthropogenic and
3 natural sources (1), usually at trace concentration levels ranging from parts per trillion
4 (ppt) to parts per billion (ppb). However, agriculture (e.g., fertilizer application and
5 animal husbandry) (2, 3) and industrial and motor vehicle (e.g., chemical production
6 and traffic emission) (4, 5) activities contribute to significant increases in local and/or
7 regional NH_3 levels. In addition, National Emissions Inventory air pollutant
8 emissions trends data prepared by the United States Environmental Protection Agency
9 (U.S. EPA) indicate that annual NH_3 emissions from the source category of electric
10 utilities have risen continuously since 2005. Gaseous NH_3 can increase particulate
11 matter (PM) mass concentrations through the formation of ammonium salts such as
12 ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$), ammonium nitrate (NH_4NO_3), and ammonium
13 chloride (NH_4Cl) via chemical reactions with sulfuric, nitric, and hydrochloric acids,
14 respectively. Experiments also reveal that NH_3 plays a vital role in aerosol
15 nucleation events (6-8).

16 The resultant PM affects the Earth's radiation budget through direct and/or indirect
17 effects and modifies the properties of clouds by serving as cloud condensation and/or
18 ice nuclei (9). Epidemiological studies also have demonstrated a strong correlation
19 between human exposure to PM and increased rates of respiratory and cardiovascular
20 illness and other adverse human health effects (10, 11). Despite these implications
21 for ammonia's negative impacts on air quality, NH_3 currently is not regulated under
22 the National Ambient Air Quality Standards by the U.S. EPA. As a result, there are

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4 1 substantial uncertainties in spatial and temporal variations of NH_3 due to the lack of
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6 2 ground-based observations.

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8 3 Conventional NH_3 studies primarily have focused on the measurements near source
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10 4 areas (e.g., farms) (12, 13) using passive samplers (e.g., annular diffusion denuders)
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12 5 with off-line analysis (e.g., ion chromatography (IC)) (14, 15). Newly developed
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14 6 NH_3 instruments using laser spectroscopy and chemical ionization mass spectrometry
15
16 7 have improved time resolution and detection limits and minimized human-induced
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18 8 errors (16, 17). Meanwhile, relatively little previous work has investigated the effect
19
20 9 of gas-particle partitioning of NH_3 and the interaction between NH_3 and acidic
21
22 10 gaseous and particulate species due to a paucity of simultaneous datasets. In
23
24 11 addition, information about NH_3 levels for the industrial and urban area of Greater
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26 12 Houston is still scarce. Nowak et al. (18) conducted a 14-day aircraft measurement
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28 13 campaign including atmospheric NH_3 along the Houston Ship Channel (HSC) area
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30 14 during the second Texas Air Quality Study (TexAQS II). Gong et al. (19)
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32 15 characterized the seasonal and diurnal patterns of gaseous NH_3 levels in Houston.
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34 16 According to a photochemical model, the estimated NH_3 mixing ratios for the
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36 17 Houston area are in the range of 1 to 15 ppb (20). In order to examine the effects of
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38 18 NH_3 on air quality in Houston, measurements of gas-phase NH_3 , nitric acid (HNO_3),
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40 19 soluble chloride (assumed to be hydrochloric acid (HCl)), and aerosol species were
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42 20 performed during the summer of 2010 by simultaneous on-line gas- and particle-phase
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44 21 instrumentation.

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1 **Materials and Methods**

2 In this study, the simultaneous measurements of trace gases and particle chemical
3 composition were carried out from August 5, 2010 to August 9, 2010. All
4 instruments were deployed in a trailer atop an 18-story (~65 m above ground level)
5 building (North Moody Tower) located on the University of Houston (UH) main
6 campus, which is influenced by many local and regional emission sources such as
7 highways, airports, and industrial facilities. Detailed information about this
8 sampling site can be found in Lefer and Rappenglück (21). Meteorological
9 parameters (e.g., temperature and relative humidity) as well as mixing ratios of some
10 important air pollutants (e.g., carbon monoxide (CO)) are measured regularly by the
11 UH research group at this location (22, 23). All data were averaged into 1-hr
12 intervals for temporal consistency.

13

14 **Gaseous species measurements**

15 Gas-phase NH_3 was measured using a 10.4- μm external cavity quantum cascade
16 laser-based sensor employing conventional photo-acoustic spectroscopy as described
17 in Gong et al. (19). This state-of-the-art optical technique achieves a sub-ppb
18 detection limit with a response time of seconds and an accuracy of ~6%. Gas-phase
19 HNO_3 and HCl were measured using a mist chamber together with IC (Dionex, Model
20 CD20-1), where the minimum detection limits of ppt levels were reached for a
21 temporal resolution of 10 minutes with an uncertainty of $\pm 10\%$ (23, 24).

22

1 Aerosol species measurements

2 Particle chemical composition was measured using a particle-into-liquid-sampler
3 (PILS) (BMI, Model 4002) coupled directly to two IC systems (Dionex, Model 1600)
4 (25, 26). Mass concentrations ($\mu\text{g}/\text{m}^3$) of water soluble inorganic components
5 including ammonium (NH_4^+), sodium (Na^+), potassium (K^+), calcium (Ca^{2+}),
6 magnesium (Mg^{2+}), sulfate (SO_4^{2-}), nitrate (NO_3^-), nitrite (NO_2^-) and chloride (Cl^-)
7 in fine particle aerosols ($D_p < 1 \mu\text{m}$) were determined at 16-min intervals.

8

9 Results and Discussion

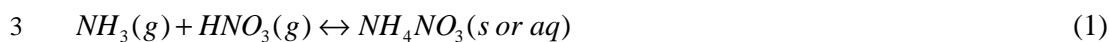
10 Effect of NH_3 on Particle Mass Concentrations

11 Figure 1 presents a time series of hourly-averaged mixing ratios (\pm one standard
12 deviation) of gaseous NH_3 (3.0 ± 2.5 ppb), HNO_3 (287.4 ± 291.6 ppt), HCl ($221.3 \pm$
13 260.7 ppt) and CO (109.8 ± 22.4 ppb) and concentrations of particulate NH_4^+ ($0.5 \pm$
14 $1.0 \mu\text{g}/\text{m}^3$), SO_4^{2-} ($4.5 \pm 4.3 \mu\text{g}/\text{m}^3$), NO_3^- ($0.3 \pm 0.2 \mu\text{g}/\text{m}^3$) and Cl^- ($0.2 \pm 0.1 \mu\text{g}/\text{m}^3$)
15 along with meteorological parameters. The NH_3 mixing ratios are a subset of the
16 data considered by Gong et al. (19). NH_3 levels were elevated around mid-day,
17 when NH_4^+ and SO_4^{2-} also dramatically increased compared to other time periods of
18 the measurements. This suggests that NH_3 played an important role in PM formation
19 and that the gas-particle conversion was highly efficient when NH_3 was available,
20 though SO_4^{2-} goes to the aerosol phase regardless of NH_3 level. However, NO_3^- and
21 Cl^- concentrations did not change significantly throughout the campaign.

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4 1 During these peaks, the wind mainly blew from the southwest in the direction of the
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6 2 second largest coal-fired power plant (W. A. Parish) in the U.S. (also verified by
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9 3 Hybrid Single-Particle Lagrangian Integrated Trajectory modeling (27)). The
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11 4 average wind speed was about 10 miles per hour when these mid-day spikes occurred,
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14 5 leading to an inference that the electricity generating station, which is approximately
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16 6 23 miles (37 km) away from the sampling site, may be a source of NH₃ in Houston
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19 7 during this period. The selective catalytic reduction (SCR) technique was installed
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21 8 to control nitrogen oxides (NO_x) emissions from Parish after 2000 (28). Interestingly,
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24 9 no NH₃ spikes in Parish plumes were reported by Nowak et al. (18). Auxiliary data
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26 10 collected atop the Moody Tower were used to assist in NH₃ source identification.
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29 11 For instance, primary pollutants such as CO emitted from automobile tailpipes are
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31 12 usually used as indicators of vehicular emissions. Since the introduction of
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34 13 three-way catalytic converters, motor vehicles have contributed to elevated NH₃ levels
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36 14 in urban areas (29, 30) when NO_x is over-reduced inside the converters (31, 32).
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39 15 Nevertheless, no enhancements in CO were coincident with enhanced NH₃ around
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41 16 mid-day, indicating that motor vehicles are less likely to cause elevated NH₃ in
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44 17 Houston during this period.

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46 18 During the five days of measurements, there were no concurrent decreases in HNO₃
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49 19 and HCl nor increases in NO₃⁻ and Cl⁻ when NH₃ levels were elevated around mid-day,
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51 20 indicating that NH₄NO₃ and NH₄Cl were not formed. This speculation is verified by
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54 21 the very low saturation ratios (<< 1) illustrated in Figure 2. The saturation ratio is
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56 22 the partial pressure product ($P_{NH_3}P_{HNO_3}$ or $P_{NH_3}P_{HCl}$) divided by the dissociation
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1 constant ($K_{NH_4NO_3}$ or K_{NH_4Cl}) that can be calculated using empirical equations (33, 34)
2 based on the reversible formation of NH_4NO_3 and NH_4Cl (eqs 1 and 2).



5 Particulate NH_4NO_3 and NH_4Cl condense when the saturation ratio is larger than one,
6 and they evaporate when the saturation ratio is smaller than one. This is in contrast
7 to the study of Nowak et al. (18) during TexAQS II who observed NH_4NO_3 formation
8 in HSC plumes with elevated NH_3 levels ranging from 5 to 80 ppb, likely due to the
9 shift in the thermodynamic equilibrium towards the aerosol phase caused by very high
10 NH_3 mixing ratios. Because the time scales to achieve thermodynamic equilibrium
11 for NH_4NO_3 and NH_4Cl usually are on the order of minutes under ambient conditions
12 (35, 36), the time since emission likely can be eliminated as the reason for the lack of
13 NH_4NO_3 and NH_4Cl formation in the present work. However, relatively high
14 temperatures (30.1 ± 2.3 °C) likely do inhibit the formation of NH_4NO_3 and NH_4Cl
15 because volatilization increases with temperature; by contrast, sulfate is considered
16 essentially non-volatile (37). The Aerosol Inorganics Model also was employed, and
17 it yielded similar results for the calculation of thermodynamic equilibrium/gas-particle
18 partitioning using measurement data from this study (38).

19 A regression between measured molar concentrations of cations and anions yields a
20 strongly linear relationship (Figure 3, $R^2 = 0.96$; $p < 0.0001$; slope = 1.53), suggesting
21 that SO_4^{2-} , NO_3^- and Cl^- (The rest of the anions were minor.) were largely associated
22 with NH_4^+ (The rest of the cations other than H^+ were minor.) and that ambient

1 aerosols were likely acidic as a result of incomplete neutralization. However, the
2 average value of the molar concentration ratio of gaseous NH_3 to total NH_3 (the sum
3 of NH_3 and NH_4^+), also known as the gas fraction ($\sigma = 0.86 \pm 0.17$), shows that NH_3
4 remained predominantly in the gas phase rather than the aerosol phase, as shown in
5 Figure 4, although sampled aerosols were ammonium-poor.

6 It is unlikely that aerosols are high in acid content when gaseous NH_3 is prevalent in
7 the atmosphere. There may be cations present in aerosols not measured with the
8 PILS-IC. One, though not the only possible, hypothesis is that amines contribute to
9 the cationic composition of PM. Amines widely exist in the atmosphere from a
10 variety of sources, and they are subject to physical and chemical processes such as
11 gas-particle partitioning (39, 40). It has been reported that aminium can displace
12 NH_4^+ in ammonium salts (41, 42). In addition, the availability of amines enhances
13 sulfuric acid-water ($\text{H}_2\text{SO}_4\text{-H}_2\text{O}$) nucleation (43, 44), which may partially account for
14 relatively high SO_4^{2-} levels (up to $33.7 \mu\text{g}/\text{m}^3$) observed during the measurements. If
15 we assume that ambient aerosols are neutral and attribute all missing cations to
16 aminium, the estimated required mixing ratio of gaseous amines is approximately 55
17 ppb following the example in Ge et al. (40). While this is a very large value,
18 observed atmospheric amine mixing ratios range from ppt to hundreds of ppb levels;
19 even parts per million (ppm) levels were found in power plant regions (45). Some
20 existing plants in the U.S. use amine-based solvent to capture post-combustion carbon
21 dioxide (46). However, to our knowledge, Parish currently uses only NH_3 tank
22 farms instead of amine technology. Given the strong linear relationship between

1 measured anions and cations, the ammonium concentrations would be correlated
2 strongly with NH_4^+ if present.

3 It is also noted that the mean gas fractions for HNO_3 ($\sigma = 0.71 \pm 0.14$) and HCl ($\sigma =$
4 0.72 ± 0.24) were larger than 0.5, as shown in Figure 4, indicating they existed mainly
5 in the gas phase. This observation may be attributed to the warm conditions during
6 the measurements, which favor volatilization of NH_4NO_3 and NH_4Cl . Figure 5
7 displays the molar concentration ratio of NH_3 to the sum of HNO_3 and HCl ($11.3 \pm$
8 9.5) over the entire course of sampling, indicating that NH_3 was much more abundant
9 than HNO_3 and HCl .

10

11 **Effect of NH_3 on Particle Number Concentrations**

12 Aerosol nucleation and growth in coal-fired power plant plumes can greatly contribute
13 to particle number concentrations near source regions. Stevens et al. (47)
14 incorporated the TOMAS aerosol microphysics module (48, 49) into the SAM
15 Large-Eddy Simulation/Cloud Resolving model (50) (SAM-TOMAS) and simulated
16 aerosol nucleation and growth in the Parish power-plant plume. In the present work
17 we also used this model to investigate how NH_3 emissions from power plants may
18 affect the nucleation and growth of particles in the plume. The model simulates the
19 aerosol size distribution using 15 size bins segregated by dry mass per particle
20 covering a size range from 3 nm to 10 μm and microphysical processes including
21 coagulation, H_2SO_4 condensation, and nucleation (47). Modeled H_2SO_4 vapor
22 formation depends on SO_2 and OH concentrations, and the OH concentrations in turn

1 depend on the amount of sunlight and the NO_x concentrations.

2 NH_3 is considered to be a potentially important participant in aerosol nucleation and

3 formation. In order to evaluate the effects of NH_3 on particle number concentration

4 along the trajectory of power plant plumes, we hypothesize that elevated NH_3 levels

5 originated from NH_3 slips at Parish, and we add NH_3 emissions from the plant to the

6 SAM-TOMAS simulations. Two ternary ($\text{H}_2\text{SO}_4\text{-H}_2\text{O-NH}_3$) nucleation schemes,

7 Merikanto et al. (51) and Napari et al. (52) (which is scaled by a factor of 10^{-5} to

8 better agree with observations (53)), are tested in SAM-TOMAS. Figure 6 shows

9 twelve simulations from SAM-TOMAS under various environmental conditions. It

10 shows the number of new particles in the plume normalized by the SO_2 emitted as a

11 function of the distance downwind from the plant. Both schemes were run with 900

12 ppt and 0 ppt NH_3 background mixing ratios. In addition, three different NH_3

13 emission scenarios (high: 0.012 kg/s; medium: 0.007 kg/s; low: 0.0012 kg/s) were

14 employed and tested based on the calculated range of NH_3 emission factors (82,500 to

15 825,000 lb/yr) from Parish based on vendor-estimated slip values (1 to 10 ppm) (54).

16 In all simulations, the number of new particles reaches a maximum near 10 km

17 downwind; beyond this point, concentrations decrease because coagulation rates

18 exceed nucleation rates. It can be seen that NH_3 emissions are very important for

19 new particle formation, especially in the simulations in which background NH_3

20 mixing ratios are low (i.e., the green and red lines show a large variation in nucleation

21 between simulations with different NH_3 emission rates). When background NH_3

22 mixing ratios were larger, the simulated effect of NH_3 emissions on nucleation was

1 more saturated and the predicted differences between NH₃ emission scenarios were
2 smaller. Specifically, the fractional increases in particle concentrations between the
3 low and high NH₃ emission simulations at 50 km downwind were 1.1 for Merikanto's
4 nucleation scheme with 900 ppt NH₃ background mixing ratio, 2.0 for Merikanto's
5 nucleation scheme with 0 ppt NH₃ background mixing ratio, 1.2 for Napari's
6 nucleation scheme with 900 ppt NH₃ background mixing ratio, and 2.5 for Napari's
7 nucleation scheme with 0 ppt NH₃ background mixing ratio, respectively. Larger
8 NH₃ emissions accelerate aerosol nucleation in the simulations, as the system exhibits
9 a high sensitivity to the amount of NH₃ slip, which emphasizes the significance of
10 future NH₃ measurements in areas near power plants that utilize SCR. In addition,
11 although Houston is currently in compliance with the mass-based PM_{2.5} standards,
12 efforts to characterize particle number concentration and size distribution
13 synchronously with measurements of gaseous and particulate species are needed to
14 better understand NH₃ impacts on both particle mass and number concentrations.

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1
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3 **List of figures**
4

5 **Figure 1.** Hourly-averaged mixing ratios of NH₃, HNO₃, HCl and CO and
6 concentrations of NH₄⁺, SO₄²⁻, NO₃⁻ and Cl⁻ as well as meteorological parameters
7 during the measurements.
8

9
10 **Figure 2.** Time series of the saturation ratios of NH₄NO₃ and NH₄Cl.
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13
$$S = P_{NH_3} P_{HNO_3} / K_{NH_4NO_3} \text{ or } P_{NH_3} P_{HCl} / K_{NH_4Cl}$$

14
15

16 where S is saturation ratio; P is partial pressure; K is dissociation constant.
17

18 $K = \exp[84.6 - 24220/T - 6.1 \ln(T/298)]$ for NH₄NO₃
19

20 $K = \exp[2.2358 \ln T - 2.13204 * 10^4 T^{-1} + 65.437516 - 8.167 * 10^{-3} T + 4.64383 * 10^{-7} T^2$
21
22

23 $- 1.10475 * 10^{-10} T^3]$ for NH₄Cl
24

25 where T is temperature in Kelvin.
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28 **Figure 3.** Linear relationship between measured cations and anions.
29

30 **Figure 4.** Time series of gas fractions for NH₃, HNO₃ and HCl.
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33 **Figure 5.** Time series of the ratio of NH₃ to the sum of HNO₃ and HCl.
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35 **Figure 6.** The number of particles formed by nucleation in the Parish plume per SO₂
36 mass emitted as a function of the distance downwind from the Parish plant.
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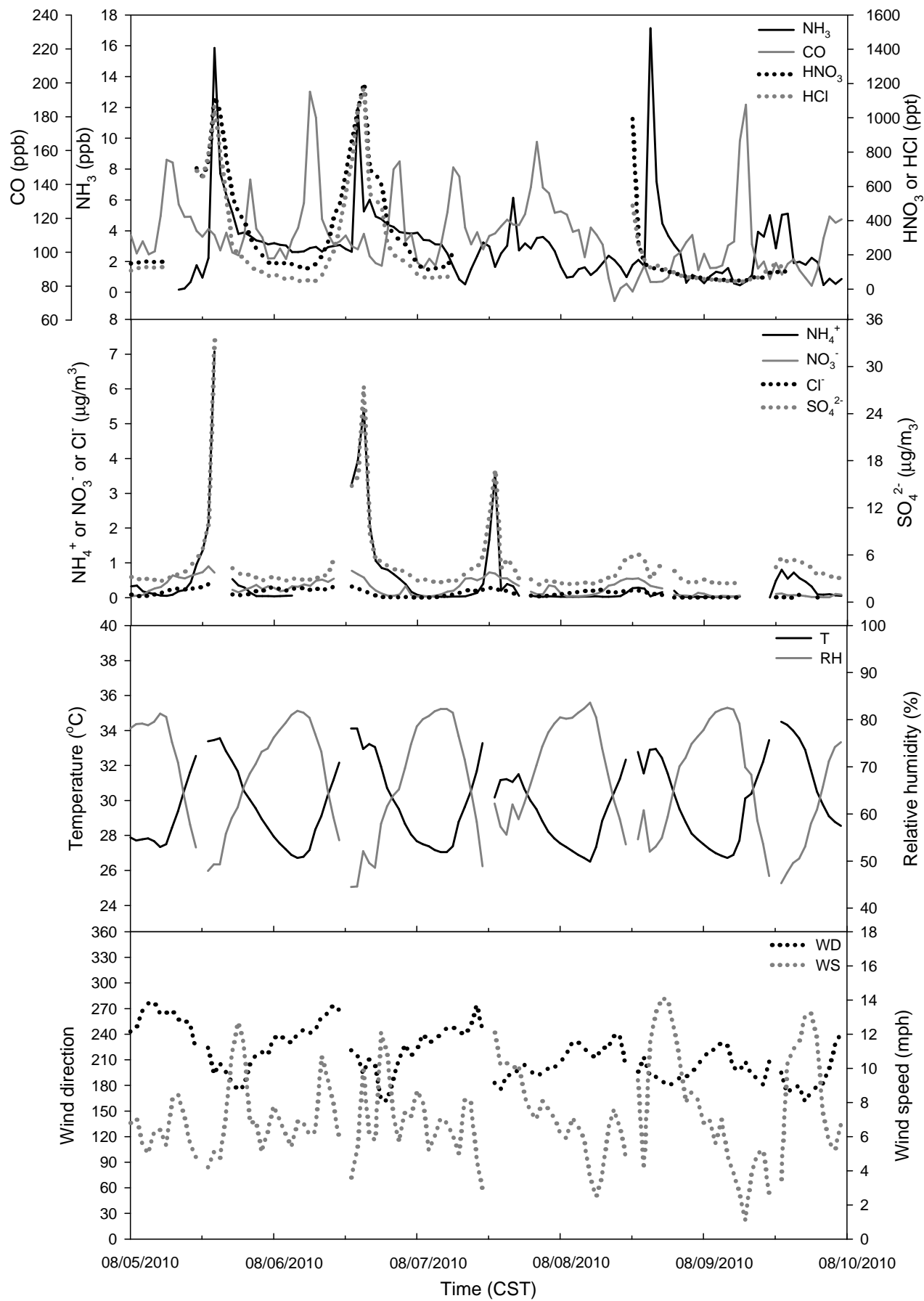


Figure 1.

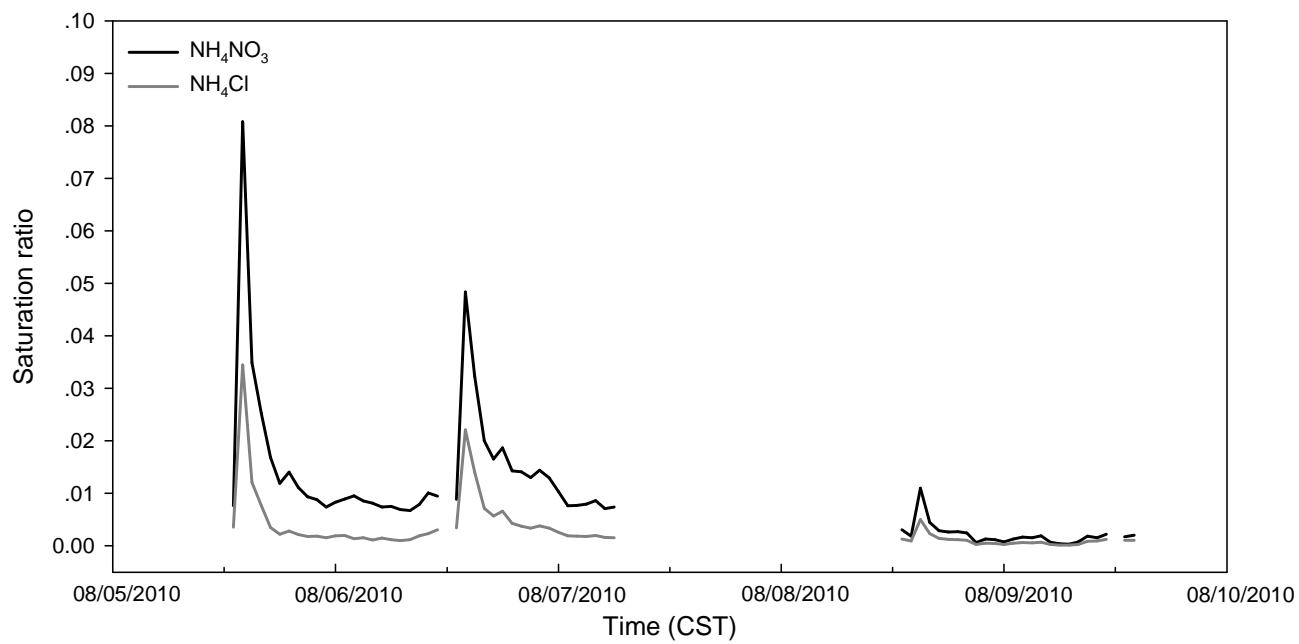


Figure 2.

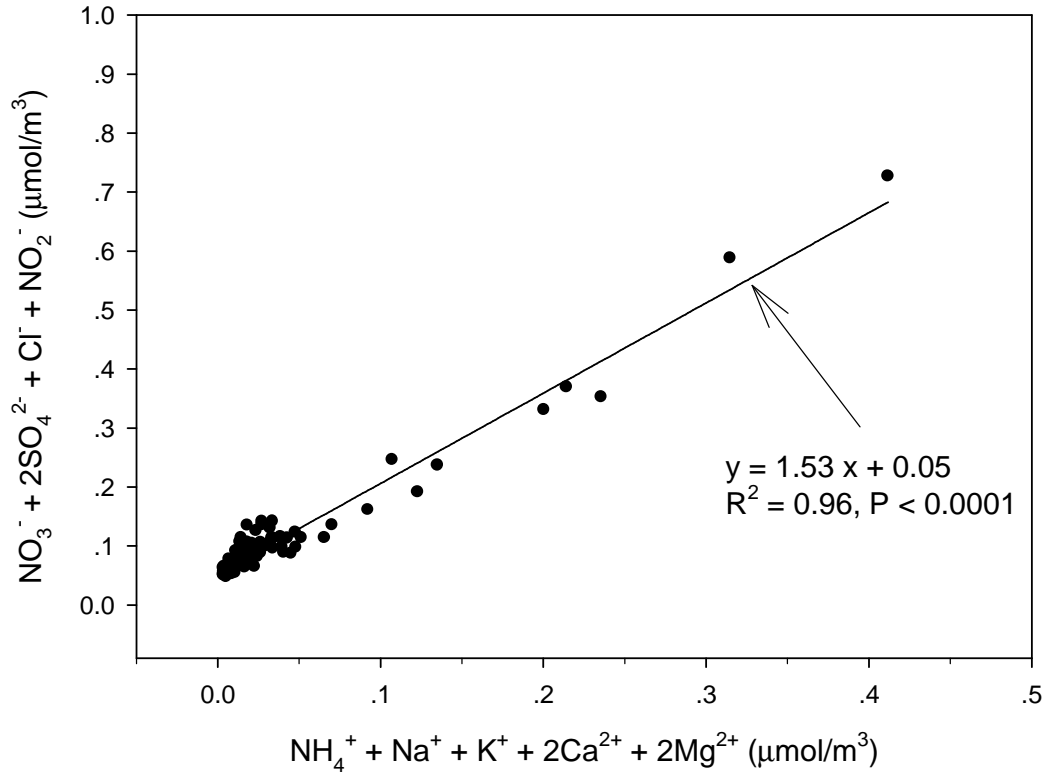


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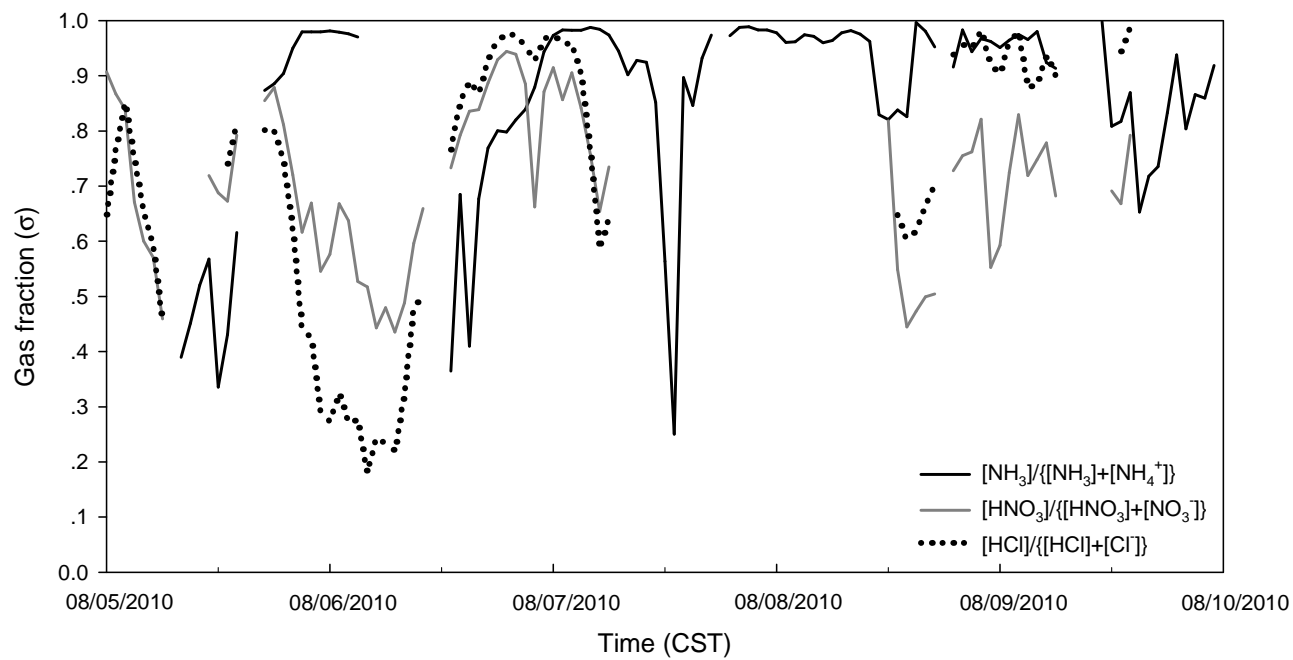


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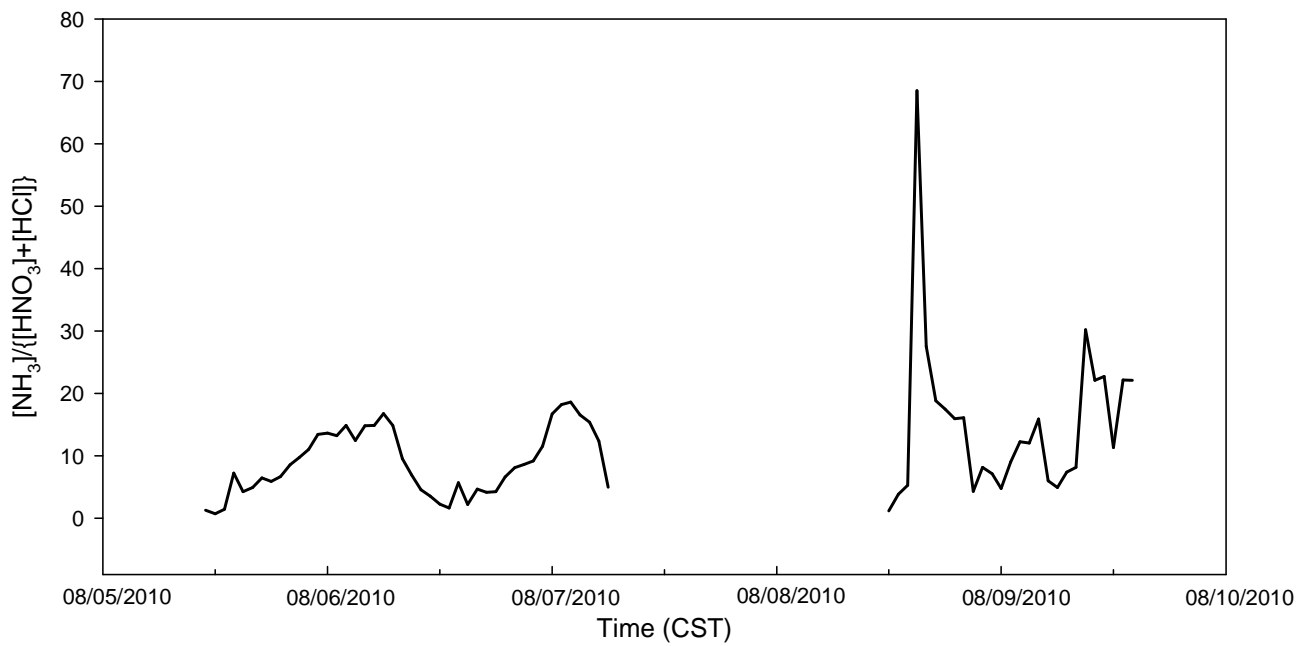


Figure 5.

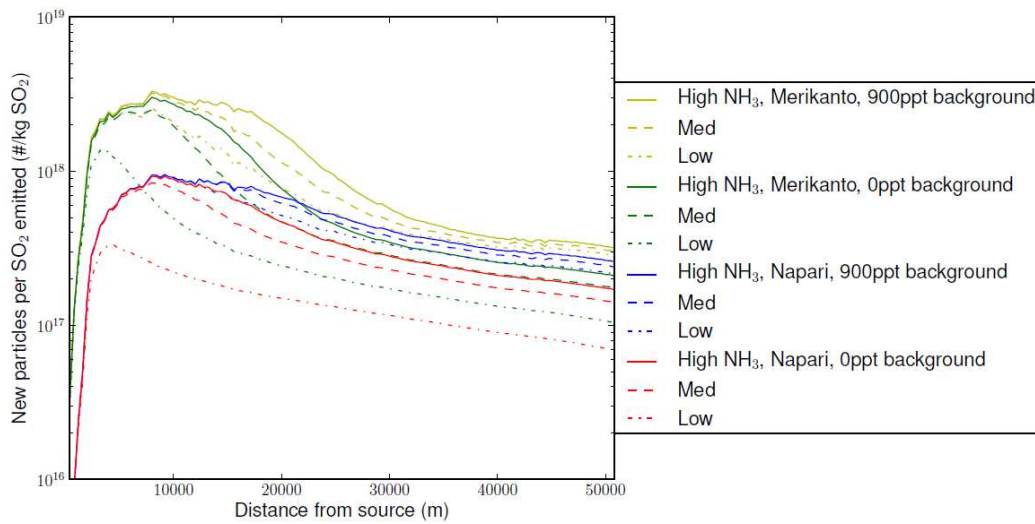


Figure 6.

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SYNOPSIS TOC



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