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Authors

Fischer, Marc L.
Littlejohn, David

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1 **Ammonia at Blodgett Forest, Sierra Nevada, USA**

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3 Marc L. Fischer and David Littlejohn

4

5 Environmental Energy Technologies Division, E.O. Lawrence Berkeley National Laboratory,

6 1 Cyclotron Rd., Berkeley CA, 94720, USA

7

8 Corresponding author address:

9

10 Marc L. Fischer, Staff Scientist

11 Atmospheric Sciences Department

12 Mail Stop 90K-125

13 E.O. Lawrence Berkeley National Laboratory

14 1 Cyclotron Rd.

15 Berkeley, CA 94720-8108

16

17 Phone: 510-486-5539

18 email: mlfischer@lbl.gov

19 **Abstract**

20 Ammonia is a reactive trace gas that is emitted in large quantities by animal agriculture and other
21 sources in California, which subsequently forms aerosol particulate matter, potentially affecting
22 visibility, climate, and human health. We performed initial measurements of NH_3 at the Blodgett
23 Forest Research Station (BFRS) during a two week study in June, 2006. The site is used for
24 ongoing air quality research and is a relatively low-background site in the foothills of the Sierra
25 Nevada. Measured NH_3 mixing ratios were quite low (< 1 to ~ 2 ppb), contrasting with typical
26 conditions in many parts of the Central Valley. Eddy covariance measurements showed NH_3
27 fluxes that scaled with measured NH_3 mixing ratio and calculated aerodynamic deposition
28 velocity, suggesting dry deposition is a significant loss mechanism for atmospheric NH_3 at
29 BFRS. A simple model of NH_3 transport to the site supports the hypothesis that NH_3 is
30 transported from the Valley to BFRS, but deposits on vegetation during the summer. Further
31 work is necessary to determine whether the results obtained in this study can be generalized to
32 other seasons.

33 1. Introduction

34

35 In California and the nation, many areas are out of compliance with federal particulate matter
36 standards designed to protect human health (NRC 1998; NRC 2000). Nationally, Congress has
37 set a goal to remediate current and prevent future impairment of visibility in over 150 federally
38 designated Class 1 Federal (Malm et al. 2000) designated sites. Ammonia (NH_3) is the primary
39 gas to form aerosols in combination with acidic species (e.g., SO_x , NO_x) that are produced in
40 combustion processes from energy related activities. While mixing ratios of combustion derived
41 species are regulated, NH_3 is not. If ammonia limits aerosol concentrations, then controls on
42 emissions of NO_x and perhaps SO_x may not be effective in controlling aerosol concentrations,
43 visibility, or protecting human health.

44

45 The magnitude of NH_3 fluxes are expected to vary enormously over space. NH_3 is emitted from
46 strong point sources (e.g. animal agriculture), medium strength distributed sources (e.g.,
47 fertilized fields and automobile catalytic converters), and exchanged with spatially vast areas of
48 soil and vegetation (Potter et al. 2001; Kirchstetter et al. 2002; Battye et al. 2003). Ammonia is
49 of particular interest in California because it is emitted in large amounts from agricultural
50 sources in the Central Valley, leading to high (20-40 ppb) surface layer NH_3 mixing ratios
51 (Fischer et al. 2003; Lunden et al. 2003; Chow et al. 2006). For example, recent work suggest
52 that San Joaquin Valley area emissions might range from 8 to 42 $\text{g N ha}^{-1} \text{ day}^{-1}$ (11 to 50 ng NH_3
53 $\text{m}^{-2} \text{ s}^{-1}$) in winter and summer respectively, with approximately 78 % of the summertime
54 emissions derived from animal agriculture (Battye et al. 2003).

55

56 While most NH_3 measurements have been made in urban areas in California, some
57 measurements have been made in rural settings. Airborne measurements in the afternoon mixed
58 layer showed that ammonium compounds (i.e., $\text{NH}_3 + \text{NH}_4^+$) were the dominant component of
59 the N budget with variable NH_3 concentrations corresponding to mixing ratios of 10 ± 7 and 2.5
60 ± 0.5 ppb in boundary layer above the foothills of the Sierra in the boundary layer above Lake
61 Tahoe respectively (Zhang et al. 2002). In contrast, a ground-based study at Lake Tahoe
62 measured significantly lower concentrations corresponding to approximate mixing ratios

63 between 0.6 to 1.5 ppb and mean summer deposition rates between 3 to 11 ng N m⁻² s⁻¹ (Tarnay
64 et al. 2001). The previous work raises the question of whether there are vertical gradients in NH₃
65 caused by dry deposition or whether the differences in NH₃ at the surface and aloft are due to
66 different measurement times.

67
68 Here we describe a short term study of the NH₃ mixing ratios and NH₃ fluxes at a rural site in the
69 foothills of the Sierra Nevada.

70

71 2. Methods

72 The methods section includes a description of the measurement site, the fast response NH₃
73 instrument, the methods used for data reduction, a filter sampling system used to provide
74 comparative NH₃ measurements, a method used to calculate the aerodynamic deposition velocity
75 expected under different meteorological conditions, and a predictive model for NH₃ mixing
76 ratios at the measurement site.

77 2.1 Measurement Site

78 UC Berkeley Blodgett Forest Research Station

79 We measured NH₃ mixing ratios and fluxes near the University of California's Sierra Nevada the
80 Blodgett Forest Research Station (BFRS), located west of the Sacramento region as shown in
81 Figure 1. The BFRS site is an attractive site for this work because it is representative of large
82 areas of forested land with acidic soils in the mountainous Western US and has been the site of
83 ongoing air quality measurements (Goldstein et al. 2000; Dillon et al. 2002; Kurpius et al. 2002;
84 Farmer et al. 2006). Although recent work at BFRS has studied mixing ratios and fluxes of
85 several reactive nitrogen species, NH₃ has not been measured previously.

86 The BFRS tower is located at 38.88°N, 120.62°W, at an elevation of 1315 m in a re-
87 growing ponderosa pine plantation. Tree heights ranged from approximately 8-10 m. Terrain is
88 gently sloping downward from east to west. Power to the site is provided by a diesel generator
89 located approximately 130 m due north of the tower site. The predominant winds are upslope
90 from the southwest during the day and downslope from the northeast during the night.

91 2.2 NH₃ Instrument

92
93 Ammonia was measured using a sensitive fast-response quantum-cascade laser (QCL)
94 spectrometer operating at a frequency of 965 cm^{-1} (Aerodyne Research Inc (ARI), similar to that
95 used for eddy covariance flux measurements of NO_2 (Zahniser 2003; Horii et al. 2004). The
96 precision of the NH_3 instrument is normally 0.3 ppb (1 sigma) for data collected at a frequency
97 of 10 Hz. The instrument provided highly automated control of high frequency data collection,
98 zero adjustments, and zero and span checks as described below using a dedicated software
99 package (TDLWintel).

100
101 In addition to the QCL spectrometer, additional data was collected. First, a sonic anemometer
102 (Gill Windmaster Pro) was used to measure fluctuations in virtual air temperature and 3-D
103 winds. The digital output from the anemometer was logged by the computer controlling the
104 QCL spectrometer. The anemometer was physically positioned so that the sensing volume was
105 located 30 cm from the inlet manifold of the NH_3 instrument. Second, a data logger (Campbell
106 CR23X) recorded gas flow rates controlled by mass flow controllers, inlet surface temperatures
107 measured with thermocouples, atmospheric temperature and relative humidity (Vaisala Y45),
108 and short wave solar radiation (Kipp and Zonen CM3).

109
110 The NH_3 and ancillary meteorological measurements were made at a height of approximately 10
111 m above the ground, sufficient to reach slightly above the nearby vegetation. The combined
112 weight of the spectrometer, support electronics and thermal control system and liquid nitrogen
113 storage dewar for automated refills of the spectrometer detector dewar (total of $\sim 200\text{kg}$)
114 required a platform scissor-lift. The scissor lift was located at a distance of approximately 8 m
115 from the main BFRS meteorological tower. During the two day period from July 24 to 25, when
116 the LBNL measurements were compared with the filter sampler, the platform was lowered to a
117 height of $\sim 6\text{ m}$ to match the height of the filter sampler. The filter sampler was deployed on the
118 main BFRS tower.

119
120 To achieve high temporal resolution necessary for eddy covariance measurements, we designed a
121 high flow rate gas sampling and calibration subsystem that transmits ambient NH_3 vapor to the
122 spectrometer with minimal residence time. A schematic of the inlet and calibration system is

123 shown in Fig. 2. A flow of ambient air is drawn into the sample manifold by the combination of
124 a manifold flow pump (at 20 slpm) and into the NH₃ spectrometer at a rate (approximately 25
125 slpm) determined by the pump speed (Varian 600 dry scroll) and the diameter of a critical orifice
126 inlet. After entering the critical orifice (which reduces the pressure to approximately 50 Torr), air
127 is passed through a 0.2 micron PTFE air filter (Gelman PALL, Acro-50), a 2 m long 1 cm
128 diameter PFA Teflon tube to the multipass optical cell contained within the QCL spectrometer.
129 All glass surfaces are siloxyl coated (General Electric) and surfaces are heated as suggested in
130 Neuman et al (1999). In our application, the temperatures of the different inlet parts were
131 maintained between 40 and 45°C by a set of four temperature control circuits, while the optical
132 bench including the optical absorption cell was maintained at 30°C.

133
134 During the measurements, the instrument zero was adjusted every 30 minutes, under control of
135 the spectrometer computer, by overfilling the inlet manifold with an approximately 60 slpm flow
136 of dry nitrogen supplied by a large liquid N₂ supply dewar. Typically, zero adjustments were
137 significantly less than 1 ppb. In addition, the instrument zero and span were checked
138 periodically. Zeros were generally checked every 30 minutes. The span of the instrument was
139 checked by reversing a backflow of 300 sccm that normally removes a 100 sccm flow of NH₃
140 supplied from a permeation tube source. After applying NH₃ for 30 s, the backflow is
141 reestablished removing NH₃ from the inlet. The response time of the instrument to an
142 approximately 15 ppb step in NH₃ mixing ratio was checked once each hour by applying a NH₃
143 from a permeation tube source to the N₂ flow. As shown in Figure 3, the response is well
144 characterized by the sum of exponential decay terms as

$$145 \quad \text{NH}_3(t) = \text{No} (a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2)), \quad (1)$$

146 where $a_1 = 0.8 \pm 0.05$, $\tau_1 = 0.35 \pm 0.05$ s, $a_2 = (1-a_1)$, and $\tau_2 = 4 \pm 1$ s. The uncertainties in
147 the values reported for the decay coefficients time constants represent variations in the best fit
148 values obtained from fits taken over the experimental period.

149

150 **2.3 Data Reduction**

151

152 The 10Hz data NH₃ were processed to estimate mean NH₃ mixing ratios and NH₃ fluxes. For
153 mean NH₃, a continuous estimate of instrument zero was estimated as a spline interpolation of

154 NH₃ values obtained during the stable period at the end of zero checks (see Figure 3). The
 155 instrument zero was less than 1 ppb for 90% of the data, until June 21st, when the instrument ran
 156 out of cryogenics. Upon restarting the instrument on June 23rd, the instrument noise level had
 157 increased by nearly an order of magnitude (to ~ 3 ppb in 1 second integration), leading to a larger
 158 variation in zero level. Following subtraction of instrument zeros, mean mixing ratios were
 159 calculated for 1 and 12 hour bins.

160
 161 NH₃ flux was computed for ½ hour intervals from the covariance of the 10 Hz NH₃ mixing ratios
 162 and the vertical wind using standard techniques (Balducchi et al. 1988). Wind fields were
 163 rotated to a coordinate system with zero mean vertical wind. Fluctuations in ammonia, NH₃',
 164 virtual temperature, T', and wind vectors, u', v', and w', were calculated by subtracting 1/2 hour
 165 block averages. Vertical fluxes were calculated as the covariance between vertical wind
 166 fluctuations, w', and other quantities. Periods during NH₃ zero or span measurements were
 167 excluded. The mean ammonia flux, $F_{\text{NH}_3} = \langle w' \text{NH}_3' \rangle$ was estimated for each ½ hour interval.
 168 The time lag between w' and NH₃', required to maximize F_{NH_3} , was determined from lag
 169 correlation plots. Typical values for the best lag were small (< 0.3 s), and roughly consistent
 170 with that expected from the measured step response of the inlet system.

171
 172 To correct for loss of high frequency NH₃ fluctuations due to finite frequency response of the gas
 173 inlet, we applied an empirically derived multiplicative correction (Horii et al. 2004). The
 174 correction was computed from the measurements of sensible heat obtained from the sonic
 175 anemometer. Here sensible heat is calculated as, $H = \rho C_p \langle w' T' \rangle$, where ρ and C_p are the
 176 density and specific heat of air respectively. We calculated the correction factor,

$$177 \quad f_{\text{corr}} = w' T' / w' T_{\text{sm}}', \quad (2)$$

178 where T_{sm}' , is obtained by convolving T' with the double exponential decay function describing
 179 the step response to NH₃ span decay in Eq (1). Typical values for F_{corr} ranged from 1 to 1.2
 180 depending on the atmospheric stability, indicating that the NH₃ captured most of the high
 181 frequency fluctuations contributing to the flux. As an additional check of the frequency response,
 182 power spectra for w'T', w'T_{sm}', and w'NH₃' were computed for ½ hour periods and compared
 183 with the -4/3 power law expected from Komolgorov similarity theory.

184

185 We determined whether the NH_3 fluxes were stationary by comparing the $\frac{1}{2}$ hour mean flux with
186 the mean of the individual fluxes determined from 5 minute sub-intervals. Data was considered
187 to be stationary when the flux calculated from the subintervals is within 30% of the $\frac{1}{2}$ hour mean
188 flux (Foken et al. 1996). Non-stationary conditions typically occur during periods of intermittent
189 turbulence which typically occurs on nights when the air is stably stratified and friction velocity,
190 $u^* = \langle -w'u' \rangle^{1/2}$ is low ($u^* < 0.1 \text{ m s}^{-1}$). Non-stationary fluxes of nitrogen oxides have also been
191 observed at BFRS, associated with emissions from the generator (Farmer et al. 2006). We
192 excluded the data ($\sim 20\%$) obtained when the wind direction was within 45 degrees of north.

193 ***2.4 Filter Sampling***

194 Ambient NH_3 concentrations were determined during a two day period (starting on the evening
195 of June 23rd and continuing into midday of June 25th) using filter samples collected with the
196 Desert Research Institutes (DRI) sampler (Chow et al. 1993). As described above, the inlet of
197 the filter sampler was located at a height of 5.5 m off the ground on the main meteorological
198 tower. In this method, two filter samples are collected simultaneously. One filter is exposed to a
199 flow of ambient air, while the other is exposed to air that has had gaseous NH_3 removed by an
200 annular denuder. Then the denuded filters collected only particulate NH_4^+ , while the undenuded
201 filter collected both gas and aerosol. Gaseous NH_3 is estimated as the difference between
202 undenuded and denuded measurements. In this experiment, four sets of paired (denuded and
203 undenuded) citric acid coated filters were exposed to air flows near 100 liters per minute
204 (measured before and after each sample was collected) over the two day period using 12 hour
205 collection times (1800-0600 and 0600-1800 PDT, or 0100-1300 and 1300-0100 GMT). Before
206 and after sample collection the filters were stored in capped, bagged, and stored in an ice chest.
207 Following collection on June, 25th, the samples were returned to DRI for analysis of NH_4^+ ions
208 captured on the citric acid.

209

210 ***2.5 Estimate of Maximum Deposition Velocity***

211 As a check on the observed NH_3 fluxes, we computed deposition velocities, $V_d = F_{\text{NH}_3}/\text{NH}_3$, for
212 each $\frac{1}{2}$ hour interval and compared it to a simple model for the maximum deposition velocity
213 expected if all NH_3 molecules are reaching the leaf surfaces are adsorbed. In general, deposition
214 velocity can be expressed in a resistance based model as,

215
$$V_d = (R_a + R_b + R_c)^{-1}, \quad (3)$$

216 where R_a , R_b , and R_c are the aerodynamic, leaf boundary layer, and stomatal resistances
 217 respectively. In the limit that the vegetation is nitrogen limited and readily accepts all NH_3
 218 reaching the leaf surface, R_c can be assumed to be small and a maximum deposition velocity can
 219 be written as

220
$$V_{d\max} = (R_a + R_b)^{-1}, \quad (4)$$

221 Using standard turbulence models for the surface layer fluxes, one can write a set of expressions
 222 for R_a and R_b (Wesely 1989; Horii et al. 2004). Here

223
$$R_a = u/u_*^2 - \chi_H / (k u_*), \quad (5)$$

224 where k is the Von Karman coefficient (~ 0.4). Under stable conditions χ_H can be expressed as

225
$$\chi_H = 5(z-d)/L, \quad (6)$$

226 where z is the measurement height, d is the displacement height (often assumed to be 0.75
 227 vegetation height), and L is the Monin–Obukhov length scale, $L = -kg\langle w'T \rangle / Tu_*^3$, and g is the
 228 acceleration due to Earth's gravity. Stable conditions are defined as when $L > 0$. Under unstable
 229 conditions ($L < 0$),

230
$$\chi_H = \exp(0.598 + 0.39 \ln(-(z-d)/L) - 0.09 (\ln(-(z-d)/L))^2). \quad (7)$$

231 Finally, the boundary layer resistance at the leaf surface can be written as

232
$$R_b^{-1} \sim u_* / 7.1 \quad (8)$$

233 Under the conditions observed at a mixed deciduous forest in Northeastern United States, Horri
 234 et al. (2004) observed $0.01 < V_d < 0.08 \text{ m s}^{-1}$.

235 **2.6 Simulation of NH_3 Mixing Ratios**

236 Measured NH_3 mixing ratios were compared with simulated NH_3 concentrations derived from
 237 and a regional emission inventory estimate of NH_3 emissions combined with a particle back
 238 trajectory calculation of time and space specific surface influence on atmospheric gas
 239 concentrations and dry deposition of NH_3 .

240
 241 A simple NH_3 emission model was used for these simulations. NH_3 emissions for June were
 242 estimated assuming that cows in dairies and feedlots generated a large fraction of the emissions
 243 in the Central Valley. The spatial distribution of cows was obtained from county level statistics
 244 for 2002 animal stocking density reported by the United States Department of Agriculture's

245 National Agricultural Statistics Service (NASS, 2004). We estimated the NH_3 emission factors
 246 for the summer conditions by scaling the annual averaged emissions factors by the ratio (2.3) of
 247 summer time animal fluxes to annually averaged animal fluxes in the San Joaquin Valley (Battye
 248 *et al.*, 2003). The resulting emissions factors are 185 and 64 g NH_3 animal⁻¹ day⁻¹ for dairy and
 249 non-dairy cattle respectively. County level NH_3 fluxes were calculated as the total NH_3
 250 emissions for each county normalized by the area and are shown in Table 1. Fluxes from
 251 Nevada were set equal to the 2 ng m⁻² s⁻¹, similar to low emission counties in California. We did
 252 not attempt to include other sources of NH_3 emission (e.g, other animal agriculture or
 253 automobiles) and hence this estimate likely represents a lower limit to NH_3 fluxes. However, we
 254 consider this simple model roughly sufficient for determining the temporal variations in NH_3
 255 expected at BFRS, particularly given the additional approximations we make in estimating the
 256 transport of NH_3 from remote locations to the site.

257
 258 The surface influence functions were calculated using the stochastic time inverted Lagrangian
 259 transport (STILT) model (Lin et al. 2003). STILT was originally derived from the NOAA
 260 HYSPLIT particle transport model (Draxler et al. 1998) for inverse model estimates of surface
 261 CO_2 fluxes (Lin et al. 2004). In our simulations, ensembles of 100 particles were released from
 262 the tower site every 2 hours and run backward in time for a period of 12 hours, which generally
 263 allowed the particles to reach locations in the central valley. STILT was driven with NOAA
 264 reanalysis meteorology (EDAS40) with 40 km spatial resolution and hourly temporal resolution.
 265 Land surface contributions to atmospheric NH_3 were assumed to be proportional to the time a
 266 particle spends within the surface boundary layer. NH_3 deposition was assumed to depend on the
 267 rate of vertical mixing in the atmosphere and parameterized as a residence time $\tau = z/V_{d0}$, where
 268 z is the particle altitude above ground and $V_{d0} = 0.02$ m s⁻¹ is an assumed mean deposition
 269 velocity. For each time step, Δt , NH_3 is updated as

$$270 \quad \text{NH}_3(t + \Delta t) = \text{NH}_3(t) e^{-\Delta t/\tau} + F_{\text{NH}_3} \Delta t/z_i v, \quad (8)$$

271 where F_{NH_3} (nmol m⁻² s⁻¹) is the surface NH_3 flux at the position of the particle, z_i is the height of
 272 the boundary layer, and v is the molecular density of air. Simulations were run both with and
 273 without the deposition loss term to estimate the concentration expected for a non-reacting gas.

274 3. Results and Discussion

275

276 **3.1 Surface NH₃ Mixing ratios**

277 Figure 4 shows the hourly averages of measured NH₃ from the LBNL laser spectrometer and the
278 mean results from the 12 hour samples collected by the DRI filter system. Both LBNL and DRI
279 data show that NH₃ was generally between 0 and 2 ppb, with a few periods of higher mixing
280 ratios. Near June 13th, a synoptic event introduced cooler air from the north with lower
281 temperatures and mild precipitation, reducing NH₃ concentrations significantly. The averages of
282 the LBNL measurements were lower than the filter samples on June 24th, and similar to or higher
283 than the filter samples on June, 25th (see Table 2). Inspection of the LBNL data suggests that a
284 significant fraction of the data was noisy and did not pass quality control criteria (~ 50% in some
285 of the 12 hour periods), perhaps causing the poor correlation between LBNL averages and the
286 DRI filter measurements.

287

288 We also examined the diurnal variations in NH₃. As shown in Figure 5, there was a significant
289 diurnal cycle with lower mixing ratios at night and higher mixing ratios during the day. This is
290 consistent with having predominantly downslope winds carrying NH₃ free air from the Sierra
291 Nevada during the night and upslope winds carrying air with NH₃ from the Central Valley during
292 the day (Dillon et al. 2002).

293 **3.2 Calculated Aerosol – Gas Equilibrium**

294

295 We considered whether the low NH₃ mixing ratios might limit ammonium-based aerosol
296 concentrations by comparing measured NH₃ with previously measured HNO₃ and the aerosol-
297 gas equilibrium coefficient, K_p, which defines the minimum NH₃*HNO₃ product required to
298 form NH₄NO₃ aerosol (Stelson et al. 1982). Figure 6 shows that K_p >> 1 ppb² for most of the
299 observation period. Earlier work at Blodgett showed that HNO₃ mixing ratios fell in a range of
300 0.3 to 1.5 ppb (5%-95%) for June-October (Murphy et al., 2006). Assuming a nominal value of
301 1 ppb HNO₃, the minimum NH₃ mixing ratio required to support aerosol NH₃*HNO₃ in
302 equilibrium with gas phase constituents is numerically equal to the value of K_p. Since the
303 measured NH₃ mixing ratio is generally significantly less than K_p, this suggests that aerosol
304 NH₃*HNO₃ will not be present in equilibrium with gases. We also note that although K_p was

305 low during points earlier in June, there were also light rains, which would likely strip NH_3 ,
306 HNO_3 , and aerosols from ambient air.

307 ***3.3 NH_3 Fluctuations, Fluxes, and Deposition Velocities***

308 Before computing NH_3 fluxes, we examined the power spectra for temporal variations in $w'T'$,
309 $w'T'_{\text{sm}}$, and $w'\text{NH}_3$ for each ½ hour period over which NH_3 fluxes were calculated. By
310 comparing the spectra of $w'T'$ and $w'T'_{\text{sm}}$, we can visually inspect the loss of high frequency
311 power in $w'T'$ introduced by smoothing T' with the finite frequency response of the NH_3 inlet
312 system. A representative set of power spectra are shown in Figure 7. As expected, the spectra
313 for $w'T'$ and $w'T'_{\text{sm}}$ are similar, consistent with the smoothing reducing $w'T'$ by a small amount,
314 and suggesting that NH_3 fluxes can be accurately recovered. We also note parenthetically that
315 the high frequency slope of all three of the spectra was not as steep as that expected for
316 turbulence in a Komolgorov similarity theory, as observed by other researchers at this and other
317 sites (Farmer et al. 2006).

318
319 The NH_3 fluxes calculated from the 10Hz data are shown in Figure 8. Most of the NH_3 fluxes
320 were small ($\sim 10 \text{ ng NH}_3 \text{ m}^{-2} \text{ s}^{-1}$) or negative. During a several day period early in the campaign
321 when NH_3 mixing ratios were highest, large negative fluxes ($-30 \text{ ng NH}_3 \text{ m}^{-2} \text{ s}^{-1}$) were observed,
322 indicating that NH_3 was being lost to the canopy by dry deposition. The mean flux during the
323 measurement period was $9.2 \pm 1.1 \text{ ng NH}_3 \text{ m}^{-2} \text{ s}^{-1}$. As a check of whether the estimated fluxes
324 were realistic, we calculated deposition velocities for a subset of the measured fluxes. The subset
325 was obtained by requiring that the NH_3 mixing was known to better than 50% (at 68%
326 confidence). As shown in Figure 9, the measured deposition velocities are all less than the
327 maximum deposition velocity estimated from the measured turbulence conditions using Eq (8),
328 with a typical ratio for the measured to maximum deposition velocity of approximately 0.5. This
329 is consistent with some combination of imperfect sticking to leaf surfaces and stomatal resistance
330 to NH_3 uptake by the leaves.

331 ***3.4 Transport Model Estimates of NH_3 Concentrations***

332 The map of the estimated surface NH_3 fluxes from cattle is shown in Figure 10. Surface fluxes
333 range over several orders of magnitude, reflecting the strong emissions from the Central Valley
334 and low emissions from the mountainous regions of the Sierra Nevada. Figure 10 includes an

335 example ensemble of 12-hour particle back-trajectories representing a measurement at BFRS at
336 1300 hours local time on June 12th, 2006. This example shows that some particle tracks sweep
337 backward into the Central Valley where they come into contact with high surface NH₃ fluxes.

338
339 The predicted NH₃ concentrations from the back trajectory simulations are compared with
340 measured NH₃ in Figure 11. Measured NH₃ is generally a factor of ~ 2 higher than NH₃
341 predicted with deposition and a factor of ~ 2 less than NH₃ predicted without deposition. The
342 temporal variations in predicted and measured NH₃ mixing ratios match reasonably well. This is
343 likely because the large variations are caused by variations in the amount of air reaching BFRS
344 from areas in the Central Valley where NH₃ fluxes are highest.

345 **4. Conclusions**

346 We performed an exploratory study of NH₃ mixing ratios and fluxes at Blodgett Forest during
347 June, 2006. The 1 hour averaged NH₃ mixing ratios ranged from non-detection (< 0.2 ppb) to
348 about 2 ppb, typical of a low-background site removed from significant sources. The diurnal
349 variations were consistent with upslope flows bringing air with higher NH₃ to the site during the
350 day. The observed NH₃ mixing ratios were not sufficient to support NH₄NO₃ aerosol in
351 equilibrium with gas phase NH₃ assuming HNO₃ was similar to that observed at the site
352 previously. NH₃ fluxes, measured using the eddy covariance method, were generally small or
353 negative, consistent dry deposition to the vegetation and no significant net emission. Calculated
354 deposition velocities were generally about half of the maximum expected for deposition to a
355 canopy with aerodynamic and leaf boundary layer resistance but no resistance to leaf uptake
356 (perfect sticking to leaves). This is not surprising given the nitrogen poor soils in the Sierra
357 foothills. Last, we predicted NH₃ at BFRS by combining a simple NH₃ emission inventory that
358 considered only emissions from cows (dairy and meat) with a particle back-trajectory model.
359 Measured and predicted NH₃ concentrations showed substantially similar temporal patterns over
360 synoptic time periods. Predictions with and without NH₃ deposition bracketed the measured
361 NH₃ mixing ratios. On the basis of these measurements, we conclude that NH₃ from the Central
362 Valley had a small but measurable effect on NH₃ mixing ratios at the BFRS site during the short
363 period of this study, but further measurements would be necessary to determine the whether the
364 same patterns prevail over longer periods, particularly between different seasons.

365

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370 shared the research infrastructure at BFRS, while David and Sheryl Rambeau provided
371 invaluable assistance with arrangements for field work at BFRS. Steven Kohl of the Desert
372 Research Institute prepared the filter sampler and performed the analysis of the integrated NH₃
373 mixing ratios. John Lin generously provided the STILT model for the atmospheric transport
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452 phosphorus in and around the Lake Tahoe Basin: Implications for possible sources of atmospheric
453 pollutants to Lake Tahoe. *Environmental Science & Technology* **36**(23): 4981-4989.
- 454

455

456 7. Tables457 Table 1. Cattle stocking, area, and estimated NH₃ flux by county.

County	Beef Cows	Dairy Cows	Other Cattle	area (km ²)	Flux (ng NH ₃ m ⁻² s ⁻¹)
Alameda	9401	6	10405	1888	8
Alpine	1560	0	551	1891	1
Amador	10112	20	9104	1518	9
Butte	8979	1261	9191	4197	4
Calaveras	14390	222	12878	2611	8
Colusa	0	0	7957	2946	2
Contra Costa	0	0	11596	1843	5
Del Norte	1018	4703	4154	2580	5
El Dorado	4115	9	3551	4380	1
Fresno	23422	90550	282547	15265	28
Glenn	17438	17304	30655	3366	22
Humboldt	22333	16732	24041	9146	8
Imperial	0	0	386634	10687	27
Inyo	0	0	8278	26120	0
Kern	36779	74708	148553	20841	14
Kings	5130	138292	126108	3561	111
Lake	4764	4	4378	3220	2
Lassen	25381	38	23905	11667	3
Los Angeles	0	0	2092	10396	0
Madera	15723	48086	82972	5468	32
Marin	9105	10309	15998	1331	31
Mariposa	10204	245	12130	3715	5
Mendocino	0	0	7691	8983	1
Merced	29534	223303	212270	4937	133
Modoc	41564	14	33615	10097	6
Mono	2989	0	2938	7794	1
Monterey	25430	1606	46025	8504	7
Napa	4300	245	3453	1930	3
Nevada	3007	108	1927	2451	2
Orange	392	0	401	2021	0
Placer	0	0	10004	3595	2
Plumas	5766	7	10644	6537	2
Riverside	3670	90359	87042	18451	14
Sacramento	16392	18337	32807	2472	31
San Benito	14408	935	24054	3556	9
San Bernardino	2918	158240	110185	51334	8
San Diego	6363	5729	13709	10752	3
San Francisco	0	0	0	120	0

San Joaquin	19629	103534	95196	3582	86
San Luis					
Obispo	38268	550	44928	8459	7
San Mateo	1474	6	941	1150	2
Santa Barbara	19482	2669	21183	7007	5
Santa Clara	0	0	12692	3304	3
Santa Cruz	984	176	2275	1140	2
Shasta	16618	562	11225	9690	2
Sierra	3339	0	3777	2441	2
Siskiyou	34750	1518	28421	16094	3
Solano	14560	3947	26605	2123	18
Sonoma	14311	31986	35301	4034	26
Stanislaus	42007	162878	221060	3824	142
Sutter	0	0	5321	1543	3
Tehama	29027	5489	33679	7555	8
Trinity	2671	12	2252	8137	0
Tulare	31171	412462	456491	12349	101
Tuolumne	6855	108	5288	5723	2
Ventura	4357	17	4544	4724	1
Yolo	6773	2012	8124	2594	6
Yuba	7419	3325	20694	1615	17

458

459 Table 2. Comparison of NH₃ mixing ratios (ppb) from DRI filter samples and averages

Date time (GMT)	Filter		LBNL	
24/06/2006 7:00	1.46	(0.05)	0.74	(0.28)
24/06/2006 19:00	1.55	(0.05)	0.36	(0.13)
25/06/2006 7:00	0.90	(0.12)	0.56	(0.32)
25/06/2006 19:00	0.58	(0.14)	0.91	(0.30)

460 8. Figure Captions

461 Fig 1. Satellite mosaic image showing the Blodgett Forest Research Station in the
462 forested western foothills of the central Sierra Nevada of California, and the mixed use
463 (agricultural and urban) areas of the nearby Sacramento Valley area.

464 Fig 2. Schematic illustration of the air sampling manifold with critical orifice flow inlet and
465 air filter. Automated instrument zero and span calibrations are performed by
466 periodically flowing N_2 into inlet, either without or with the addition of NH_3 from a
467 permeation tube source.

468 Fig 3. Time series of NH_3 mixing ratio showing transient decay following removal of NH_3 span
469 gas from zero air flow to instrument inlet.

470 Fig 4. Hourly NH_3 mixing ratios measured at Blodgett Forest in June, 2006. NH_3 data
471 from the laser-spectrometer (black symbols) are averaged into 12 hour bins for
472 comparison with integrating filter samples (blue symbols) collected with a sampling
473 system provided by the Desert Research Institute.

474 Fig 5. Mean diurnal variation in surface NH_3 mixing ratio from June 11th to 26th, 2006.

475 Fig 6. Comparison of NH_3 mixing ratio (black) and aerosol-gas equilibrium partitioning
476 coefficient, K_p (red), indicating minimum product of gas phase NH_3 and HNO_3 mixing
477 ratios necessary for NH_4NO_3 aerosol to be found in equilibrium with gas phase
478 constituents.

479 Figure 7. Power spectra of covariance in vertical wind speed with sonic temperature,
480 $w' T'$, smoothed sonic temperature, $w' T'_{sm}$, and fluctuations in NH_3 mixing ratio,
481 $w' \text{NH}_3'$. The straight line in upper right shows $-4/3$ slope expected for fluctuation
482 spectra in an inertial sublayer.

483 Figure 8. Eddy covariance measurement of NH_3 flux for all time points (crosses) and for those
484 passing quality control criteria for use in calculating deposition velocities (filled squares).

485 Figure 9. Scatter plot comparison of measured deposition velocity, v_d , and maximum deposition
486 velocity in the case that all molecules reaching the leaf surface are absorbed, v_{dmax} .

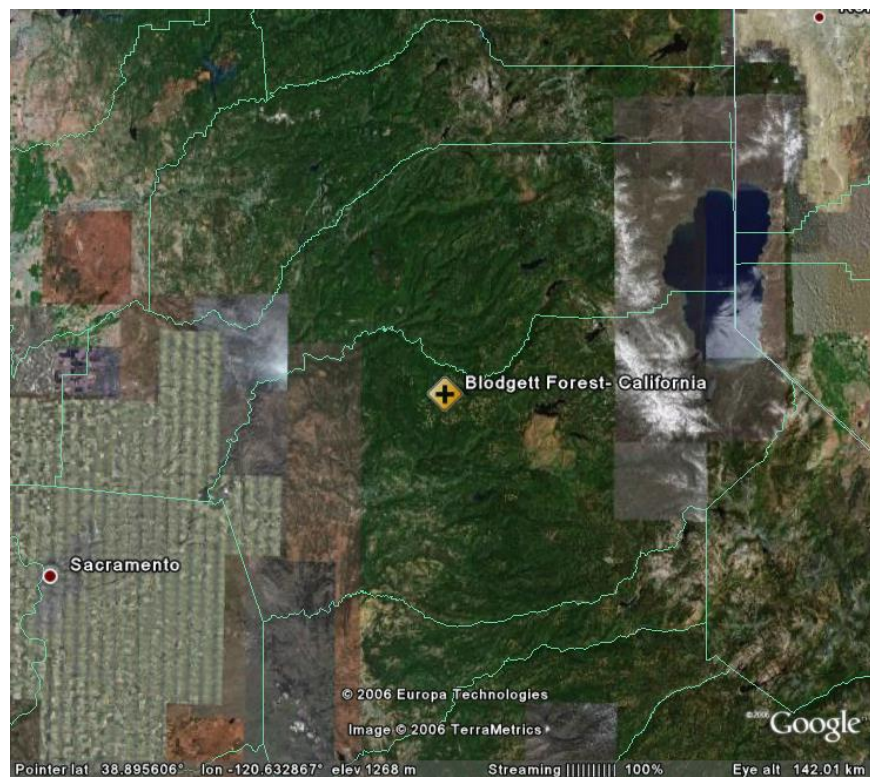
487 Figure 10. Map of California showing estimated NH_3 emissions ($\text{ng NH}_3 \text{ m}^{-2} \text{ s}^{-1}$) and
488 an example 12hr back trajectory calculation of showing particles converging at BFRS at midday
489 on June 12th, 2006.

490 Figure 11. Measured hourly NH_3 mixing ratios from LBNL system (black points), DRI 12 hour
491 integrated sampler results (blue points), and predicted NH_3 mixing ratios predicted from the back
492 trajectory calculations and cattle-only NH_3 emission inventory. Predicted NH_3 is scaled to fit on
493 plot so that NH_3 predicted without deposition (red line) is scaled by a factor of 0.5, while NH_3
494 predicted with deposition (green line) is scaled by a factor of 2.

495 9. Figures

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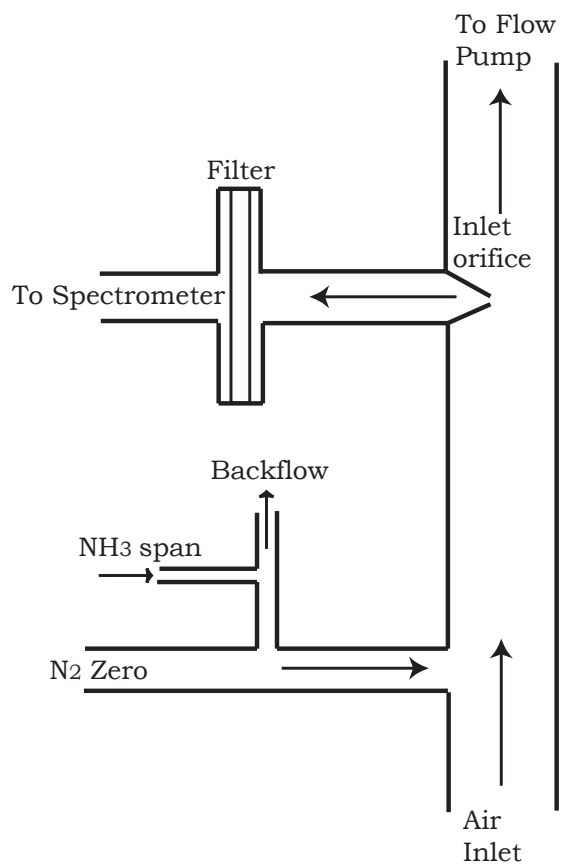
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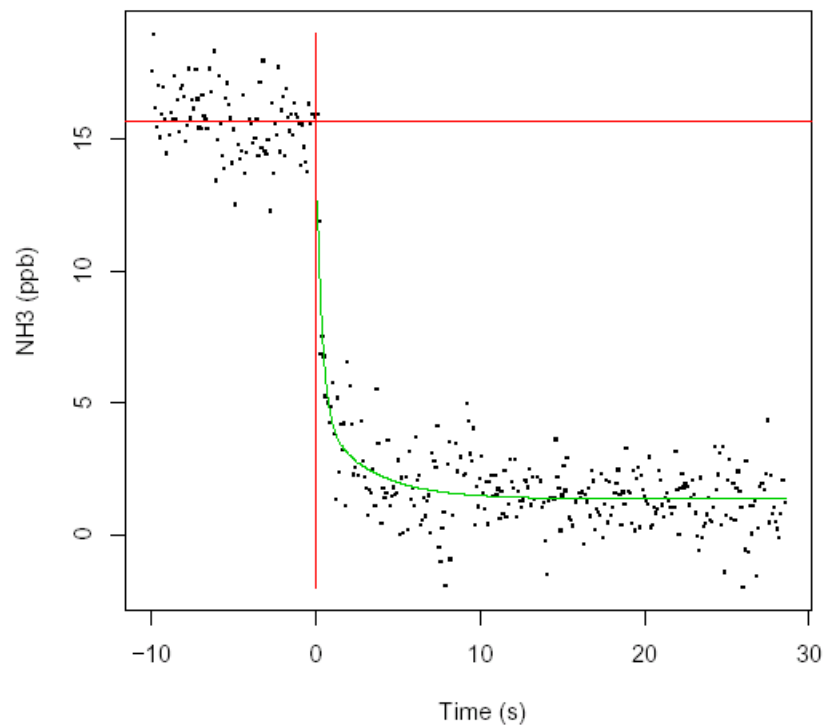
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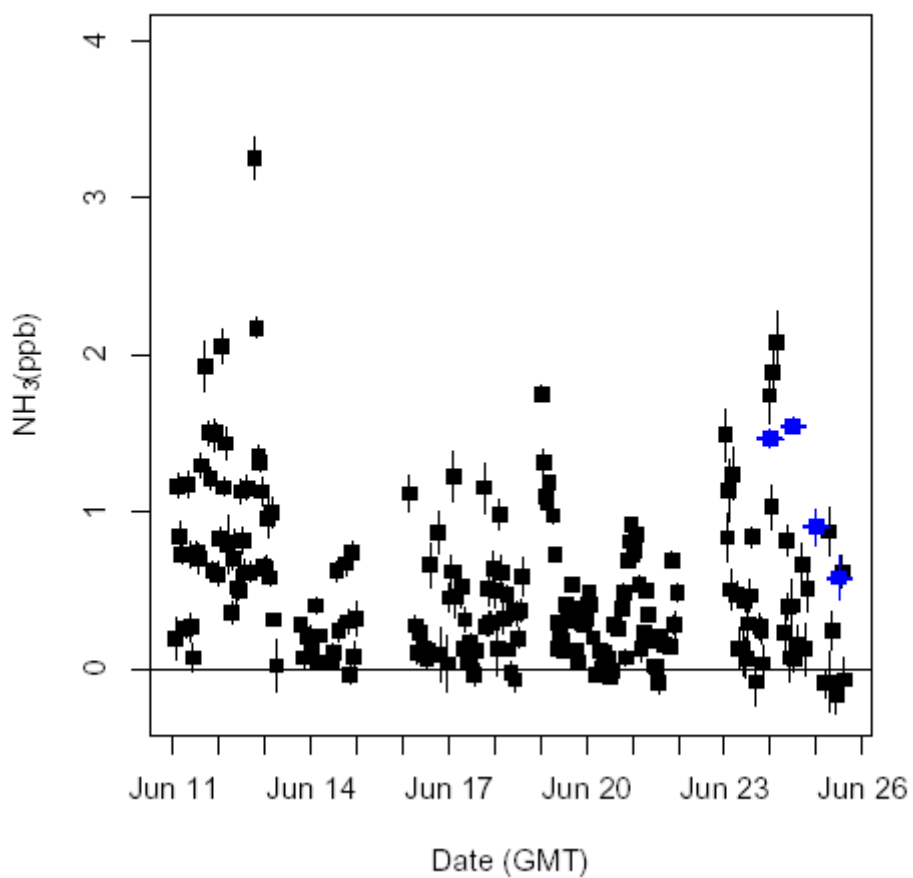


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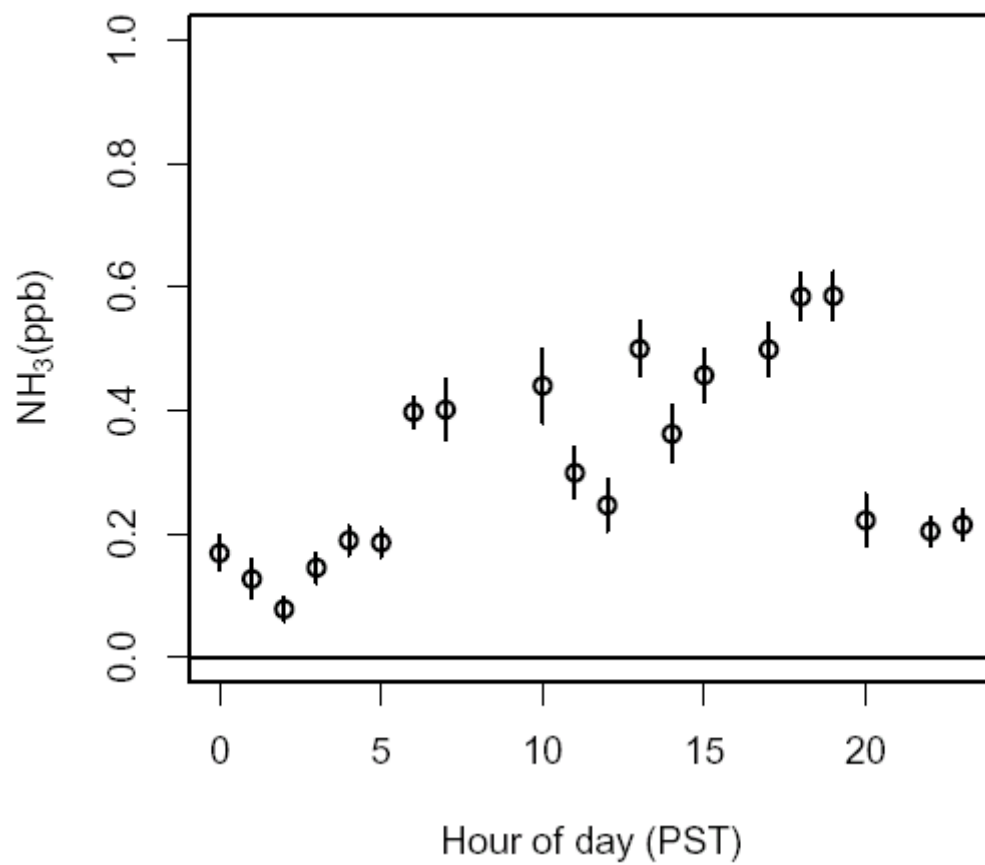
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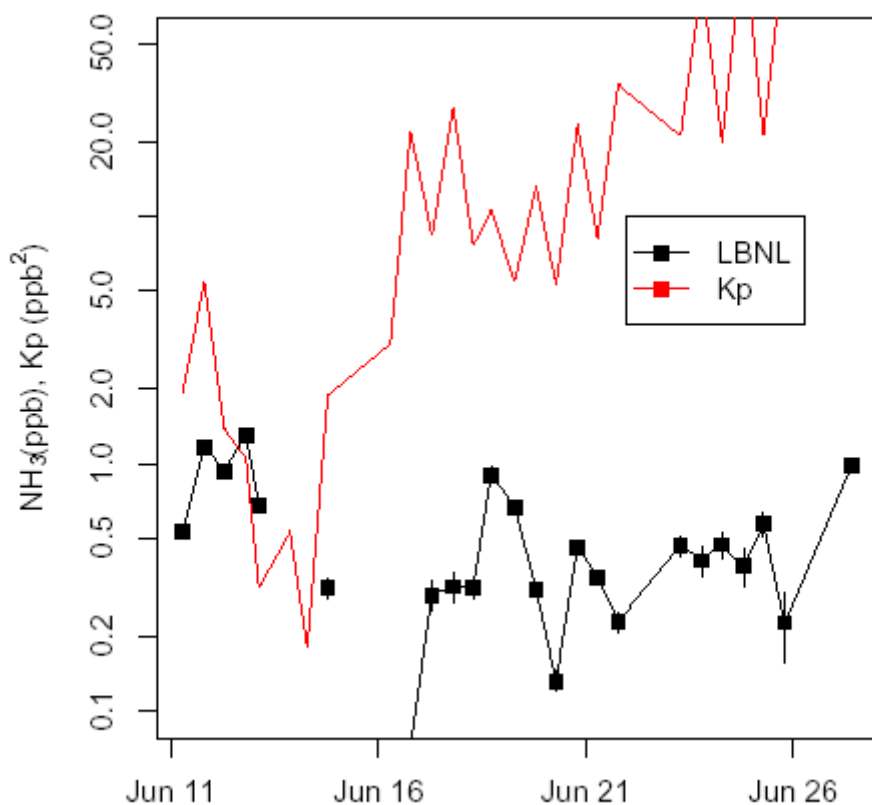
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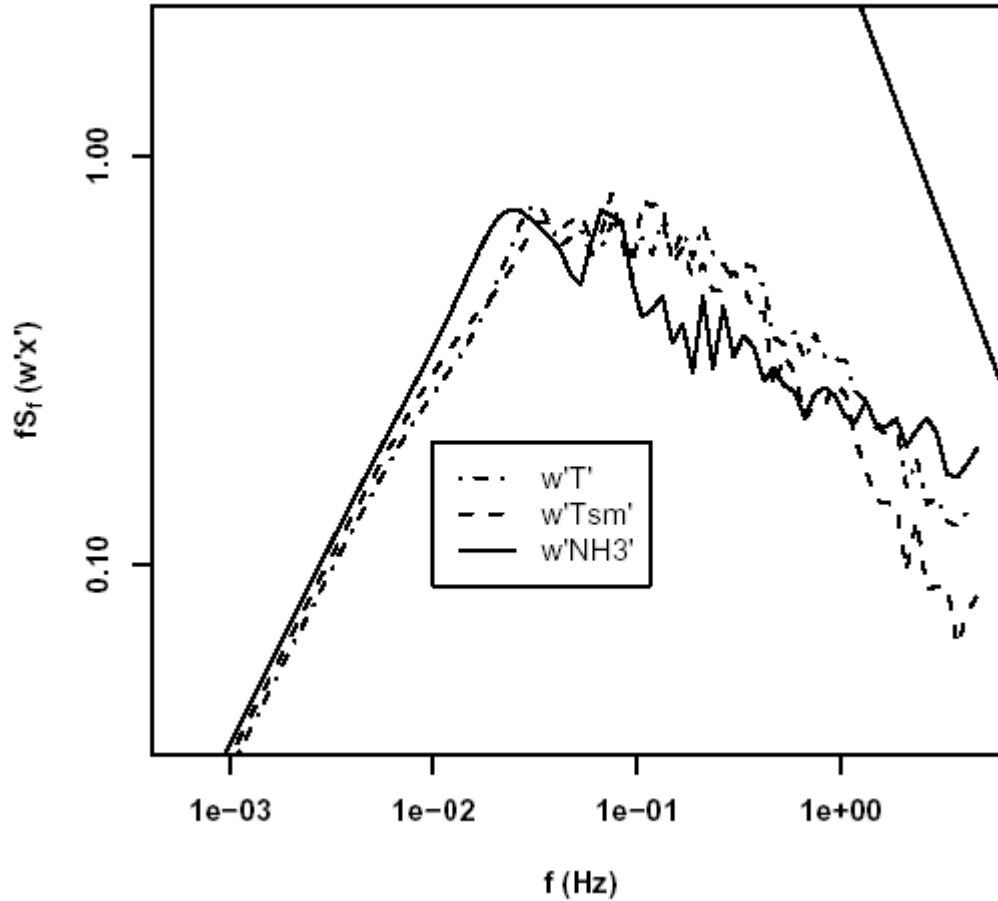
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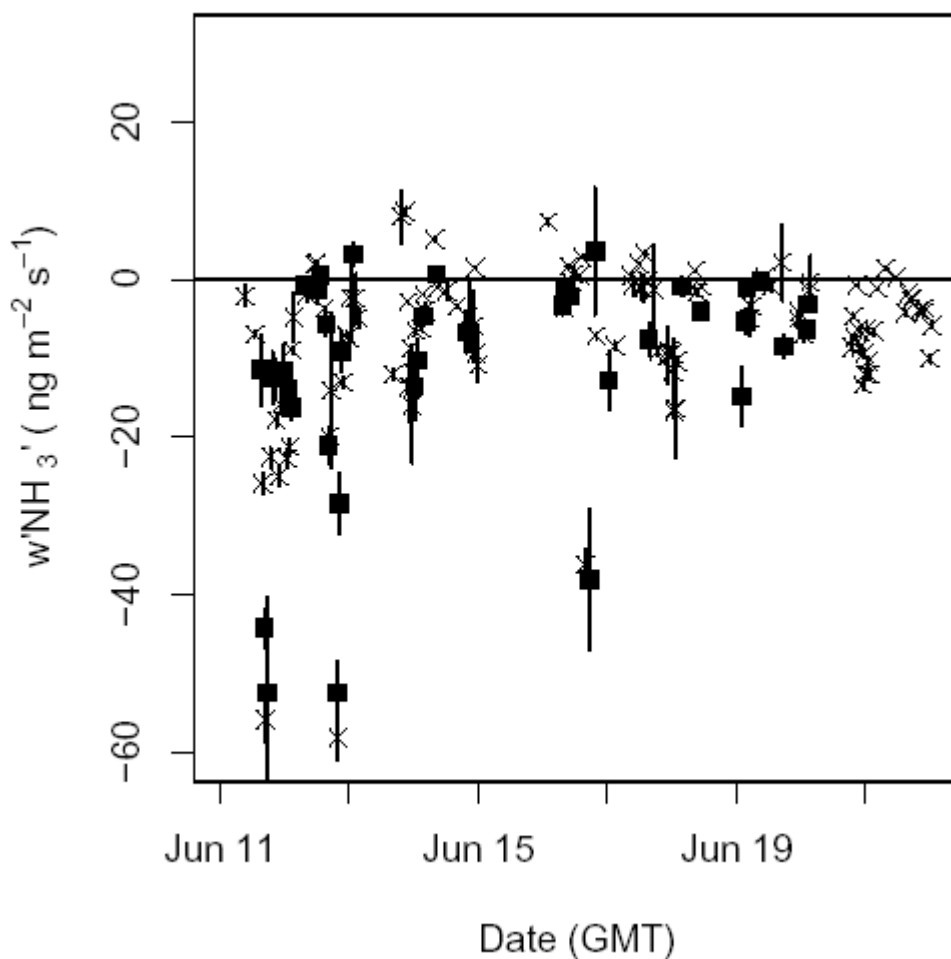
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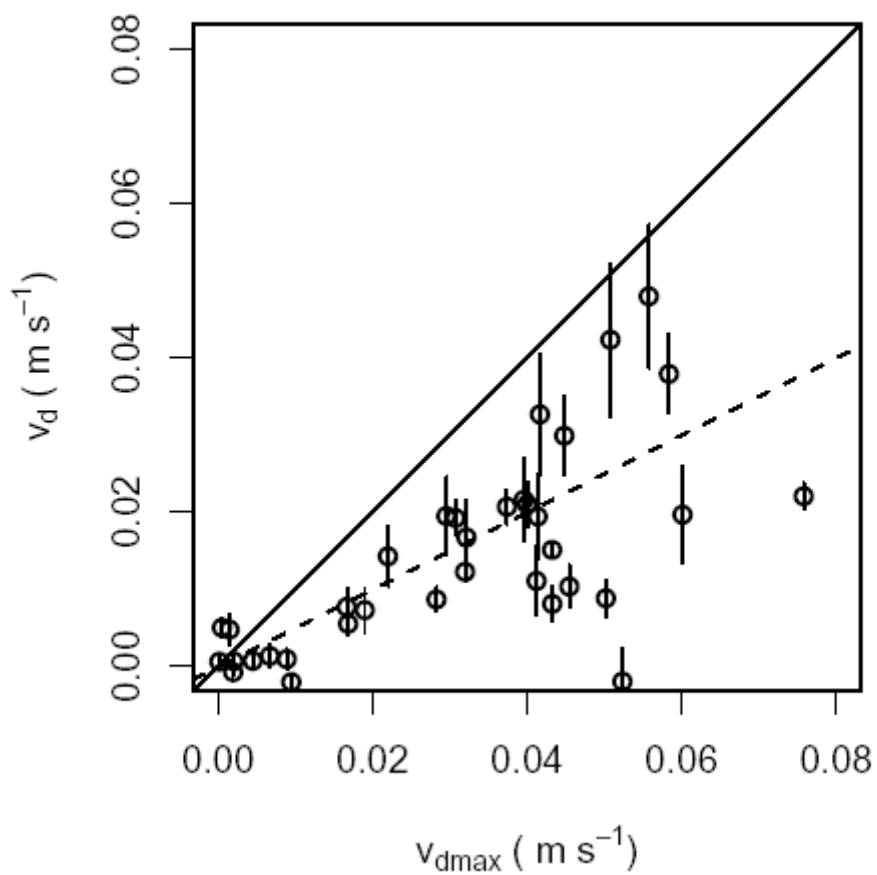


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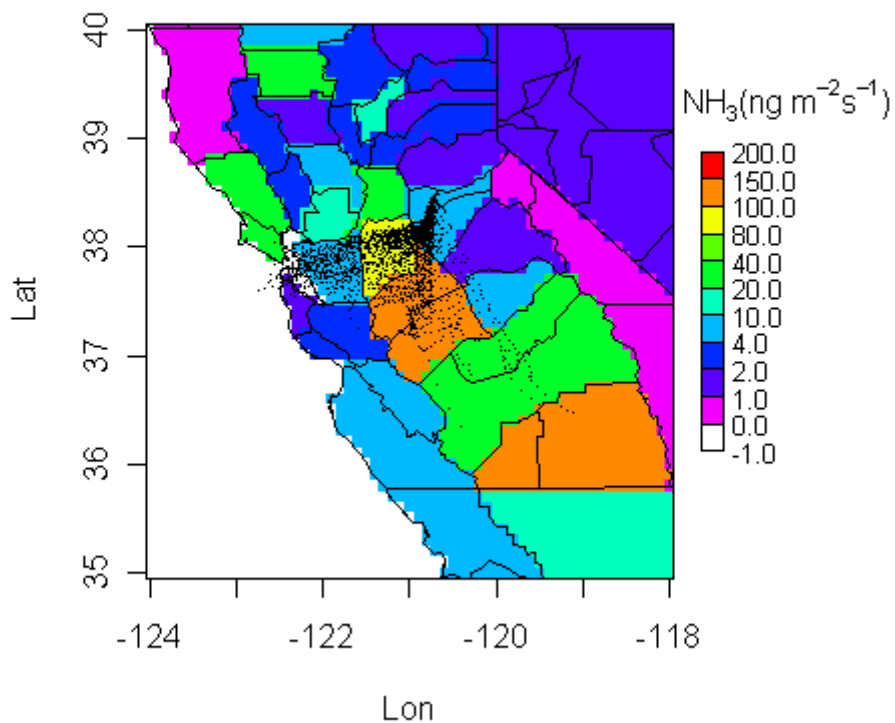
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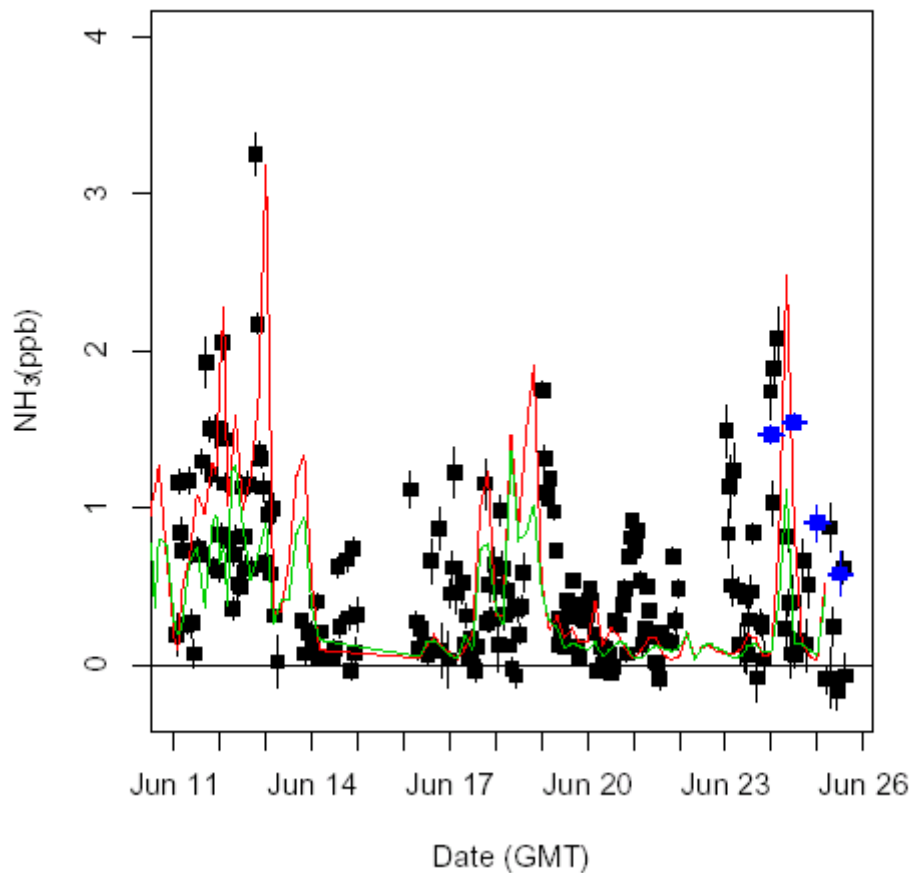


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