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Atmospheric Measurement Techniques Discussions

A relaxed eddy accumulation system for measuring vertical fluxes of nitrous acid

X. Ren[1,*], J. E. Sanders[1], A. Rajendran[1,], R. J. Weber[2], A. H. Goldstein[2], S. E. Pusede[3], E. C. Browne[3], K.-E. Min[3], and R. C. Cohen[3,4]**

[1]Resenstiel School of Marine and Atmospheric Science, Unirversity of Miami, Miami, FL, USA
[2]Department of Environmental Science, Policy, and Management, University of California at Berkeley, Berkeley, CA, USA
[3]Department of Chemistry, University of California at Berkeley, Berkeley, CA, USA
[4]Department of Earth and Planetary Science, University of California at Berkeley, Berkeley, CA, USA
[*]now at: Air Resources Laboratory, National Oceanic and Atmospheric Administration, Silver Spring, MD, USA
[**]now at: Department of Epidemiology and Public Health, University of Miami, Miami, FL, USA

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Correspondence to: X. Ren (xren@rsmas.miami.edu)

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Abstract

A relaxed eddy accumulation (REA) system combined with a nitrous acid (HONO) analyzer was developed to measure atmosperhic HONO vertical fluxes. The system consists of three major components: (1) a fast-response sonic anemometer measuring vertical wind velocity and air temperature, (2) a fast-response controlling unit separating air motions into updraft and downdraft samplers by the sign of vertical wind velocity, and (3) a highly sensitive HONO analyzer based on aqueous long path absorption photometry measuring HONO concentations in these updrafts and downdrafts. A dynamic velocity threshold ($\pm 0.5\sigma_w$, where σ_w is a standard deviation of the vertical wind velocity) was used for valve switching determined by the running means and standard deviations of the vertical wind velocity. Using measured temperature as a tracer and the average values from two field deployments, the flux proportionality coefficient, β, was determined to be 0.42 ± 0.02, in good agreement with the theoretical estimation. The REA system was deployed in two ground-based field studies. In the California Research at the Nexus of Air Quality and Climate Change (CalNex) study in Bakersfield, California in summer 2010, measured HONO fluxes appeared to be upward during the day and were close to zero at night. The upward HONO flux was highly correlated to the product of NO_2 and solar radiation. During the Biosphere Effects on Aerosols and Photochemistry Experiment (BEARPEX 2009) at Blodgett Forest, California in July 2009, the overall HONO fluxes were small in magnitude and were close to zero. Causes for the differences in HONO fluxes in the two different environments are briefly discussed.

1 Introduction

The traditional eddy covariance (EC) technique for flux measurement requires the use of sensors that can respond at fast frequencies (~10 Hz). This constraint can not always be met for the measurement of many atmospheric chemical species. The relaxed eddy accumulation (REA) method thus represents great potential as a suitable

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alternative for the EC technique for micrometeorological flux measurement of atmospheric species when fast response sensors are not available. The REA method was derived from the eddy accumulation (EA) method that was first suggested by Desjardins (1972) and involves sampling the air depending on the magnitude and direction of the vertical wind velocity. The REA method, proposed by Businger and Oncley (1990), separates the air samples into updraft and downdraft reservoirs at a constant flow rate, based solely on the sign of the vertical wind. Concentrations in the updraft and downdraft eddy motions are determined by an analytical sensor and the flux is calculated proportional to the difference in concentration between the updrafts and downdrafts (Meyers et al., 2006). Details on the theory and derivation of the REA technique can be found in the literature (e.g., Businger and Oncley, 1990; Baker et al, 1992; Dabberdt et al., 1993; Pattey et al., 1993). Because in-situ concentration measurements are not necessary, the REA technique also allows for the use of laboratory instrumentation, which may have higher accuracy than portable sensors but is too bulky or delicate for field use (Nie et al., 1995).

The REA technique has increased in popularity and has been successfully used to measure the fluxes of a number of traces gases and aerosols, for example volatile organic compounds (Guenther et al., 1996; Valentini et al., 1997; Bowling et al., 1998; Pattey et al., 1999; Gallagher et al., 2000; Schade and Goldstein, 2001; Olofsson et al., 2003; Hornsby et al., 2009), ammonia (Zhu et al., 2000), stable isotope of $^{13}C^{16}O_2$ and $^{12}C^{18}O^{16}O$ (Bowling et al., 1999), nitrous oxide (Xi et al., 1996), total gaseous mercury (Cobos et al, 2002; Olofsson et al., 2005; Bash and Miller, 2008), and aerosol particle numbers (Schery et al., 1998; Gaman et al., 2004). There are only a few attempts to measure atmospheric nitrous acid (HONO) fluxes, mostly derived from the gradient method (e.g., Harrison and Kitto, 1994; Neftel et al., 1996; Honrath et al., 2002; Stutz et al., 2002; Beine et al., 2004; 2005). To our knowledge, there are very limited HONO flux measurements using the REA method (Bertman et al., 2003; Zhou et al., 2011). Nitrous acid (HONO) plays an important role in atmospheric chemistry because of its photolysis to form the hydroxyl (OH) radical, the most important atmospheric oxidant

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(Alicke et al., 2003; Kleffmann et al., 2005; Ren et al., 2006; Mao et al., 2010). Significant daytime HONO levels and fast HONO loss through its photolysis indicate that a strong HONO production rate exists in many environments. This suggests that HONO plays an important role in total reactive nitrogen (NO_y) cycling (Ren et al., 2010), despite the fact that HONO usually constitutes a small fraction of NO_y. Measurement of HONO concentrations and fluxes is thus of great interest and is important to understand the roles HONO plays in atmospheric photochemistry and nitrogen budget.

In this paper, we present the development of a REA system for the measurement of atmospheric HONO fluxes. The REA system was characterized and deployed in two recent field studies: the California Research at the Nexus of Air Quality and Climate Change (CalNex 2010) study in Bakersfield, California in summer 2010 and the Biosphere Effects on Aerosols and Photochemistry Experiment (BEARPEX 2009) at Blodgett Forest, California in July 2009. Measurement results of HONO fluxes in these two field studies are briefly discussed.

2 Methods

2.1 Relaxed eddy accumulation

A relaxed eddy accumulation (REA) system was developed to measure atmospheric HONO vertical fluxes. The system samples wind eddies based on the sign of vertical wind velocity over an extended time interval. Updraft (w^+) and downdraft (w^-) air samples are collected into separate HONO samplers when the vertical wind velocities are out of a deadband (defined below). The vertical mass flux of HONO (F_{HONO}) can be determined by the following equation (Businger and Oncley, 1990):

$$F_{HONO} = \beta \sigma_w (\bar{C}_{up} - \bar{C}_{down}) \quad (1)$$

where, σ_w is the standard deviation of the vertical wind velocity, $\bar{C}_{up}$and $\bar{C}_{down}$ are the average HONO concentrations in the updrafts and downdrafts, respectively, and β is the flux proportionality coefficient. The calculation of β is described in Sect. 3.1.

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A dynamic velocity deadband of $0.5\sigma_w$ was implemented to maximize the difference between updraft and downdraft concentrations. Such a varying threshold made the flux proportionality coefficient, β, independent of observation conditions (Gaman et al., 2004). Instantaneous vertical wind velocity was sampled and the moving averages ($\bar{w}$) and standard deviations (σ_w) of vertical wind velocity during the predefined running average interval (set to 5 min, which is used by a REA method (e.g., Nie et al., 1995)) were calculated. When the deviation of current vertical wind velocity ($w^+ = w - \bar{w}$) was greater than $+0.5\sigma_w$, the air sample flow was diverted to the updraft sampler to measure HONO in the updraft air samples ($\bar{C}_{up}$). When the deviation of vertical wind velocity ($w^- = w - \bar{w}$) was smaller than $-0.5\sigma_w$, the air sample flow was diverted to the downdraft sampler to measure HONO in the downdraft air samples ($\bar{C}_{down}$). Concentrations of HONO in the updraft and downdraft samples were then measured by a HONO analyzer as described in Sect. 2.2.

Our REA-HONO system consists of a 3-D sonic anemometer (Campbell Scientific, Model CST3), a controlling unit to divert air into updraft and downdraft samplers depending on the sign of vertical wind velocity, and a HONO analyzer (described in Sect. 2.2). The sonic anemometer collects 3-dimensional wind components: two horizontal components (u and v) and one vertical component (w), and virtual temperature of air. The controlling unit includes a computer with data acquisition hardware/software and two fast-response 3-way solenoid valves (Fluorocarbon Delta Solenoid Valve, Model DV3-144D2), one each for updraft and downdraft sampling. The wind and temperature signals from the anemometer are collected by the computer through a USB analog to digit converter (Measurement Computing, Model USB-1208FS) at a sampling frequency of 10 Hz. Moving averages and standard deviations (σ_w) of vertical wind velocity with a 5 min interval are updated instantaneously. The computer then determines the motion of air (updraft or downdraft) as described previously and holds the previous air motion status for the about 350 ms until the air arrives at the solenoid valve system. The computer then operates the valves accordingly to divert the air into the updraft sampler or downdraft sampler, or in case the air motion falls in the deadband

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(i.e., the deviation of current vertical wind velocity greater than $-0.5\sigma_w$, but less than $0.5\sigma_w$), the valves are switched to positions to sample zero air. In summary, this REA system was operated according to the following steps, repeated after every sample interval of 0.1 s:

1. Vertical wind velocity and air temperature are read from the anemometer via a universal serial bus (USB) analog to digital converter.
2. Moving average and standard deviation in a previous 5 min interval are calculated and updated.
3. Based on the instantaneous vertical wind velocity and threshold of $\pm 0.5\sigma_w$, valve positions are determined and the corresponding command is sent via USB port to update the valve status after waiting for the time for the air to travel through the sample line.
4. Depending on the REA valve positioning, the number of data points and average temperature statistics in the updraft/downdraft/deadband vertical wind speed interval are updated.

At the end of each averaging period (usually 30 min) for flux calculation, the percentages of time for updraft, downdraft and deadband sampling and the corresponding average temperatures are calculated and the average statistics are saved for further analyses. The computer used for the REA-HONO system has a Windows XP operation system and a data acquisition program based on Visual Basic to conduct the above calculations, control the valves, and acquire data from the anemometer and the HONO analyzer. A schematic of the REA system for HONO vertical flux measurement and its field installation are shown in Fig. 1.

2.2 HONO analyzer

In our REA system, a HONO analyzer is used to measure HONO concentrations in updraft and downdraft air samples. Its technique is based on aqueous coil scrubbing

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followed by nitrite derivatization to a highly light-absorbing azo dye, which is then detected with liquid waveguide long path absorption photometry. A detailed description of this instrument can be found elsewhere (Ren et al., 2010). Here a brief description is given. Ambient air was pulled through a light-shielded Teflon tubing (OD = 6.35 mm, and ID = 3.96 mm, length = 5.3 m) to a manifold at flow rate of about 11 l min^{-1}, 2 l min^{-1} of which was fed either the HONO instrument's updraft or downdraft sampler. The instrument was housed in an instrument rack near the anemometer. The inlet of the sampling tubing was mounted next to the anemometer sensor at a height of 13.5 m above the ground. Inside each sampler, ambient air was pulled through 10-turn glass coil by a vacuum pump and the air flow rate was controlled by a mass flow controller at 2 l min^{-1}. A phosphate buffer with a concentration of 1.0 mmol l^{-1} was used as a scrubbing solution to collect HONO in the air sample. After the separation from the gas phase, the scrubbing solution was mixed with sulfanilamide (SA) and N-(1-naphthyl) ethylenediamine (NED) reagents. The mixture was then pumped through a Teflon derivatization coil, where nitrite was converted to an azo dye, which was detected by a long path absorption photometer.

The HONO instrument was calibrated using sodium nitrite ($NaNO_2$) standard solutions as well as a HONO generation system (Ren et al., 2010). The detection limit of the HONO analyzer was about 3 pptv with a 2-min integration time required by the HONO sampling and analysis and the measurement uncertainty was about ±15 % at a 2σ confidence level.

As shown in Fig. 1, the REA system consisted of a manifold with air flow split into two flow paths: the sample flow for either the updraft or downdraft sampler and the bypass flow (mass flow control #1 (MFC#1) in Fig. 1). In order to keep the air flow rates through the updraft and downdraft samplers constant, HONO-free zero air from a zero air generator (Perma Pure, LLC) was fed into the samplers when an air motion fell in a "deadband" or when one sampler was sampling zero air while the other sampler was sampling ambient air in either updraft or downdraft case. The zero air flow rate was controlled by a mass flow controller at 4.5 l min^{-1}, which exceeds the total

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sampling flow rate of 4 l min^{-1} during deadband periods. Extra zero air flow was vented to the ambient air through a tee connection to maintain the zero air pressure at the atmospheric pressure.

2.3 Site description

The REA-HONO system was deployed at two field sites: one in Bakersfield, California as part of the CalNex study in summer 2010 and the other at Blodgett Forest, California during the BEARPEX II study in summer 2009. The site of the CalNex study is located at the southern end of the San Joaquin Valley in Bakersfield, California, about 6 km southeast of downtown Bakersfield (35°20′46.2″ N, 118°57′55.9″ W, 120 m elevation). There are two nearby major highways: Highway 58 located at about 800 m north of the site and Highway 99 located at about 6 km west of the site. During the day, the site was influenced by the prevailing wind from downtown Bakersfield. HONO vertical fluxes were measured from 16 May to 29 June 2010 in this study.

The BEARPEX site is located at Blodgett Forest in the western foothills of the Sierra Nevada mountains (38°58′42.4″ N, 120°38′3.4″ W, 1315 m elevation) and has been described in detail elsewhere (e.g., Goldstein et al., 2000; Wolfe et al., 2009; Ren et al., 2010). During this study, HONO vertical fluxes were measured from 4 July to 30 July 2009.

In both field studies, other chemical species, including ozone, detailed nitrogen species (NO, NO_2, HONO, HNO_3, alkyl nitrates, and peroxy nitrates), CO, volatile organic compounds (VOCs), and meteorological parameters, including temperature, pressure, relative humidity, wind direction, wind speed, and solar radiation, were also measured concurrently. The relatively complete suite of chemical and meteorological measurements in the both studies provides a great opportunity to examine the relationship between the measured HONO fluxes and other parameters.

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3 Characterization of the REA system

3.1 Proportionality coefficient, β

The proportionality coefficient, β, is needed to calculate REA fluxes based on Eq. (1). The β-value is thought to depend on atmospheric stability (Ammann and Meixner, 2002; Andreas et al., 1998; Milne et al., 2001). Under ideal atmospheric turbulence conditions such as over flat and homogenous terrain, the proportionality, β, in Eq. (1) has a value of approximately 0.6 (Businger and Oncley, 1990; Baker et al., 1992; Katul et al., 1996) when a vertical velocity threshold of zero is used. When a non-zero threshold issued, the proportionality coefficient is generally constant and commonly calculated from sensible heat flux and vertical air temperature that correspond to the sampled up and downdrafts (Businger and Oncley, 1990; Katul et al., 1996; Bowling et al., 1998; Schade and Goldstein, 2001), as shown in the following equation:

$$\beta = \frac{\overline{w'T'}}{\sigma_w(\bar{T}_{\text{up}} - \bar{T}_{\text{down}})} \tag{2}$$

where w' and T' are the fluctuating components of the instantaneous measured vertical wind velocity (w) and air temperature (T), i.e., $w' = w - \bar{w}$ and $T' = T - \bar{T}$, $\bar{T}_{\text{up}}$ and $\bar{T}_{\text{down}}$ denote the average temperatures of the same updrafts and downdrafts as the HONO samples, and σ_w is the standard deviation of the vertical wind velocity over a 30-min collection period. Large uncertainties can be introduced into this calculation when the denominator in Eq. (2) is very small, i.e., during near neutral atmospheric stability, commonly observed during times when the sensible heat flux changes sign in the morning and evening hours (Park et al., 2010).

According to Businger and Oncley (1990), the β-value can also be estimated using the following formula based on numerical simulations:

$$\beta = \beta_0 \exp\left(\frac{-0.75|w_0|}{\sigma_w}\right) \tag{3}$$

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where $\beta_0 = \beta$ ($|w_0| = 0$) ≈0.6, $|w_0|$ is the magnitude of the velocity threshold for up and down sampling (usually between 0 and σ_w) (Gaman et al., 2004). Using this equation, we calculate a β-value of 0.412 for our REA-HONO system, where $|w_0| = 0.5\sigma_w$ was used. During the field deployment, the 3-D sonic anemometer collected virtual temperature concurrently with wind data. Using concurrent observations of vertical wind velocity and temperature during the two field studies, we calculated the averaged daytime β-values to be 0.410 ± 0.018 for CalNex 2010 and 0.441 ± 0.008 for BEARPEX 2009 using Eq. (2), which are close to the value estimated from Eq. (3). The actual β-values determined from Eq. (2) were used in the two field studies to calculate HONO fluxes.

3.2 Time lag and flow dynamics

In order to minimize the time lag, i.e., the total travel time for the air through the sampling line, a manifold was used to pull a large bypass air flow (~9 l min^{-1}) in addition to the sample flow of 2 l min^{-1} (Fig. 1). The time lag was estimated to be about 350 ms based on the total air flow rate and the volume in the sample line. With a tubing inner diameter of 3.96 mm and a length of 5.3 m, the calculated Reynolds number is ~4100 and is greater than the critical Reynolds number of 2300. Thus the flow in the sampling line was most likely turbulent (Bird, 1960).

3.3 Updraft and downdraft statistics

With the use of a dynamic velocity threshold of $\pm 0.5\sigma_w$ to determine the air motion, the average fraction of time when air motion was updraft or downdraft was about 22 % in the both field studies, while the air motion fell in the deadband for the rest 56 % of the time. The HONO concentrations in the updrafts and downdrafts were corrected for the sampling time fractions.

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3.4 Possible sampling artifacts due to sampling line

In the REA-HONO system, a piece of 5.3-m long Teflon tubing was used as a sample inlet and there might be some sampling artifacts due to certain wall reactions forming HONO. The possible interferences have been tested with our HONO analyzer in the laboratory and there was no HONO loss through a longer piece of Teflon tubing (Ren et al., 2010). Furthermore, in the field we conducted an additional test with a dry annular denuder coated with sodium carbonate by connecting the denuder to the sample inlet. The denuder removes HONO efficiently but retains most of the particles, NO_2, PAN, and other organic nitrates in the air flow. The signals obtained from the ambient air through the denuder were essentially the same as the signals from zero air, indicating no significant HONO interferences through the sample line. By using a large manifold flow (totally ~11 l min^{-1}) in our configuration (Fig. 1), the possible artifacts due to sample tubing were significantly suppressed. Even if there is a small amount of artifact present, it would appear in both updraft and downdraft samples and be cancelled out because only the difference of HONO concentration between updraft and downdraft samples was used in the HONO flux calculation.

4 Applications

The developed REA system was deployed to measure HONO fluxes in two field studies: CalNex 2010 in Bakersfield, California and BEARPEX 2009 at Blodgett Forest, California. Measurement results of HONO fluxes, other chemical species, and meteorological parameters in the two field studies are briefly discussed below.

4.1 CalNex 2010

The time series of observed HONO fluxes and HONO concentrations are shown in Fig. 2. The HONO flux varied from a minimum of −0.3 nmol m^{-2} s^{-1} (downward) to a maximum of 0.5 nmol m^{-2} s^{-1} (upward). The observed HONO exhibits a typical diurnal

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variation with a lowest concentration in the late afternoon of ~30 pptv and a highest concentration in the early morning of 2000 pptv. The observed HONO and HONO flux levels are comparable to the measurements at other urban/suburban locations (e.g., Harrison and Kitt, 1994; Stutz et al., 2002). For instance, Harrison and Kitt (1994) observed HONO fluxes varying from −0.21 to 0.53 nmol m^{-2} s^{-1} over a grassland in eastern England. Zhou et al. (2011) reported similar upward HONO fluxes with a maximum flux of ~0.19 nmol m^{-2} s^{-1} during the day at the Program for Research on Oxidants: PHotochemistry, Emissions, and Transport (PROPHET) site located in a forested area in northern Michigan, despite lower levels of NO_x observed at the site compared to typical urban/suburban sites.

The diurnal variations of chemical species and meteorological parameters are shown in Figure 3. On average, HONO fluxes appeared to be upward during the day with a maximum of ~0.1 nmol m^{-2} s^{-1} observed in the morning and were close to zero (-0.007 ± 0.017 nmol m^{-2} s^{-1}) at night. The observed daytime HONO fluxes are reasonable considering the moderate levels of reactive nitrogen species existing in San Joaquin Valley. Highest HONO fluxes were observed when winds were from northwest, where downtown Bakersfield is located.

Previous studies have found that there are a few photochemical homogeneous and heterogeneous processes that can produce HONO. The reaction of photolytically excited NO_2 (NO_2^*) with water (Li et al., 2008) can produce HONO and OH, although the reaction rate and yield of HONO and OH are still under debate and this mechanism likely contributes insignificantly to atmospheric HONO formation (Carr et al., 2009; Sörgel et al., 2011). Several heterogeneous processes involving photolysis can also form HONO. For example, the photosensitized reduction of NO_2 on organic surfaces such as aromatics and humic acids can produce HONO (George et al., 2005; Stemmler et al., 2006). The photolysis of surface adsorbed nitric acid (HNO_3) and nitrate can act as a source of HONO and thus serve as an important pathway for the remobilization of deposited HNO_3 (Zhou et al., 2002, 2003, 2011). The conversion of NO_2 on fresh soot particles and secondary organic aerosols is also a source of HONO

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(Ammann et al., 1998; Arens et al., 2001; Monge et al., 2010), although the roles of these processes are still under discussion (Arens et al., 2001; Bröske et al., 2003; Aubin and Abbatt, 2007; Sörgel et al., 2011). Lastly, the photolysis of o-nitrophenol and its methylated analogues can produce HONO (Bejan et al., 2006), but this mechanism is only important in urban areas where concentrations of nitrophenols are high.

The photochemical production of HONO near the earth surface can contribute to HONO vertical fluxes. During CalNex 2010, we observed a very strong correlation (r^2 = 0.985) between HONO flux and the product of NO_2 concentration and solar radiation during the daytime from late morning to early evening, when the boundary mixing layer was expected to be fully developed (Fig. 4). A similar correlation between NO_2 and upward HONO fluxes was observed by Harrison and Kitto (1994), although in this study the upward HONO fluxes were usually associated with higher NO_2 levels (>10 ppbv) than the daytime NO_2 levels (~3–5 ppbv) observed during this study. The correlation is poor between the HONO flux and NO_2 only (r^2 = 0.21) or between the HONO flux and solar radiation only (r^2 = 0.27), suggesting that the reduction of NO_2 involving sunlight might be an important HONO source in this environment, in agreement with the finding during the DOMINO (Diel Oxidant Mechanism In relation to Nitrogen Oxides) campaign in southwest Spain (Sörgel et al., 2011).

4.2 BEARPEX 2009

Measurements of HONO concentration and flux at Blodgett Forest during BEARPEX 2009 were quite different from those during CalNex 2010. The measured HONO levels are about one order of magnitude lower than those during CalNex 2010 (Figs. 5 and 6). This is expected because of relatively low levels of reactive nitrogen at Blodgett Forest compared to those in San Joaquin Valley. The HONO levels during BEARPEX 2009 are comparable to the levels observed at the same site during BEARPEX 2007 (Ren et al., 2010).

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Compared to CalNex 2010, the daytime HONO fluxes during BEARPEX 2009 were much lower (Figs. 3 and 6). The average daytime HONO flux was close to zero (-0.004 ± 0.024 nmol m^{-2} s^{-1}) at this forested site. Because of the lower HONO fluxes during BEARPEX 2009 compared to those of CalNex 2010, the correlation between HONO flux and the product of NO_2 and solar radiation is much weaker ($r^2 = 0.43$) during BEARPEX 2009, compared to the strong correlation observed during CalNex 2010. If we apply the relationship between HONO flux and the product of NO_2 and solar radiation during CalNex 2010 in Fig. 4 (a slope of $\sim 3 \times 10^{-8}$ nmol m^{-2} s^{-1} per pptv of NO_2 and per W m^{-2} of solar radiation) to BEARPEX 2009, the corresponding HONO flux is about 0.007 nmol m^{-2} s^{-1} in the midday when the NO_2 concentration was about 300 pptv and the solar radiation was about 800 W m^{-2} during BEARPEX 2009. This value is about the average level we observed at Blodgett during the day and is below the detection limit of the REA-HONO system (~0.01 nmol m^{-2} s^{-1}).

Much smaller HONO fluxes were observed during BEARPEX 2009 compared to the PROPHET site in a broadleaf forest in Northern Michigan, where significant daytime upward HONO fluxes were observed with a maximum of HONO flux of 0.19 nmol m^{-2} s^{-1} observed around noontime (Zhou et al., 2011). This difference is consistent with the lower observed HONO concentrations (~20–30 pptv) during the midday at Blodgett Forest compared to HONO levels (60–120 pptv) at the PROPHET site (Zhou et al., 2011) and some other forested areas (Acker et al., 2006; Ren et al., 2006). We attribute this difference to the overall low acid precipitation in the western US including California and thus less HONO production from the photolysis of deposited HNO_3/nitrate in this more basic environment (Ren et al., 2010; Zhou et al., 2011).

5 Summary

In this work a REA-HONO system was developed to measure atmosperhic HONO vertical fluxes. With a dynamic velocity threshold of $\pm 0.5\sigma_w$ to determine air motion and using measured temperature as a tracer, the flux proportionality coefficient, β,

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was determined to be 0.42 ± 0.02 in two field deployments, in good agreement with the theoretical estimation of 0.412.

The developed relaxed eddy accumulation (REA) system was successfully deployed in two field studies to measure vertical HONO fluxes. The measurements show significant daytime upward HONO fluxes in San Joaquin Valley during CalNex 2010, with a maximum HONO flux of ~0.1 nmol m^{-2} s^{-1} observed in the morning. The upward fluxes correspond to significant HONO production near the surface. HONO fluxes appeared to be close to zero at night. During CalNex 2010, a strong linear correlation between HONO flux and the product of NO_2 and solar radication was observed for the daytime hours when the boundary mixing layer was fully developed, indicating that the photochemical production of HONO involving NO_2 and sunlight may be dominant in HONO production and thus the upward fluxes in this evnironment.

On the other hand, the HONO fluxes observed at Blodgett Forest during BEARPEX 2009 were low in magnitude and close to zero on average, partly because of the overall low reactive nitrogen levels in the environment. The low HONO fluxes observed at Blodget Forest are quite different from the observations at the PROPHET site in northern Michigan (Zhou et al., 2011). This is consistent with the lower daytime HONO levels observed at Blodget Forest compared to the HONO observations at the PROPHET site and in other forested areas probably due to the lower acid deposition in the Blodgett Forest region.

In order to better understand the vertical HONO flux and its role in atmospheric HONO chemistry, more measurements of HONO flux are needed, especially in a variety of environments, including polluted urban environments. The REA-HONO system will be further deployed in future field studies.

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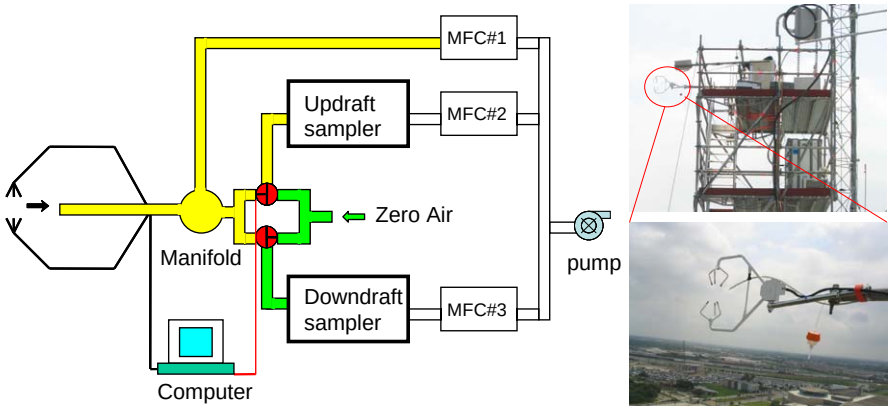

Fig. 1. Left: schematic of a Relaxed Eddy Accumulation (REA) system for HONO flux measurement. Right: pictures showing the actual instrumentation during a field study. Both the REA system and the HONO analyzer were installed on a tower.

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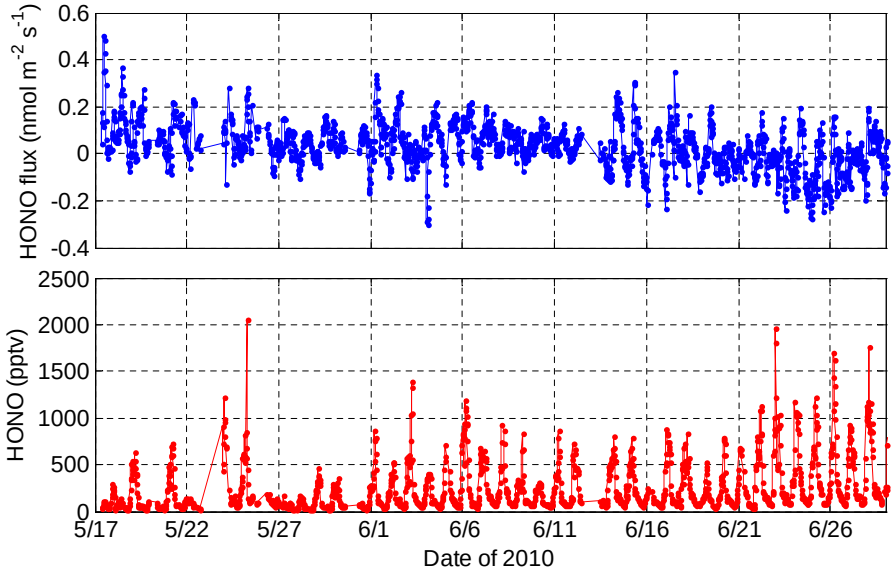

Fig. 2. Time series of HONO flux (top) and HONO concentration (bottom) measured during CalNex 2010.

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A REA system for HONO flux measurement

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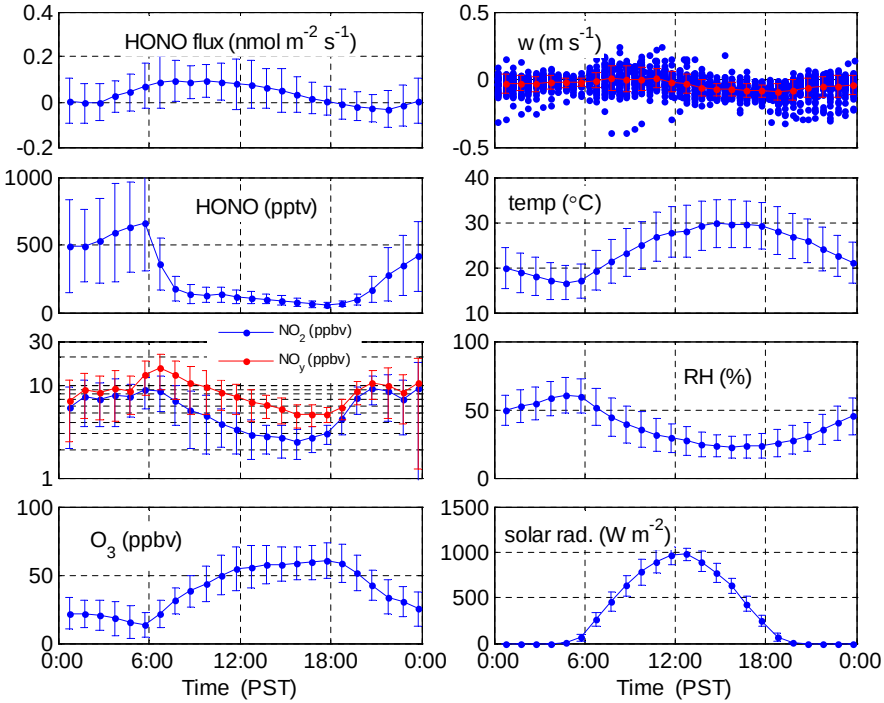

Fig. 3. Composite diurnal variations of HONO flux, HONO, NO_2/NO_y, O_3, vertical wind velocity (w), temperature, relative humidity (RH) and solar radiation measured during the CalNex 2010 field study. Hourly diurnal mean values are shown and error bars represent 1σ deviations of the measurements in the hourly bins. For vertical wind velocity (w), individual 30-min averages are also plotted as blue dots to show the variations in the data.

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A REA system for HONO flux measurement

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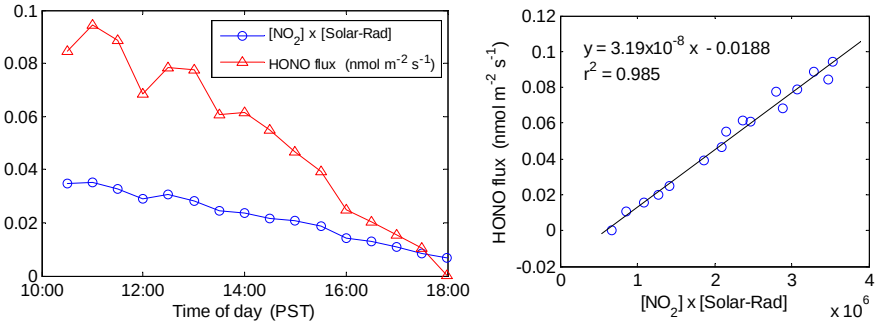

Fig. 4. Left: mean diurnal variations (in 30 min intervals) of HONO flux (in nmol m^{-2} s^{-1}, red triangles) and the product (multiplied by a factor of 1×10^{-8}, blue circles) of $[NO_2]$ (in pptv) and solar radiation (in W m^{-2}). Right: scatter plot of HONO flux versus the product of $[NO_2]$ and solar radiation. Data are shown for hours between 10:00 and 18:00 (Pacific Standard Time, PST) when the boundary mixing layer was expected to be fully developed.

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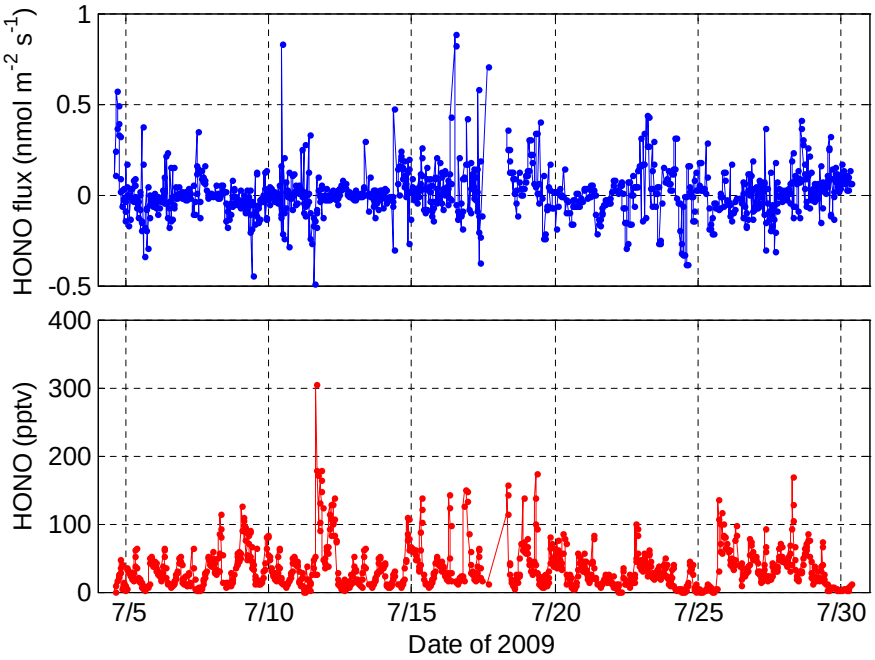

Fig. 5. Time series of HONO flux (top) and HONO concentration (bottom) observed during BEARPEX 2009.

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A REA system for HONO flux measurement

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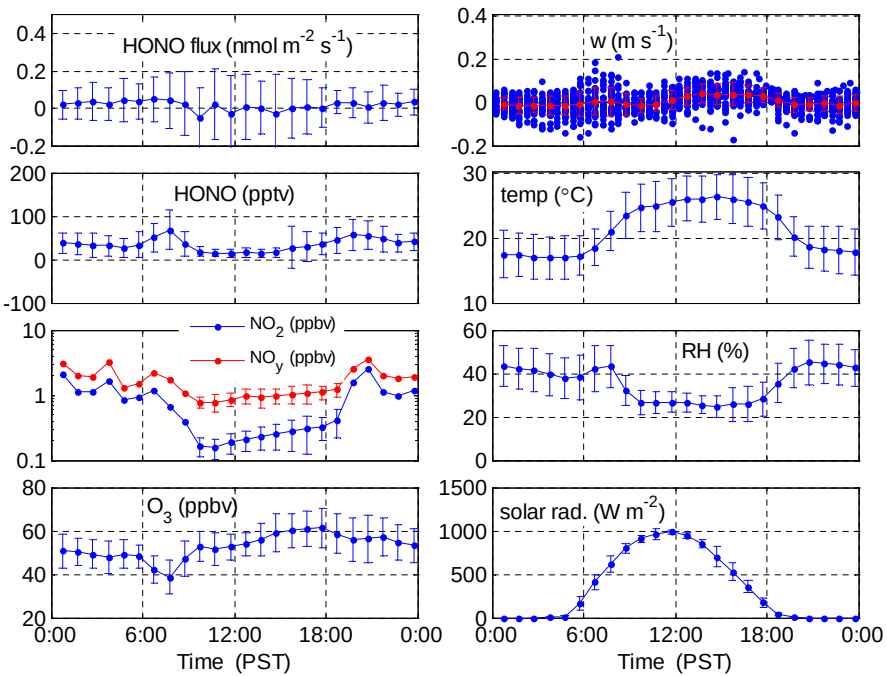

Fig. 6. Diurnal variations of HONO flux, HONO, NO_2/NO_y, O_3, vertical wind velocity (w), temperature, relative humidity (RH) and solar radiation measured during the BEARPEX 2009 field study. Hourly diurnal mean values are shown and error bars represent 1σ deviations of the measurements in the hourly bins. For vertical wind velocity (w), individual 30-min averages are also plotted as blue dots to show the variations in the data.

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