Relaxed eddy accumulation measurements of ammonia, nitric acid, sulfur dioxide and particulate sulfate dry deposition near Tampa, FL, USA

LaToya Myles¹,³, Tilden P Meyers¹ and Larry Robinson²

¹ NOAA/Air Resources Laboratory, Atmospheric Turbulence and Diffusion Division, 456 South Illinois Avenue, Oak Ridge, TN 37830, USA
² Environmental Sciences Institute, Florida A&M University, 1520 South Bronough Street, Tallahassee, FL 32307, USA
E-mail: LaToya.Myles@noaa.gov

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Abstract

The relaxed eddy accumulation (REA) method was utilized to measure fluxes of key atmospheric species, specifically ammonia (NH₃), nitric acid (HNO₃), sulfur dioxide (SO₂) and particulate sulfate (SO₄²⁻) to vegetation that is characteristic throughout the Tampa Bay Watershed. Three annular denuder systems (ADS), each consisting of two annular denuders and a filter pack in series, were deployed to accumulate gaseous constituents and fine-fraction particulates (Dₚ < 2.5 μm) in updraft and downdraft eddies, as well as in the mid-draft velocity range. Relaxed eddy accumulation samples, which were analyzed by ion chromatography, and continuous meteorological data were collected during the May 2002 Bay Regional Atmospheric Chemistry Experiment (BRACE) near Sydney, FL. For the chemical species of current interest, concentrations were 1.64 ± 0.23 for NH₃, 2.06 ± 0.24 for HNO₃, 3.49 ± 0.50 for SO₂ and 4.64 ± 0.31 μg m⁻³ for SO₄²⁻, and the deposition velocity (Vd) estimates for NH₃, HNO₃, SO₂ and SO₄²⁻ were 1.27 ± 0.65, 3.63 ± 1.47, 0.45 ± 0.98 and 0.42 ± 1.00 cm s⁻¹, respectively. The results obtained confirm the expectation that the deposition of ammonia, nitric acid and particulate sulfate was controlled by aerodynamic and quasi-laminar layer resistances and that sulfur dioxide is relatively dependent upon stomatal conditions.

Keywords: dry deposition velocity, relaxed eddy accumulation, annular denuder system, BRACE

1. Introduction

Historically, excess nutrient loading into Tampa Bay has substantially depreciated the water quality and biological diversity of this estuarine ecosystem [1]. Increased nutrient concentrations often amplify rates of algal primary production and cause eutrophication in aquatic bodies. High levels of nutrients, especially nitrogen, promoted the 40% loss of benthic seagrasses in Tampa Bay from 1950 to 1980. This dramatic loss of food and habitat stressed native fish and other aquatic organisms throughout the bay’s food web; however, implementation of water quality programs has reduced total nitrogen (TN) input to levels that have allowed notable resurgences of seagrass communities [2]. Estimates of TN loading from 1992 to 1994 were 3.8 × 10⁶ kg yr⁻¹ with 1.1 × 10⁶ kg yr⁻¹ ascribed to atmospheric deposition processes [3]. Almost half of the TN deposition to the surrounding Tampa Bay Watershed (500 700 ha surface area) is the result of dry deposition (~3.87 kg N ha⁻¹ yr⁻¹) [4].
Certain atmospheric species, which are linked to aquatic nutrient loading, are incorporated into precipitation (wet deposition) or aerodynamically transferred to the Earth’s surface through dry processes (dry deposition). One such species is ammonia (NH\textsubscript{3}), which is a primary pollutant mainly emitted from agricultural operations. Low emission source heights in conjunction with ammonia’s brief atmospheric residence time drive deposition rates, especially in proximity to large sources [5]; however, NH\textsubscript{3} fluxes are highly episodic and show a strong dependence on meteorological conditions [6]. Nitric acid (HNO\textsubscript{3}) is an oxidation product of NO\textsubscript{2} (NO + NO\textsubscript{2}). Nitric acid usually exhibits variable rates of dry deposition during daytime hours, perhaps due to small surface changes and its high solubility and surface affinity rates [7].

Another important atmospherically deposited species is sulfur dioxide (SO\textsubscript{2}), which is largely emitted as a result of fossil fuel combustion. Strong aerosol formation tendencies compete with dry deposition processes for removal of SO\textsubscript{2} in the troposphere. Particulate SO\textsubscript{4}\textsuperscript{2−} is formed primarily through the oxidation of SO\textsubscript{2}.

The aim of this study is to measure the dry deposition fluxes of NH\textsubscript{3}, HNO\textsubscript{3}, SO\textsubscript{2} and SO\textsubscript{4}\textsuperscript{2−} over low grassland vegetation near Tampa, FL with a relaxed eddy accumulation system and to utilize the data to estimate the associated dry deposition velocities.

2. Methodology

2.1. Relaxed eddy accumulation

The relaxed eddy accumulation (REA) system that was utilized to determine fluxes of atmospheric species was first described by Businger and Oncley [8]. Relaxed eddy accumulation is a conditional sampling variant of the eddy accumulation method used by Desjardins [9]. This technique utilizes isolated reservoirs to sample vertical wind eddies based on direction over an extended time interval. Updraft (\(w^+\)) and downdraft (\(w^-\)) air samples are collected into separate accumulators with the mean vertical wind velocity assumed to be zero and the flow rate constantly maintained [10]. The vertical mass flux of a scalar (\(F_s\)) may be determined by

\[
F_s = F_{\text{HI}}(\beta \sigma_w (\bar{C}_w - \bar{C}_d))
\]

where \(\beta\) is an empirical coefficient, \(\sigma_w\) is the standard deviation of the vertical wind velocity, and \(\bar{C}_w\) and \(\bar{C}_d\) are the average concentrations of the scalar in the updrafts and downdrafts, respectively [11]. A dynamic velocity deadband of 0.3\(\sigma_w\), where \(\sigma_w\) is the standard deviation of the vertical wind velocity, was implemented to maximize the difference between updraft and downdraft concentrations. When the vertical wind velocity fell below 0.3\(\sigma_w\), the sample flow was diverted to a mid-channel annular denuder system (ADS). The switching frequency of the REA system was 1 s, which Meyers et al [6] found minimizes the potential loss of flux. In order to obtain more efficient scalar fluxes, the \(\beta\) coefficient was computed from data collected by a 3D sonic anemometer with the following equation:

\[
\beta = F_{\text{HI}}(\sigma_w(\bar{T}_{w^+} - \bar{T}_{d^-}))^{-1}
\]

where \(F_{\text{HI}}\) is the sensible heat flux (\(w^'c_p\)) and \(\bar{T}_{w^+}\) and \(\bar{T}_{d^-}\) denote the average temperatures of the updrafts and downdrafts, respectively [12].

Nemitz et al [13] and Sutton et al [14] validated the REA method for NH\textsubscript{3} flux measurements through comparisons with the conventional flux-gradient method. The REA method has also been configured to measure particle fluxes [15]. Different accumulators may be used to collect updraft and downdraft REA samples. In the present study, annular denuders and filter packs served as REA accumulators. Zhu et al [16] and Pryor and Klemm [17] used denuders with the REA method to successfully collect NH\textsubscript{3} and HNO\textsubscript{3}, respectively. The current REA method with annular denuders and filter packs was applied to assess NH\textsubscript{3} flux over grassland and soybeans [18]. Overall, the REA method offers an ideal alternative to the other traditional techniques because it does not require fast-response sensors for each experimental scalar. Fast-response sensors are necessary to allow eddy correlation measurement of fluxes. The REA system can also provide deposition information for several species during a single experiment [19]. Supplementary material concerning this REA system is detailed by Meyers et al [6].

In order to incorporate dry deposition parameters into atmospheric models, an estimate of deposition velocity is necessary. The deposition velocity (\(V_d\)) is an engineering factor defined as the ratio of the vertical flux (\(F\)) to the concentration (\(C\)) of a scalar at a height (\(z\)) [20]:

\[
V_d = -\frac{FC}{z^{'}}\text{.}
\]

The measured concentrations and calculated fluxes from REA samples may be used to estimate deposition velocity.

2.2. Sample collection and analysis

Annular denuders and filter packs (URG Corp, Chapel Hill, NC) were used to collect reactive basic and acidic gases as well as strongly acidic particles in updraft, mid-draft and downdraft wind eddies. The three experimental annular denuder systems (ADS), as well as one field blank ADS, were attached to a sampling manifold. This arrangement allowed the 20 L min\(^{-1}\) sample flow to enter the system through a single inlet, a Teflon\textsuperscript{®}-coated glass elutriator-impactor, which eliminated atmospheric particles with an aerodynamic diameter of 2.5 \(\mu\)m or greater and maximized sample collection efficiency at 20 L min\(^{-1}\). A Teflon\textsuperscript{®}-coated plastic rain shield prevented precipitation from entering the elutriator-impactor and causing interference. Two sizes of annular denuders were coupled in series to the manifold for sample collection. Acid-coated denuders were placed first in series before base-coated denuders. In preliminary studies, the authors found no measurable difference between this configuration and a base-then-acid series configuration. Figure 1 shows the ADS and other REA equipment attached to the experimental tripod. From 1 to 7 May 2002, all short denuders (30 mm o.d. \(\times\) 150 mm length, three-channel with 1 mm annular spacing) were coated with 10 mL of 1\% citric acid solution to collect NH\textsubscript{3}. In order to increase collection efficiency and prevent NH\textsubscript{3} volatilization, all subsequent acid coatings were made...
with a 1% phosphorus acid coating solution, which was found to have a greater collection efficiency by Perrino and Gherardi [21]. Each long denuder (30 mm o.d. × 242 mm length, three-channel with 1 mm annular spacing) was coated with 10 mL of a 1% sodium carbonate solution in 2% glycerin in methanol to collect HNO₃ and SO₂. The final component of the ADS was a two-stage filter pack assembly (47 mm o.d.), which housed a Whatman® PTFE membrane filter with a polypropylene back (1 μm pore size) to collect the particulate SO₄²⁻. Guidelines for the ADS preparation and extraction were developed from the US EPA Compendium Method IO 4.2: ‘Determination of Reactive Acidic and Basic Gases and Strong Acidity of Atmospheric Fine Particles (<2.5 μm)’ [22].

After sample collection, denuders were extracted with 20 mL of 18 MΩ deionized water; exposed filters were extracted with a solution of 90% deionized water and 10% methanol. Sample extracts were analyzed with a Dionex DX-80 (Dionex Corp, Sunnyvale, CA) ion chromatograph (IC). The DX-80 was outfitted with an IonPac AS14A—5 μm (3 × 150 mm) analytical column and a GS14A guard column for anion separation that utilized an eluent solution of 0.16 M Na₂CO₃ and 0.02 M NaHCO₃. Ammonium was separated from the sample solution with an IonPac CS12A—5 μm (3 × 150 mm) analytical column and a CS12A guard column with 0.4 M methanesulfonic acid solution as the eluent. Flow rates were regulated at 1 mL min⁻¹ and sample loops held at 10 μL each.

2.3. Sampling program
The field experiment was conducted near Sydney, FL on the Valrico Advanced Wastewater Treatment Plant’s tertiary sprayfield (N 27°57.5’, W 82°13.8’), which served as the core experimental site for the Bay Regional Atmospheric Chemistry Experiment (BRACE). The sprayfield is approximately 263 acres with 1715 sprayheads that have a design capacity of 41,548 L min⁻¹ and is bordered by three ponds on the northeast and southern sides. Spraying of treated effluent on the study area was suspended during the BRACE study. Vegetation on the sprayfield was primarily grass, probably bahiagrass and bermudagrass, interspersed with tufts of cogongrass. Average vegetation height was approximately 8–10 cm with scattered patches greater than 30 cm.

All equipment was mounted on a tripod located approximately 30 m to the south of the research buildings. Data from winds in the direction of the research buildings (north of the sampling equipment) were excluded from this analysis. The 3D sonic anemometer and impactor inlet were mounted on the tripod at a height of 2 m (figure 2). Air flow to the system was supplied by a diaphragm pump and the flow rate of 20 L min⁻¹ was maintained by a mass-flow controller (Sierra Instruments, Monterey, CA). Constant air flow through the system was directed to one of the three ADS (updraft, downdraft and mid-channel), based on the vertical wind velocity (w). When the value of w fell below the deadband value (0.3σ_w), the airflow switched to the mid-channel ADS. The effective sampling volume of each channel was ≈1.6 m³. In laboratory testing of the sampling system, the precisions (coefficients of variation, CV = σ̅x⁻¹ where σ is the standard deviation and ̅x is the mean) of measured NH₃, HNO₃, SO₂ and SO₄²⁻ were 4.2%, 3.4%, 2.0% and 2.1%, respectively. Differences between updraft and downdraft sample concentrations were often an order of magnitude greater than the analytical precision for each species. The minimum relative differences in updraft and downdraft concentrations were 5.1% for NH₃, 4.6% for HNO₃,
2.2% for SO$_2$ and 2.4% for SO$_2^{-4}$. The mean concentration gradients for each species were $0.70 \pm 0.14 \, \mu g \, m^{-3}$ for NH$_3$, $0.31 \pm 0.08 \, \mu g \, m^{-3}$ for HNO$_3$, $0.51 \pm 0.08 \, \mu g \, m^{-3}$ for SO$_2$ and $0.80 \pm 0.10 \, \mu g \, m^{-3}$ for SO$_2^{-4}$. The estimated analytical uncertainty of the measured fluxes is $\sim 18\%$. Samples were collected from 28 April to 31 May 2002 (Julian Days 118–151) for two 4 h periods per day (approximately 0700–1100 EST and 1130–1530 EST). Measurements were not taken during precipitation events.

### 3. Results and discussion

The updraft concentrations, downdraft concentrations, fluxes and deposition velocities of NH$_3$, HNO$_3$, SO$_2$ and SO$_2^{-4}$ are listed in table 1. All concentrations were blank corrected and the mean values represent averages of species concentrations in the measured wind eddies. The relatively large extraction volumes (20 mL) may have diluted some samples to concentrations below instrument detection levels. The average standard deviation of the vertical wind velocity ($\sigma_w$) from the 46 4 h sampling periods presented here was $0.43 \pm 0.01 \, m \, s^{-1}$. The mean $\beta$ coefficient for the entire sampling period was $0.54 \pm 0.02 \, (n = 46)$, which was calculated by equation (2). This agreed well with the range of $\beta$ values from previous studies by Baker [11] and Milne et al [10]. The morning and afternoon sampling periods preclude the application of this data set to the determination of diurnal trends since samples were not collected during evening and overnight hours. However, the sampling periods do provide data that are useful in the characterization of daytime fluxes over grass for the species measured. The ranges of concentrations and flux values are indicative of both the experimental error and natural variability of each species.

#### 3.1. Ammonia (NH$_3$)

The mean NH$_3$ concentration and standard error was $1.64 \pm 0.23 \, \mu g \, m^{-3}$ for all of the collected samples (updraft, downdraft and mid-channel). The mean value is similar to concentrations reported by Meyers et al [6] over crops without recent fertilization. Comparison with other REA-based NH$_3$ measurements is difficult given that studies frequently measure NH$_3$ volatilization from fertilized vegetation. Only 7 of the 18 sample runs exhibited larger concentrations in downdrafts than in updrafts, which indicated deposition of NH$_3$ to the canopy (table 1). The values of these negative fluxes were relatively large compared to the positive flux quantities (i.e. emission). Therefore, ammonia’s mean deposition rate and standard error was $-0.036 \pm 0.055 \, \mu g \, N \, m^{-2} \, s^{-1}$, which is in the range of values measured by Phillips et al [5]. Confidence limits at the 95% level for the mean NH$_3$ flux were $-0.047$ and $-0.024 \, \mu g \, N \, m^{-2} \, s^{-1}$.

#### 3.2. Nitric acid (HNO$_3$)

For the 14 HNO$_3$ samples, the mean concentration was $2.06 \pm 0.24 \, \mu g \, m^{-3}$. The HNO$_3$ concentration falls in the range of values measured by Danalatos and Glavas [23] in a coastal area during midday in the spring season. Nitric acid was deposited on the surface in 13 of the 14 viable samples (table 1). The resulting mean HNO$_3$ flux was $-0.057 \pm 0.015 \, \mu g \, N \, m^{-2} \, s^{-1}$. Confidence limits of the mean HNO$_3$ flux at the 95% level were $-0.088$ and $-0.027 \, \mu g \, N \, m^{-2} \, s^{-1}$.

#### 3.3. Sulfur dioxide (SO$_2$)

Sulfur dioxide exhibited moderately large concentration maxima of $8.08 \, \mu g \, m^{-3}$ in the updraft samples and $9.60 \, \mu g \, m^{-3}$ in the downdraft samples (table 1). The mean SO$_2$ concentration for the entire experiment was $3.49 \pm 0.50 \, \mu g \, m^{-3}$. 

![Figure 2. Schematic of the REA system with annular denuders and filter packs.](image-url)
Table 1. Relaxed eddy accumulation parameters including updraft concentrations ($C_u$), downdraft concentrations ($C_d$), fluxes and deposition velocities ($V_d$) for each species. Also included are empirical coefficients ($\beta$) and standard deviations of the vertical wind velocity ($\sigma_u$).

| Day  | $C_u$ (µg m⁻³) | $C_d$ (µg m⁻³) | Flux NH₃ (µg m⁻³ s⁻¹) | V_h NH₃ (µm s⁻¹) | Flux HNO₃ (µg m⁻³ s⁻¹) | V_h HNO₃ (µm s⁻¹) | Cₑ SO₂ (µg m⁻³) | Flux SO₂ (µg m⁻³ s⁻¹) | V_h SO₂ (µm s⁻¹) | Cₑ SO₂⁺ (µg m⁻³) | Flux SO₂⁺ (µg m⁻³ s⁻¹) | V_h SO₂⁺ (µm s⁻¹) | $\beta$ | $\sigma_u$ (m s⁻¹) |
|------|----------------|----------------|------------------------|------------------|-----------------------|------------------|----------------|------------------|------------------|----------------|------------------|------------------|-------|----------------|
| 118-1| —              | —              | —                      | —                | —                     | —                | —              | —                | —                | —              | —                | —                | —     | —              |
| 119-1| 0.56           | 0.71           | 0.041                  | 6.46             | —                     | —                | —              | —                | —                | —              | —                | —                | —     | 0.52           |
| 120-1| —              | —              | —                      | —                | —                     | —                | —              | —                | —                | —              | —                | —                | —     | —              |
| 121-1| —              | —              | —                      | —                | —                     | —                | —              | —                | —                | —              | —                | —                | —     | —              |
| 122-1| —              | —              | —                      | —                | —                     | —                | —              | —                | —                | —              | —                | —                | —     | —              |
| 123-1| —              | —              | —                      | —                | —                     | —                | —              | —                | —                | —              | —                | —                | —     | —              |
| 124-1| —              | —              | —                      | —                | —                     | —                | —              | —                | —                | —              | —                | —                | —     | —              |
| 125-1| —              | —              | —                      | —                | —                     | —                | —              | —                | —                | —              | —                | —                | —     | 0.26           |

Mean: 1.68 1.79 — 0.036 1.27 1.93 2.23 — 0.057 3.63 3.75 3.88 — 0.034 0.45 4.61 4.79 — 0.038 0.32 0.42 0.54 0.43
Median: 1.68 1.79 — 0.036 1.27 1.93 2.23 — 0.057 3.63 3.75 3.88 — 0.034 0.45 4.61 4.79 — 0.038 0.32 0.42 0.54 0.43
Std dev: 1.06 1.30 — 0.233 1.59 0.79 0.93 — 0.054 5.51 2.40 2.55 — 0.140 4.90 7.67 — 0.176 0.22 0.20 0.32 0.10
Std err: 0.31 — 0.055 0.36 0.21 0.25 0.05 1.04 0.51 0.08 0.30 0.05 0.10 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.01
Min: 0.46 0.64 — 0.059 — 0.233 0.68 0.06 0.213 1.36 0.09 0.043 — 0.043 — 0.26 0.12 0.02 0.01 0.02 0.01 0.02
Max: 4.56 5.26 0.45 0.461 3.19 3.55 4.03 0.019 21.66 9.08 9.60 0.189 10.88 7.98 9.05 0.357 11.92 1.15 0.15 0.02 0.15 0.02

Note: The values are given in micromoles per cubic meter (µg m⁻³) for concentrations, micromoles per cubic meter per second (µg m⁻³ s⁻¹) for fluxes, and centimeters per second (cm s⁻¹) for deposition velocities and vertical wind velocities.
Higher mean concentration values were found in afternoon samples (mean = 3.98 ± 0.71 μg m\(^{-3}\)) versus the concentrations in morning samples (mean = 2.87 ± 0.65 μg m\(^{-3}\)), though the difference is not statistically significant. The mean deposition rate for SO\(_2\) was -0.034 ± 0.028 μg m\(^{-2}\) s\(^{-1}\). At the 95% level, the confidence interval for SO\(_2\) flux was -0.091 and 0.024 μg m\(^{-2}\) s\(^{-1}\).

3.4. Particulate sulfate (SO\(_{2}^-\))

The SO\(_{2}^-\) mean concentration during the experiment was 4.64 ± 0.31 μg m\(^{-3}\). During the second week of sampling, several rain events occurred which lowered the ambient levels of SO\(_{2}^-\). However, the calculated SO\(_{4}^2\) deposition rates did not vary much over the length of the experiment, with a difference of less than 1.0 μg m\(^{-2}\) s\(^{-1}\) between the minimum and maximum fluxes, -0.60 μg m\(^{-2}\) s\(^{-1}\) and 0.34 μg m\(^{-2}\) s\(^{-1}\), respectively (table 1). The SO\(_{4}^2\) mean flux was -0.038 ± 0.035 μg m\(^{-2}\) s\(^{-1}\). At the 95% level, the confidence interval for particulate SO\(_{4}^2\) flux was -0.11 and 0.034 μg m\(^{-2}\) s\(^{-1}\).

3.5. Calculations of scalar deposition velocities

Deposition velocities (\(V_d\)) of NH\(_3\), HNO\(_3\), SO\(_2\), and SO\(_{2}^-\) were derived from experimental data by modifying equation (3) to

\[
V_d = -F_a[(\bar{C}_{up} + \bar{C}_{dn})0.5]^{-1}
\]

(4)

where \(F_a\) is the scalar flux and \(\bar{C}_{up}\) and \(\bar{C}_{dn}\) are the average values of the concentrations in the updrafts and downdrafts [15]. Mean deposition velocities were 1.27 ± 3.65 cm s\(^{-1}\) for NH\(_3\), 3.63 ± 1.47 cm s\(^{-1}\) for HNO\(_3\), 0.45 ± 0.98 cm s\(^{-1}\) for SO\(_2\), and 0.42 ± 1.00 cm s\(^{-1}\) for SO\(_{2}^-\) (table 2). Dry deposition velocity estimates of atmospheric gases may also be determined by utilizing the resistance analogy based on Ohm’s law [24]. The resistance model assumes a zero scalar concentration at the receptor surface (\(X_r = 0\)) which allows the deposition flux (\(F\)) to be expressed as the following equation:

\[
F = -\chi_a(R_a + R_b + R_c)^{-1}
\]

(5)

where \(\chi_a\) is the atmospheric concentration, \(R_a\) is the aerodynamic resistance, \(R_b\) is the quasi-laminar boundary layer resistance and \(R_c\) is the surface resistance. Therefore, the deposition velocity of atmospheric gases becomes a function of these resistance terms:

\[
V_d = (R_a + R_b + R_c)^{-1}
\]

(6)

Micrometeorological data were utilized to determine \(R_a\) and \(R_b\) from the following equations:

\[
R_a = \bar{u}^2\alpha_u^{-1}
\]

(7)

\[
R_b = 5(S_c 0.67 u_a^{-1})
\]

(8)

where \(\bar{u}(\alpha)\) is the mean streamwise wind speed, \(u_a\) is the friction velocity and \(S_c\) is the Schmidt number, which is calculated by dividing the kinematic viscosity of air (\(\nu\)) by the molecular diffusivity coefficient (\(D\)) of the scalar gas [20, 24].

The surface resistance, \(R_s\), is assumed to be zero for NH\(_3\) because it exhibits bidirectional movement (deposition and emission) at the canopy surface. Upon determination of resistance analogy deposition velocities from equation (6), comparisons between deposition velocity estimates from concentration and flux data and those from the resistance analogy were made to determine the validity of the \(R_s = 0\) assumption. For NH\(_3\), the deposition velocity values were similar and appeared to uphold the supposition that the receptor surface does not resist uptake of these species (table 2). The generally low NH\(_3\) concentrations for nearly all of the experiment resulted in high run to run variability in NH\(_3\) deposition velocities and a large coefficient of variation. The large uncertainty in NH\(_3\) fluxes precludes any detailed analysis of the experimental data to definitively assess the compensation point, although it is probably small given the low concentrations observed during the experimental period. The bi-directionality of NH\(_3\) fluxes also suggests that two-source models (e.g. soil, canopy) are used although, in this case, NH\(_3\) fluxes to or from the sandy soils were probably low and no attempt was made to separate out the soil fluxes of NH\(_3\) from the total flux measured above the canopy. The estimated deposition velocity was higher than the resistance analogy value for HNO\(_3\), which may have resulted from an underestimation of \(R_s\), which was similarly noted by Meyers et al [7].

For SO\(_2\), the \(R_s = 0\) assumption was not valid. The surface resistance parameterization from Wesely [25], which is sensitive to seasonal category and land use type, produced an \(R_s\) value of 222 s m\(^{-1}\) for SO\(_2\). When this value was placed into equation (6), the resistance analogy deposition velocity of SO\(_2\) was determined as 0.39 cm s\(^{-1}\), which was more in line with, but slightly lower than, the estimated value of 0.45 cm s\(^{-1}\). Matt et al [26] found a similar relationship between measured and modeled SO\(_2\) deposition velocities and attributed the difference to stomatal resistance influence upon the \(R_c\) parameter.

The dry deposition velocity of atmospheric particles may also be determined from the resistance model as shown below:

\[
V_d = v_t + (R_a + R_b + (R_c R_b v_t))^{-1}
\]

(9)

where \(v_t\) is the terminal settling velocity of the particle:

\[
v_t = D_p^2\rho_\gamma g C(18\mu)^{-1}
\]

(10)
Here $D_b$ is the particle diameter, $\rho_p$ is the particle density, $g$ is the acceleration due to gravity, $C$ is the slip correction factor and $\mu$ is the absolute viscosity of air. The $R_a$ parameter is calculated in the same manner for particles and gases (equation (7)) while the $R_b$ parameter for particles is reliant upon Brownian diffusion and is determined from the following equation:

$$R_b = \left( u_{*} \left( \frac{S}{C^2 \mu} + \frac{10^{-3/3}S}{} \right) \right)^{-1} (11)$$

where $S$ is the Stokes number, which is the dimensionless ratio of particle stop distance ($s_p$) to the characteristic length of flow ($L$) [27, 28]. Equation (9) yielded a deposition velocity of 0.01 cm s$^{-1}$ for SO$_2^-$ (table 2). The estimated value of 0.42 cm s$^{-1}$ is clearly much greater than the value predicted by the methodologies represented by equations (9)–(11), for reasons that remain poorly understood. Allen et al [29] and references therein note the quite large range of SO$_2^-$ deposition velocities. However, there are many reports of measured deposition velocities for particles that are much higher than expectations [30, 6]. The present reports of measured deposition velocities for particles that are much higher than expectations [30, 6]. The present results agree with the methodologies represented by equations (9)–(11), for reasons that remain poorly understood.

4. Conclusions

Concentrations of NH$_3$, HNO$_3$, SO$_2$ and SO$_2^-$ were measured with a relaxed eddy accumulation system over a low grassland sprayfield near Tampa, FL. Mean concentrations of NH$_3$, HNO$_3$, SO$_2$ and SO$_2^-$ were 1.64 ± 0.23, 2.06 ± 0.24, 3.49 ± 0.50 and 4.64 ± 0.31 $\mu$g m$^{-3}$, respectively. Mean fluxes were calculated with standard errors as $-0.036 \pm 0.055 \mu$g N m$^{-2}$ s$^{-1}$ for NH$_3$, $-0.057 \pm 0.015 \mu$g N m$^{-2}$ s$^{-1}$ for HNO$_3$, $-0.034 \pm 0.028 \mu$g m$^{-2}$ s$^{-1}$ for SO$_2$ and $-0.038 \pm 0.035 \mu$g m$^{-2}$ s$^{-1}$ for SO$_2^-$. Deposition velocity estimates from measured concentration and flux data for NH$_3$, HNO$_3$, SO$_2$ and SO$_2^-$ were 1.72 ± 3.65, 3.63 ± 1.47, 0.45 ± 0.98 and 0.42 ± 1.00 cm s$^{-1}$, respectively. These values compared well with resistance analogy deposition velocities for all species, except HNO$_3$ and SO$_2^-$. The zero surface resistance assumption seems to hold for NH$_3$ though it is noted that low concentrations during the experiment preclude the determination of a compensation point. The relatively large surface resistance of SO$_2$ seems to indicate a dominance of stomatal resistance.

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