



Deliquescence induces eddy covariance and estimable dry deposition errors

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Abstract

The effects of deliquescent processes on eddy covariance estimates of dry deposition are considered, both theoretically and using some representative data. Turbulent and latent heat fluxes near the Earth's surface imply a vertical "saturation ratio flux" (Fairall, C.W., *Atmospheric Environment*, 18 (1984) 1329). Deliquescence, instantaneous relative to turbulent time-scales, responds to saturation ratio (or relative humidity) fluctuations and induces covariance between vertical winds and size-resolved number concentrations of hygroscopic aerosols. The induced covariance represents an error in the estimation of surface exchange by direct application of the eddy covariance technique. Under deliquescent conditions (high relative humidity), resulting errors in dry deposition estimates are shown to be often as large as typical deposition velocities reported for small particles, depending on the shape of the number distribution and the magnitudes of heat and vapor fluxes in the boundary layer. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The accurate measurement of atmospheric particle dry deposition is a significant challenge in contemporary geophysical science. Atmospheric particles, or aerosols, originate from both natural and anthropogenic sources. Aerosol concentrations influence human health, visibility, terrestrial remote sensing, and global climate (Charlson et al., 1987). Dry deposition is a removal mechanism for these particles, and is believed to contribute to fertilization (Lloyd, 1999), as well as acidification and eutrication of terrestrial ecosystems (Erisman et al., 1997). Accurate measurements are needed to understand and model aerosol cycling, and to define emission limits for acceptable air quality.

The bulk of atmospheric particulate matter grows and shrinks with water phase change via deliquescence, a process that has important consequences for the

measurement and modeling of dry deposition. In fact, 'dry deposition' is something of a misnomer, since hygroscopic (wet) aerosols constitute most of particulate mass. These very small, nearly spherical solution droplets change size rapidly to reach equilibrium with ambient relative humidity (hereafter normalized and expressed as saturation ratio). Deliquescent growth near a moist surface can enhance deposition, a strongly size-dependent process (Slinn and Slinn, 1980; Zufall et al., 1998). However, deliquescence can also affect measurements of dry deposition, and not only the physical process itself (Businger, 1986).

In stationary atmospheric flow over homogeneous terrain, surface exchange can be estimated from the turbulent scalar flux measured as an eddy covariance (Baldocchi et al., 1988). This approach is applied widely to the estimation of dry deposition, and is considered to be very accurate (Pleim et al., 1999). A turbulent flux is defined generally as a half-hour covariance between some conservative atmospheric scalar and the wind component normal to the surface. Conservative

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variables are those for which the material derivative in atmospheric flow is zero, such that no sources or sinks exist.

For non-conservative scalars, surface exchange does not uniquely determine the eddy covariance (Kowalski et al., 1997), which can also depend on chemical and thermodynamic transformations (de-Arellano et al., 1995). Kowalski and Vong (1999) found that condensation, a scalar source in the air, can reverse the sign of near-surface cloud water fluxes measured in a mean updraft. The combination of surface uptake and mean, pseudo-adiabatic liquid water production was found to yield an upward flux, which could have been interpreted erroneously as water droplet emission by the forest. Compared to (relatively enormous) cloud droplets, sub-micron particles grow and shrink even more dramatically due to deliquescent phase change. Observations of apparent emission fluxes of aerosol are hardly infrequent (e.g., Buzorius et al., 1998; Ruijgrok et al., 1997; Katen and Hubbe, 1985), and can present problems for interpretation unless the non-conservative nature of particles is considered (van-Oss et al., 1998).

The distinction should be noted, however, between phase change associated with mean motions, as when measurements are made in a consistent updraft, and phase change associated with turbulent fluctuations. This article focuses exclusively on the effects of turbulent latent and sensible heat fluxes on size-resolved measurements of particle counts. Nonetheless, any process representing a source or sink of a non-conservative variable potentially can confound the relationship between covariance and surface exchange.

Size-resolved particle concentrations are not conservative due, in part, to deliquescence; neither gas-particle conversions nor coagulation are considered here. Deliquescence may be neglected when dry particle size is measured (Gallagher et al., 1997), but this is not always the case (Sievering, 1987). Given the profound size dependence of aerosol distributions (Junge, 1963), deliquescent size change can dramatically affect the particle count in a defined size interval. The saturation ratio responds non-linearly to temperature and water vapor fluctuations, and deliquescence represents a source/sink of particles in different size intervals. Deliquescent fluctuations which correlate with vertical winds contaminate eddy covariance estimates of particle deposition (Fairall, 1984). Although such measurements have become widespread, the effects of this humidity contamination have not yet been quantified.

In this paper, a series of relationships are derived to estimate the particulate eddy covariance induced by deliquescence which can lead to erroneous conclusions about dry deposition. The saturation ratio flux (Fairall, 1984) is defined in terms of atmospheric state variables and the fluxes of latent and sensible heat typically measured in eddy covariance campaigns. Approximate

thermodynamic fluxes are compared with those computed directly from measured temperature and water vapor fluctuations. The particle count covariance is formulated in a simplified manner based on deliquescent response to saturation ratio fluctuations and an assumed shape of the particle number distribution. Perceived deposition velocities (errors) associated with deliquescent covariance are found to be sometimes as large as the deposition velocity magnitudes reported in many studies.

2. Data and treatment

Raw time series of winds (u, v, w), temperature (T), and water vapor pressure (e) from a representative eddy covariance campaign were considered as boundary layer conditions for deliquescence-induced covariance. The data come from the BOREAS Aspen site in Canada during the summer of 1994. The measurements and logging system are described by Black et al. (1996). Data from the 39.5 m measurement height were used for this analysis. A DAT-310 sonic anemometer (Kaijo-Denki, Japan) measured winds and temperature, and a 6262 infrared gas analyzer (LICOR, USA) measured the water vapor concentration. Time series from the sonic anemometer were delayed by 1.2 s in order to synchronize eddy sampling with the closed-path gas analyzer, which is subject to a tube delay. A two-dimensional coordinate rotation was employed to align the 'vertical' velocity normal to mean streamlines, as described by McMillen (1988). The terrain at the Aspen site has a gentle slope; the effects of mean vertical velocities and adiabatic expansion/compression have been neglected in this analysis. Fluxes were computed as block, half-hour covariances between gas concentrations and surface-normal winds (with neither high-pass filtering nor detrending).

Two days from the late summer of 1994 were selected, representing a range of atmospheric humidity conditions. Although each day begins and ends at midnight GMT, data are presented using local time. Saturation ratios were computed directly from measured temperature and moisture fluctuations, and the covariance with vertical winds was computed to determine the saturation ratio flux (labelled $w'S'$). The 5th August was warm and humid, with small and variable fluxes of latent and sensible heat, indicative of a cloudy day on the Canadian plains (Fig. 1). For these conditions, the saturation ratio flux was usually upward with a magnitude of about 1 mm s^{-1} . The 31st of August was a cool, dry summer day, with larger latent and sensible heat fluxes that followed a relatively smooth diurnal trend (Fig. 2). Under these conditions the saturation ratio flux was more variable, but still usually upward and typically somewhat larger in magnitude than for the cloudy day.

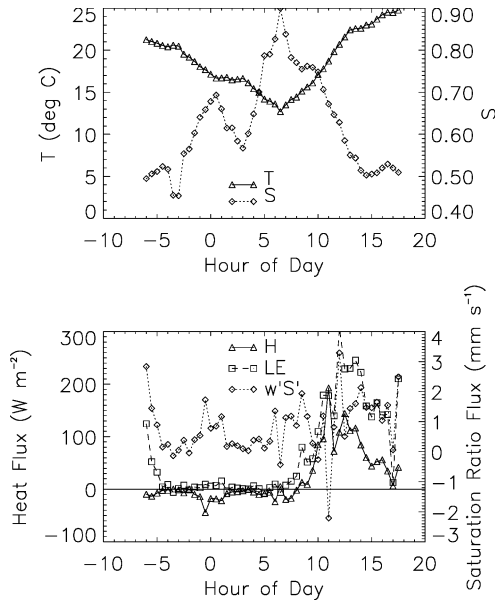


Fig. 1. Diurnal plots of boundary layer conditions on 4 and 5 August, a warm, humid day: (a) temperature (T) and saturation ratio (S); (b) fluxes of sensible (H) and latent heat (LE), and the saturation ratio flux ($w'S'$) computed from raw time series of temperature and water vapor fluctuations.

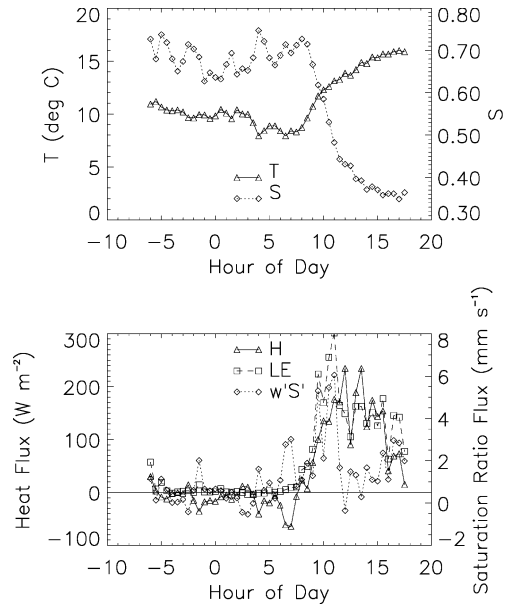


Fig. 2. Diurnal plots of boundary layer conditions on 30 and 31 August, a cool, dry day: (a) temperature (T) and saturation ratio (S); (b) fluxes of sensible (H) and latent heat (LE), and the saturation ratio flux ($w'S'$) computed from raw time series of temperature and water vapor fluctuations.

3. Notation and theory

In this section, notation is defined, derivations presented, and certain approximations evaluated. Beginning with temperature and water vapor fluctuations typically measured in eddy covariance studies, an expression is written for the saturation ratio flux. The deliquescence-induced covariance between particle count and vertical velocity is then formulated following four essential assumptions: (1) that all particles are hygroscopic and deliquescent; (2) that hydrated aerosol size is measured; (3) that certain non-linear functions can be approximated linearly over a small range (these approximations are evaluated explicitly); and (4) that the distribution of particle number with size follows the familiar power law. For convenience, the derived covariance is normalized by particle concentration and expressed as an error in the deposition velocity.

Following convention, time series of variables describing atmospheric state, motion, or gas and particle concentrations in the atmosphere are partitioned into components defined as temporal means and turbulent perturbations. For an arbitrary variable ϕ , this is expressed as

$$\phi = \bar{\phi} + \phi'. \quad (1)$$

The prime notation denotes instantaneous fluctuations about the mean over an appropriate averaging

period; the mean is expressed by the over-bar. In the event that ϕ is a non-linear function of another variable ξ , it can be useful (shown later) to approximate this dependence with a linear relationship over a limited range. Using the notation defined above, the first-order Taylor polynomial approximation for such a non-linear dependence can be expressed as

$$\phi' = \left. \frac{\partial \phi}{\partial \xi} \right|_{\bar{\xi}} \xi'.$$

The saturation vapor pressure (e_s , in units of mb) is a function of temperature (T , in °C), and is approximated very accurately (Bolton, 1980) by the empirical formula

$$e_s = A \exp\left(\frac{BT}{T+C}\right), \quad (2)$$

with $A = 6.112$ mb, $B = 17.67$ (dimensionless) and $C = 243.5^\circ\text{C}$. Although this curve is highly nonlinear, the mean saturation vapor pressure can be expressed by a function with identical form, using the mean temperature

$$\bar{e}_s = A \exp\left(\frac{B\bar{T}}{\bar{T}+C}\right). \quad (3)$$

This introduces an error of less than half a percent for typical boundary-layer temperature fluctuations measured during BOREAS (data not presented).

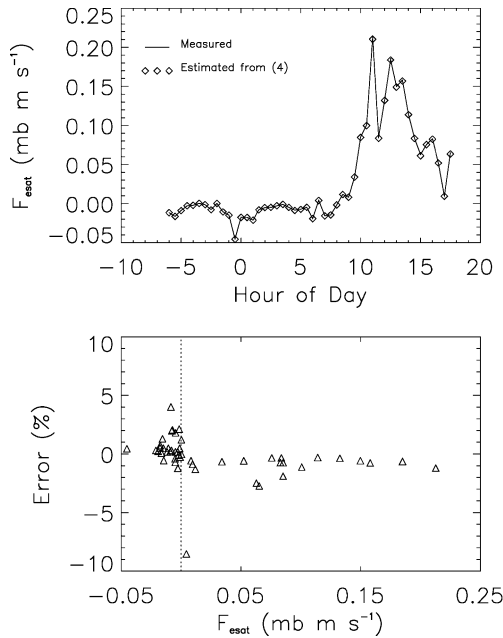


Fig. 3. Saturation vapor pressure fluxes from 4 to 5 August: (a) measured values and those approximated by Eq. (4); (b) the percent error in the approximation as a function of the measured value.

Using a Taylor polynomial approximation, again over a small range, the perturbation saturation vapor pressure (e'_s) can be expressed as a linear function of the temperature perturbation. Thus, the covariance between the saturation vapor pressure and vertical winds, termed the saturation vapor pressure flux, is a simple linear function of the kinematic heat flux

$$\overline{w'e'_s} = \bar{e}_s \frac{BC}{(\bar{T} + C)^2} \overline{w'T'} \quad (4)$$

In Figs. 3 and 4 the saturation vapor pressure flux for 5 and 31 August is represented as F_{esat} . These data show that the error in the approximation represented by Eq. (4) is generally very small, exceeding 5% only when the heat flux is near zero. Because of the extreme non-linearity of the Clausius–Clapeyron relationship approximated here, Eq. (4) typically underestimates the true saturation vapor flux, particularly at night.

The saturation ratio (S) is defined as the ratio of the water vapor pressure (e) to e_s ; this is the relative humidity, normalized such that unity indicates saturation. The true saturation ratio flux (shown previously in Figs. 1 and 2) has been computed directly from measurements, but it can be useful to approximate this as well. With Reynolds' averaging, and neglecting products of perturbation quantities, the perturbation component of the saturation ratio can be

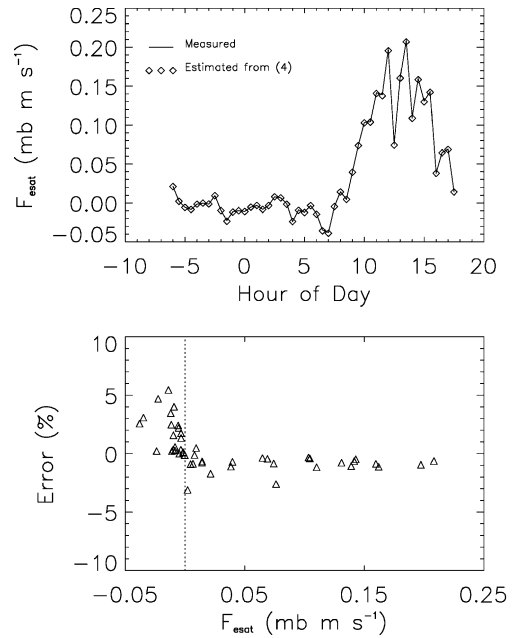


Fig. 4. Saturation vapor pressure fluxes from 30 to 31 August: (a) measured values and those approximated by Eq. (4); (b) the percent error in the approximation as a function of the measured value.

approximated as

$$S' = \frac{1}{\bar{e}_s} (e' \bar{e}_s - \bar{e} e'_s), \quad (5)$$

and the saturation ratio flux (covariance between S and vertical winds) is thus

$$\overline{w'S'} = \frac{1}{\bar{e}_s} (\overline{w'e'} - \bar{S} \overline{w'e'_s}), \quad (6)$$

which is a linear combination of the water vapor flux and, when Eq. (4) is used to estimate saturation vapor pressure fluctuations, the heat flux. Figs. 5 and 6 show that Eq. (6) gives a very accurate estimation of the saturation ratio flux for BOREAS boundary layer conditions.

Given this useful approximation for the saturation ratio flux in terms of readily measurable quantities, we examine how deliquescence converts fluxes of latent and sensible heat into a perceived particle flux. For the purpose of determining correlation with vertical winds, deliquescence can be considered as immediate (Fairall, 1984). The radius (r) of a particular hygroscopic aerosol is a function of the ambient saturation ratio according to

$$r = r_0 \left(1 + \frac{K_f}{1 - S} \right)^{1/3}, \quad (7)$$

where r_0 is the dry particle size and the constant K_f depends on the chemical composition of the particle

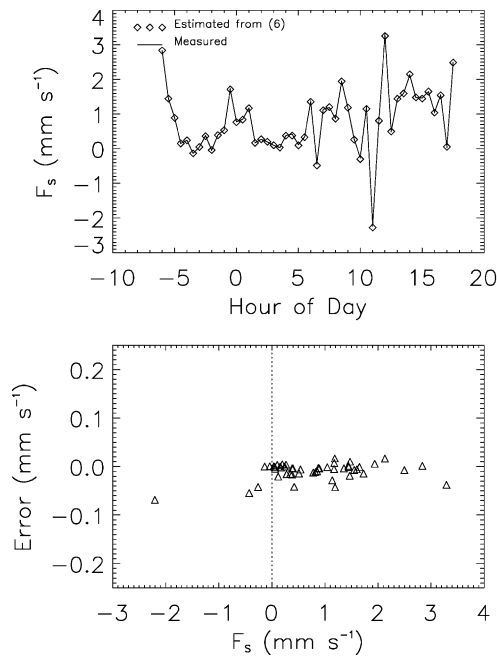


Fig. 5. Saturation ratio fluxes from 4 to 5 August: (a) measured values and those approximated by Eq. (6); (b) the percent error in the approximation as a function of the measured value.

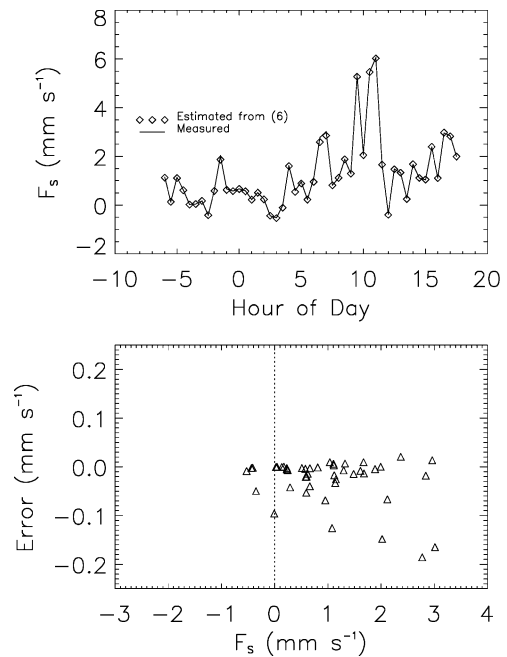


Fig. 6. Saturation ratio fluxes from 30 to 31 August: (a) measured values and those approximated by Eq. (6); (b) the percent error in the approximation as a function of the measured value.

(Businger, 1986; Fairall, 1984; Fitzgerald, 1975). Thus, the saturation ratio flux, Eq. (6), implies a covariance between vertical winds and individual particle size. In order to use a Taylor polynomial approximation to estimate this covariance, the dependence of particle size on saturation ratio must be defined by taking the derivative of Eq. (7) with respect to S and evaluating it at the mean over the averaging period

$$\frac{\partial \bar{r}}{\partial \bar{S}} = \frac{K_F \bar{r}}{3(1 - \bar{S})^2 + 3K_F(1 - \bar{S})}. \quad (8)$$

For appropriate ranges of the saturation ratio, this approximation is evaluated in Figs. 7 and 8, which compare the approximation, Eq. (8), with a more exact estimate from Eq. (7). For a particle of relevant size, deviations from the mean radius computed via Eq. (7) were compared with those predicted by Eq. (8), using the measured range of S over all data. Clearly, the error in making this linear assumption is small.

The typical instrument, used in eddy correlation assessments of dry deposition, measures particle number concentrations within a defined interval in (hydrated) particle radius. A measurement of particle number (N) is represented as the concentration (per unit air volume) of particles between two fixed limits in radius. The covariance between N and the surface-normal wind component w , usually is interpreted as a flux (F),

$$F = \overline{w'N'}. \quad (9)$$

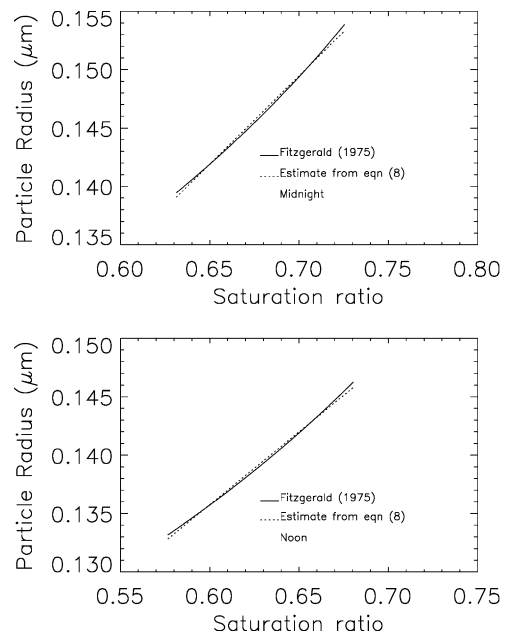


Fig. 7. Particle radius over a range of saturation ratio (mean \pm three standard deviations) for two half-hour periods on 5 August: (a) from midnight to 00:30; (b) from noon to 12:30. In each case, the first-order Taylor polynomial approximation, Eq. (8), is compared with the more exact formula of Fitzgerald (1975).

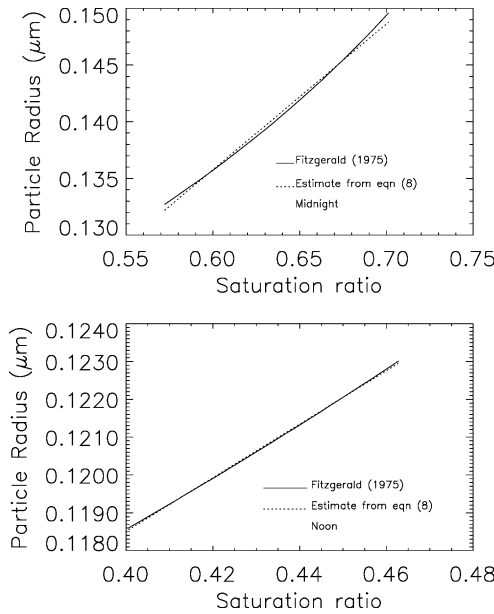


Fig. 8. Particle radius over a range of saturation ratio (mean \pm three standard deviations) for two half-hour periods on 31 August: (a) from midnight to 00:30; (b) from noon to 12:30. In each case, the first-order Taylor polynomial approximation, Eq. (8), is compared with the more exact formula of Fitzgerald (1975).

Most often, interest is focused on the so-called deposition velocity, usually defined as the covariance normalized by the scalar mean concentration

$$v_d = -\frac{\overline{w'N'}}{\bar{N}} = -\overline{w' \left(\frac{N'}{\bar{N}} \right)}. \quad (10)$$

The rules of averaging have been used to express this in a useful way (shown later). The negative sign arises because the deposition velocity is conventionally defined as positive towards the surface while the flux is negative due to the sign convention used for vertical velocity.

In this theoretical examination of the effects of deliquescence on measured covariance, surface exchange is explicitly excluded. Thus, variations in N are restricted to deliquescent size change whereby particles shrink or grow across the limits of the defined particle radius increment. Under these conditions, the velocity scale defined in Eq. (10) is not a deposition velocity, but rather an error term in the interpretation of covariance traditionally attributed to deposition. This will be denoted as Δv_d .

Deliquescent size change of particles across defined size intervals causes fluctuations in N that can correlate with vertical winds. The deliquescence-induced, temporal perturbation in the particle number distribution can be expressed as the sum of two effects. In the first case, the number distribution shifts in the radial domain, and

the induced change in N is the product of the radius change (r') and the slope of the distribution. A second term arises because of the change in the definition of the size intervals over which the distribution is expressed. The number of particles is independent of the deliquescent state at which they are measured. Thus $\bar{N}(\bar{r})d\bar{r} = N'(r')dr'$, where $d\bar{r}$ and dr' are related to S via Eq. (8). These two effects yield

$$N' = r' \left(\frac{\partial \bar{N}}{\partial \bar{r}} + \frac{\bar{N}}{\bar{r}} \right). \quad (11)$$

Commonly, and in this preliminary treatment, the dependence of particle concentration on size is approximated by

$$\bar{N} = K_J \bar{r}^{-(\beta+1)}, \quad (12)$$

the so-called Junge power law (Junge, 1963), where K_J is a constant, and β is typically about three. Note that some form of averaging is always implied by the power law, whether spatial or temporal as expressed explicitly in Eq. (12). The power law is easily differentiated with respect to particle size, and allows simplification of Eq. (11):

$$\frac{N'}{\bar{N}} = -\beta \frac{r'}{\bar{r}}. \quad (13)$$

Combining Eqs. (8), (10) and (13) defines the perceived particle deposition velocity due to fluctuations in saturation ratio and deliquescence as

$$\Delta v_d = \frac{-K_F \beta}{3(1 - \bar{S})^2 + 3K_f(1 - \bar{S})} \overline{w'S'}. \quad (14)$$

In Eq. (14), all but the last term can be taken as constant over a half-hour averaging period, and can be either measured or prescribed according to climatic conditions. The remaining term represents the covariance between the vertical winds and the saturation ratio, defined previously in Eq. (6). Finally, combining Eqs. (4), (6) and (14) allows an expression for the error in deposition velocity as a function of constants, mean quantities, and the kinematic fluxes of temperature and water vapor:

$$\Delta v_d = \frac{-K_F \beta}{3\bar{e}_s(1 - \bar{S})^2 + 3K_f\bar{e}_s(1 - \bar{S})} \times \left[\overline{w'e'} - \bar{e} \frac{B}{(\bar{T} + C)^2} \overline{w'T'} \right]. \quad (15)$$

4. Deposition velocity errors

It should be recognized that the full set of assumptions put forth in Section 2 will not always be valid. Most importantly, not all aerosols are deliquescent at any given time and place. The relative humidity at many sites does not always exceed the deliquescent point,

typically between 15% and 80% for the chemical composition of atmospheric aerosols (Fitzgerald, 1975). Thus, the errors presented here represent potential deliquescent effects. If dry aerosol size is measured (Gallagher et al., 1997) then deliquescence has no effect whatsoever on eddy covariances (note, however, that even the dry-size particle count is not conservative due to processes of coagulation and new particle production). The final two assumptions appear to be valid for the conditions considered in this paper: the approximate thermodynamic relations have been examined and shown valid, and the Junge power law may be considered as generally valid. Where the number distribution follows the Junge power law, no size dependence is predicted for errors induced by deliquescence. However, the true size dependence of such effects depends on the details of the aerosol spectra, and individual eddy covariance campaigns assessing dry deposition should take advantage of the measured shape of the number distribution, rather than simply assuming that $\beta = 3$ provides a full description.

For the two days of data from the BOREAS Aspen site, the errors in perceived deposition velocities due to deliquescent covariance are shown in Figs. 9 and 10. The approximated deposition velocity errors are practically identical to those computed directly from measured fluctuations in saturation ratio. This indicates that Eq. (15), which approximates the saturation ratio flux using a linear combination of the latent and sensible heat fluxes, gives an accurate representation of potential deliquescent effects over the range of atmospheric conditions examined. Recall that both Eqs. (14) and (15) rely heavily on the assumption that the aerosol size distribution follows the Junge power law.

Unlike the latent and sensible heat fluxes on which they are based, the diurnal trends in deposition velocity error and saturation ratio flux do not allow for simple interpretation, since they are not directly related to solar forcing. Rather, they appear to be positive quantities throughout much of the day and night, with exceptions during certain, perhaps non-stationary, periods. The saturation ratio flux is usually upward, as is the perceived particle flux, reflecting a negative error in deposition velocity. That the perceived particle flux should have the same sign as the saturation ratio flux is evident, given the monotonically decreasing nature of particle number with particle size; higher humidity allows smaller, more numerous, particles to grow into a given size increment.

For both days, the potential deliquescence-induced errors in deposition velocity are largest during the morning hours. Between 6 a.m. and noon (local time), perceived deposition velocities are of order 0.2 cm s^{-1} , similar to magnitudes reported from recent eddy covariance dry deposition studies (e.g., Buzorius et al.,

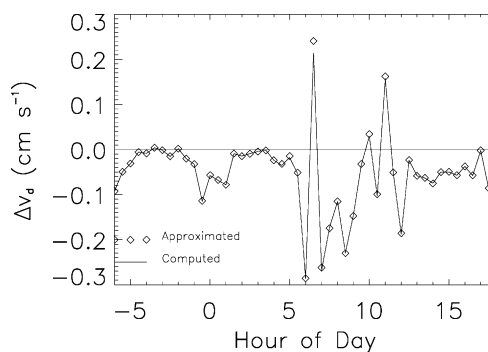


Fig. 9. Perceived deposition velocities induced by deliquescent covariance for 5 August. Both direct computations from Eq. (14) and approximations based on latent and sensible heat fluxes via Eq. (15) are shown.

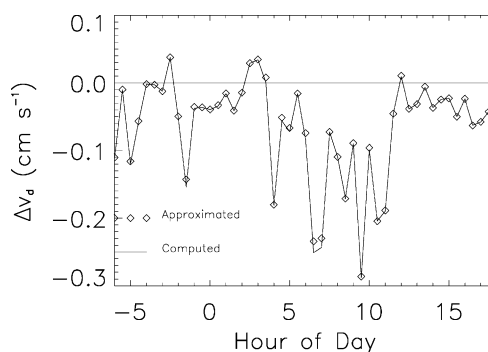


Fig. 10. Perceived deposition velocities induced by deliquescent covariance for 31 August. Both direct computations from Eq. (14) and approximations based on latent and sensible heat fluxes via Eq. (15) are shown.

1998; Erisman et al., 1997; Gallagher et al., 1997). During afternoon hours, the magnitudes are somewhat smaller, typically less than 0.1 cm s^{-1} , but still quite important. Not surprisingly, both days exhibit large variability near dawn, when the boundary layer typically undergoes a transition from nocturnal conditions of weak and intermittent turbulence toward the well-mixed daytime case. The two days presented are not intended to characterize magnitudes of perceived deposition over a range of climatic or seasonal conditions, but simply to demonstrate the efficacy of the derived approximations, and that deliquescence cannot always be neglected.

The deposition velocity error terms were typically larger on 31 August, a cooler, dryer day, than for the warm, humid conditions of 5 August. However, under these conditions it is uncertain that deliquescence would be important, depending upon aerosol composition. From Eq. (15), it is clear that the sign of the deposition velocity error term depends on four time-varying

boundary layer properties: mean temperature and humidity, and fluxes of latent and sensible heat. In fact, it is linked directly to the saturation ratio flux, but as noted before this is not an easily modeled quantity unless these four properties are known. The sign of saturation ratio flux (and error in deposition velocity) is related to a threshold in the Bowen ratio (ratio sensible to latent heat flux), but this threshold varies with mean atmospheric state. Thus, to learn about the general behavior of the saturation ratio flux, and perceived deposition velocity, Eqs. (6) and (15) can be applied at numerous sites where latent and sensible heat fluxes have been measured.

5. Conclusions

Latent and sensible heat fluxes in the atmosphere imply a saturation ratio flux, and deliquescent size change potentially can translate this into an error in the dry deposition velocity inferred from the direct application of eddy covariance. The covariance arises from size change of deliquescent particles responding immediately to saturation ratio fluctuations. Data from the BOREAS Aspen site have been used to evaluate “representative” magnitudes for summertime conditions over a mid-latitude forest. For these conditions, a series of derivations has yielded accurate approximations for the saturation ratio flux and normalized particle count covariance induced by deliquescence, which represents an error in the dry deposition velocity for deliquescent particles.

Errors in the perceived dry deposition velocity caused by deliquescence are found to be as large as the deposition velocity magnitudes often reported from eddy covariance campaigns. Most often, the effects of deliquescence are to induce a positive covariance. This represents either an underestimation of surface uptake or a perceived upward flux which might be interpreted as surface emission, and may explain previously reported results from various studies. The derived equations may prove useful for correcting eddy covariance estimates of dry deposition which utilize instruments measuring hydrated particle size.

For accurate estimates of particulate dry deposition by eddy covariance, it is best to avoid the effects of deliquescence altogether. This can be achieved in several ways. One possibility is to measure dry particle size (Gallagher et al., 1997) or another relatively conservative species such as sulfur mass (Hicks et al., 1983). The measurements can be restricted to conditions when humidity fluctuations are small (Duan et al., 1988). The use of condensation particle counters (Buzorius et al., 1998) eliminates ambient deliquescent effects at the expense of size-resolution, and may allow abundant small particles to dominate the total count. Perhaps the

best practical option is to pre-heat the air sample before measurement. The relative humidity can be brought below the aerosol deliquescence point; for most atmospheric aerosol, a relative humidity below 40% is sufficiently dry (Tang and Munkelwitz, 1994). Where none of these options are feasible, corrections of the form suggested above may be the most practical way to arrive at accurate estimates of dry deposition via eddy covariance.

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