Relative Humidity Effect on the High-Frequency Attenuation of Water Vapor Flux Measured by a Closed-Path Eddy Covariance System

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ABSTRACT

In this study the high-frequency loss of carbon dioxide (CO2) and water vapor (H2O) fluxes, measured by a closed-path eddy covariance system, were studied, and the related correction factors through the cospectral transfer function method were calculated. As already reported by other studies, it was found that the age of the sampling tube is a relevant factor to consider when estimating the spectral correction of water vapor fluxes. Moreover, a time-dependent relationship between the characteristic time constant (or response time) for water vapor and the ambient relative humidity was disclosed. Such dependence is negligible when the sampling tube is new, but it becomes important already when the tube is only 1 yr old and increases with the age of the tube. With a new sampling tube, the correction of water vapor flux measurements over a Scots pine forest in Hyytiälä, Finland, amounted on average to 7%. After 4 yr the correction increased strongly, ranging from 10%–15% during the summer to 30%–40% in wintertime, when the relative humidity is typically high. For this site the effective correction improved the long-term energy and water balance.

Results suggest that the relative humidity effect on high-frequency loss of water vapor flux should be taken into account and that the effective transfer function should be estimated experimentally at least once per year.

On the other hand, this high correction can be avoided by a correct choice and periodic maintenance of the eddy covariance system tube, for example, by cleaning or changing it at least once per year.

1. Introduction

The estimation of energy and scalar turbulent fluxes by eddy covariance (EC) technique is well established and widespread in the micrometeorological community. Long-term measurements of the surface energy balance components and the atmosphere–biosphere exchange of trace gases are essential for assessing the role of vegetation in the climate change perspective.

Closed-path eddy covariance (EC) systems are widely used in the flux tower network (Fluxnet) sites around the world to measure carbon dioxide and water vapor fluxes between the biosphere and the atmosphere. The advantages of the closed-path setups include low maintenance efforts and costs, long-term stability, and good accuracy. However, the measured fluxes need to be corrected in order to minimize any systematic error arising from the EC system setup and flux-averaging methodology (Aubinet et al. 2000). The underestimation of the EC fluxes due to the system characteristics results from the physical limitations in the response times, separation distances, size of the sensors, the use of sampling line filters, and the sampling tube dimensions. Therefore, these limitations concern mainly the high-frequency band of the scalar fluctuations. In the case of a closed-path EC system, the attenuation of scalar fluctuations in the sampling tube causes typically the largest part of the high-frequency underestimation (Aubinet et al. 2000). The attenuation of the EC fluxes at low frequencies, on the other hand, arises...
from the mean-removal methods (Rannik and Vesala 1999) and limited flux-averaging period (Sakai et al. 2001; Finnigan et al. 2003).

The transfer function method (Moore 1986; Horst 1997; Massman 2000) has been extensively used to account for the loss of the flux and to estimate the corrected or unattenuated EC fluxes. The transfer function characterizing the high-frequency loss ranges from 1 (at low frequencies) to 0 (at high frequencies), and the frequency at which the transfer function reduces the power by a factor 2 is called the cutoff frequency ($f_c$).

Moncrieff et al. (1997) gave a complete description of theoretical transfer functions for the most recent fast response instruments. However, Aubinet et al. (2000) showed that the transfer function predicted by the theory can significantly depart from the one estimated experimentally. They pointed out that the main reason for the higher theoretical than experimental cutoff frequency is most probably due to the fact that the theoretical approach ignores the impact of the sampling line filters on the transfer function.

Leuning and Judd (1996) compared transfer functions for the sampling tube before and after cleaning it and observed a degradation of the response time $\tau_s = (2\pi f_c)^{-1}$ of H$_2$O for the dirty sampling tube. They emphasized that the rates of physical absorption and desorption of water vapor to and from the walls of the gas tubing and filters could change, because of the presence of dust, pollen, and salt crystals in the walls of the tubing (Leuning and Judd 1996). Su et al. (2004, their table VII) reported the attenuations associated with water vapor fluctuations at two experimental sites for several years. They found that the response time of the system increased each year for water vapor, but not for the CO$_2$. Moreover, Ibrom et al. (2007) found that the cutoff frequency of a closed-path EC system for water vapor concentration measurements is not constant but decreases with increasing relative humidity (RH). Recently Massman and Ibrom (2008) proposed a semiempirical model that describes the attenuations associated with water vapor fluctuations. Their model seems to reasonably predict the experimental data of Lenschow and Raupach (1991), but they conclude that more experimental data are needed, and at the moment the physical basis of such a phenomenon is unknown.

In this study we first show that a similar dependency of the response time of water vapor mixing ratio on relative humidity becomes important even when a significantly short (7 m) and heated sampling tube is used. We also show that the effect of RH on the $\tau_{H_2O}$ increases strongly when the tube gets older and then dirtier inside. We present the effect of the improved correction on water vapor fluxes in different ambient conditions. Then we briefly present the implications on long-term energy and water balance, and finally we discuss potential mechanisms responsible of such effect, and possible scenarios that need to be evaluated when we want to estimate effective values of $\tau_{H_2O}$.

2. Site description

For this study the experimental data collected at the Station for Measuring Forest Ecosystem–Atmosphere Relations (SMEAR II) field measurement station located in Hyytiälä, southern Finland, have been used. The site is characterized by a 46-yr-old (in 2008) Scots pine (Pinus sylvestris L.) stand, which is homogeneous at least about 200 m in all directions, and maximally extends to the north about 1 km. For longer distances other stand types different in age/composition are also present. The average height of the trees is about 15 m, and the total (i.e., not projected) leaf area index is 6 m$^2$ m$^{-2}$. A detailed description of the site in micrometeorological context can be found in Rannik (1998) and Vesala et al. (2005).

3. Measurements

Turbulent fluxes of momentum, heat, CO$_2$, and H$_2$O were measured using the eddy covariance technique. The system, located at 23.3-m height above the ground, includes an ultrasonic anemometer (Solent Research 1012R2, Gill Ltd., Lymington, Hampshire, Britain) to measure the three wind velocity components and sonic temperature, and a closed-path infrared gas analyzer (LI-6262, LiCor Inc., Lincoln, Nebraska) that measures CO$_2$ and H$_2$O concentrations.

The sample line is 7 m long, and the outside–inside diameter is 6–4 mm. Until May 2002, the tube material was entirely (PTFE) Teflon. On 9 May 2002, the sample line was renewed, and the old tube was replaced with an electro-polished seamless stainless steel tube. The surface of this kind of metal tube is less porous than Teflon, so it was thought to be better for measurement of fluctuations than the Teflon one. Also the incorporation of an aerosol particle counter sample line to the CO$_2$–H$_2$O analyzer’s sample line necessitated the use of a metal tube. At the end of the line in front of the LI-6262 analyzer an about 0.5-m-long piece of new Teflon tube was installed to provide necessary flexibility to the line. Also the use of a dust filter (sintered brass) at the inlet of the line was not continued any more because of the measurement of aerosol particles. A 1.0-$\mu$m pore size membrane filter (Gelman Acro 50, PTFE element, polypropylene support plate and housing, Pall Corporation, East Hills, New York) recommended by LiCor, Inc., is used at the inlet of the LI-6262 analyzer to keep
clean its measurement cell. The filter is changed whenever the pressure drop increases to about double of the initial value with a clean filter. The filter is also changed earlier if the pressure drop appears to depend on ambient relative humidity and/or it is not stable over a day, because in these situations the attenuation of water vapor signal would be obvious. The frequency of the filter change varies from a few weeks to about 2 months, depending on the cleanliness of the air. To avoid condensation of water vapor in the sampling line is heated with a power of about 5 W m\(^{-1}\) using standard floor warming cable. The heating power creates, in practice, an increase of a couple of degrees Celsius in the sample air temperature. The flow rate inside the sampling line is 6.1 L min\(^{-1}\). The ambient RH was calculated from the measured dewpoint temperature (chilled-mirror sensor, M4 dewpoint monitor, General Eastern, Woburn, Massachusetts) and a measured air temperature (Pt-100 resistance thermometer) at 23-m height.

4. Methods

The eddy covariance fluxes were calculated as 30-min block-averaged covariances between the scalars (or horizontal wind speed) and vertical wind velocity according to commonly accepted procedures (Aubinet et al. 2000). The carbon dioxide and water vapor fluxes were corrected for high- and low-frequency losses, because of the limited temporal resolution of the EC system and the finite time-averaging period used for calculating the fluxes, respectively. This study concerns and discusses only the correction of the flux for high-frequency underestimation (low-pass filtering). However, the low-frequency attenuation is included in the final flux values using a first-order transfer function with a high-pass time constant corresponding to block averaging, according to Massman (2000). When the low-pass time constant is also known, a linear superposition of the high- and low-pass transfer functions, together with a cospectral model (Kaimal et al. 1972; Horst 1997), let us estimate the flux attenuation factor (Moncrieff et al. 1997).

a. Attenuation of CO\(_2\) and water vapor fluxes for high-frequency loss

Several methods have been proposed in the literature to deal with the sensor-related attenuation effects (Massman and Clement 2004). In this study we used a cospectral transfer function method because it has been previously used for our EC system (Rannik et al. 2004), and it is reasonably accurate (Laubach and McNaughton 1999).

The estimation of the flux attenuation factor for a scalar \(S\) can be defined as

\[
F_a = \left( \frac{c}{d} \right) = \frac{\int_0^\infty H_{w_s}(n)C_{w_s}(n) \, dn}{\int_0^\infty C_{w_s}(n) \, dn}, \tag{1}
\]

where \(n\) is natural frequency (in hertz), \(w\) and \(s\) are the fluctuations of the vertical velocity and scalar concentration, \((w_s)_m\) and \(w_s\) are the measured and the unattenuated covariance, and \(C_{w_s}(n)\) is the cospectral density of the scalar flux \(w_s\). The \(H_{w_s}(n)\) is a net transfer function formed as the product of a set of transfer functions characteristic to the particular EC system and the scalar \(S\). Assuming that the normalized cospectrum of all scalars has the same form (scalar similarity) and that the cospectrum \(C_{w_0}(n)\) of the potential temperature flux \(w_0\) can be measured with adequate accuracy, the flux attenuation can be determined as

\[
F_a = \frac{\int_0^\infty H_{w_s}(n)C_{w_0}(n) \, dn}{\int_0^\infty C_{w_0}(n) \, dn}. \tag{2}
\]

Thus, in order to apply Eq. (2), the knowledge of the normalized cospectrum and the net transfer function are needed.

b. Empirical cospectral models for temperature flux

Because of the lack of universal analytical formulas for scalar cospectrum in the roughness sublayer, many authors have used surface layer cospectral models (Kaimal et al. 1972) for estimating the flux attenuation \(F_a\) (Moore 1986; Horst 1997; Massman 2000; Su et al. 2004). In this study we used the formulations proposed by Horst (1997), which are based on Kansas cospectra (Kaimal et al. 1972). In unstable and near-neutral stratification, the \(w_0\) cospectra are clustered in a narrow band (Kaimal and Finnigan 1994), and the near-neutral formulation of Kaimal et al. (1972) is suitable:

\[
\frac{nC_{w_0}(n)}{w_0} = \begin{cases} \beta_1 f_0 & \text{for } f \leq 1 \\ \beta_2 f_0^{1/4} & \text{for } f \geq 1 \end{cases}, \tag{3}
\]

where \(\beta_1 = 1.05, \beta_2 = 1.33, \beta_3 = 0.387,\) and \(\beta_4 = 0.38\) are empirical constants (Horst 1997); \(f = n(z - d)/U\) is the dimensionless frequency; \(z\) is the EC measurement level (23.3 m); \(d\) is the displacement height (10.5 m).
to Rannik et al. 2004); $U$ the mean wind speed in meters per second; and $f_0$ is the frequency at which the logarithmic cospectrum $nC_{\omega_\theta}^m(n)$ attains its maximum value.

For stable stratification, the temperature flux cospectrum is described by the formula proposed by Kaimal et al. (1972),

$$\frac{nC_{\omega_\theta}^m(n)}{w\theta} = \frac{\beta_5 f / f_0}{1 + \beta_6 (f / f_0)^{2\tau}}^T, \quad (4)$$

where, again, $\beta_5 = 0.637$ and $\beta_6 = 0.91$ are empirical constants (Horst 1997).

The frequency $f_0$ should be broadly constant in unstable stratification and increase with stability in stable stratification. For our site the average values of $f_0$ were empirically estimated by Rannik et al. (2004):

$$\begin{cases} f_0 = 0.092 & \text{for } \frac{z - d}{L} \leq 0 \\ f_0 = 0.09 \left[ 1 + 4.5 \left( \frac{z - d}{L} \right)^{0.78} \right] & \text{for } \frac{z - d}{L} > 0 \end{cases}, \quad (5)$$

where $L$ is the Obukhov length. This parameterization is close to that proposed by other studies (Horst 1997).

c. Empirical estimation of the low-pass transfer function

The cospectral transfer function for a scalar $S$ measured with a first-order response sensor can be experimentally estimated by using the measured normalized cospectrum of the scalar (CO$_2$ or H$_2$O) and temperature flux by

$$H_{\omega_\theta}^n(n) = \left[ \frac{C_{\omega_\theta}^m(n)}{w\theta} \right]^{-1} \left[ \frac{C_{\omega_\theta}^m(n)}{w\theta} \right]^{-1} \left[ 1 + (2\pi \tau_s n)^2 \right]^{-1}, \quad (6)$$

where $\tau_s$ is the characteristic time constant of the sensor response (in seconds) (Horst 1997), here also called the response time. The superscript $m$ indicates a measured variable. Such methodology assumes that the temperature measurements are not attenuated, and the normalized factors ($\frac{wS_n^m}{w\theta}$ and $\frac{wS_n^m}{w\theta}$) are calculated over frequencies not affected by attenuation (Aubinet et al. 2000). To exclude the low-frequency attenuation effects, we estimated the time constant $\tau_s$ for CO$_2$ and H$_2$O fluxes through a nonlinear fit of Eq. (6) for $n > 0.01$ Hz. Moreover, in Eq. (6) we neglect the phase shift term, assuming that the quadrature spectrum is much smaller than the cospectrum in absolute value, which is generally true for the high-frequency cospectral region (Horst 1997).

To reduce the random uncertainty, the nonlinear fit was applied to ensemble-averaged cospectra using the following procedure. First, the scalars (CO$_2$ and H$_2$O) and the vertical velocity time series were shifted in time to account for the time lag, determined by maximizing the cross-covariance function. Second, single cospectral densities were calculated using fast Fourier transforms (FFT) on linearly detrended segments of $2^{10}$ data points. For further analysis we selected only the periods with fluxes exceeding certain thresholds (25 W m$^{-2}$ for sensible and latent heat fluxes and 2 $\mu$mol m$^{-2}$ s$^{-1}$ for CO$_2$ flux) and well-shaped cospectra indicating no apparent deviations from the Kolmogorov scaling in the inertial subrange, grouped the single cospectra into eight relative humidity bins, and then performed the ensemble averaging. Then, we fitted Eq. (6) to the ensemble-averaged cospectra and estimated $\tau_s$ for CO$_2$ and H$_2$O within each relative humidity bin. This procedure was applied for each year studied using data from April to October. Finally, an empirical function,

$$\tau_{H_2O} = a + b \left( \frac{RH}{100} \right)^c, \quad (7)$$

where $a$, $b$, and $c$ are empirical constants and RH the relative humidity (in percent), was used to describe the dependency of the H$_2$O time constant on RH for each year.

In the next section we present the results obtained using the data collected during the period 2001–06. The change of the air-sampling tube of the closed-path EC system in May 2002 offered us an opportunity to study the effect of tube age on the high-frequency attenuation of CO$_2$ and H$_2$O concentrations.

5. Results

a. Empirical estimation of cospectral transfer functions

Following the methodology explained above, the first-order cospectral transfer functions were calculated on an annual basis. Figure 1 shows the predicted and measured scalar cospectra calculated for 2002 (new tube) and 2006 (4-yr-old tube) in two different relative humidity situations [30% < RH < 40% (left) and 70% < RH < 80% (right)]. Here the predicted cospectra for CO$_2$ and H$_2$O refer to the product between the normalized temperature cospectrum and the estimated transfer functions for CO$_2$ and H$_2$O, respectively. In all analyzed cases, the coefficients of determination between the predicted and measured cospectra were larger than 97%, suggesting the suitability of a first-order transfer function for simulating the low-pass-filtering effect of the EC system used in this study.
For both years presented in Fig. 1, the H2O cospectra attenuated faster than CO2 cospectra, as already reported by previous studies (Aubinet et al. 2000; Ibrom et al. 2007). Values of $f_c$ for H2O were smaller than for CO2. The attenuation of the CO2 cospectrum did not show any marked dependency on either RH or tube age, and the calculated cutoff frequency has a constant value of about 1 Hz. The relative humidity effect was negligible in 2002, when the tube was new (Fig. 1a), but it increased with the tubing age. For the year 2006, when the tube was 4 yr old, we observed a strong effect of relative humidity on the high-frequency attenuation of the water vapor cospectra. While under low-relative-humidity conditions (Fig. 1c) the estimated $f_c$ for H2O has the same value as found for the new tube (Fig. 1a), the high-frequency attenuation of water vapor increases strongly with increasing relative humidity for high values of RH (Fig. 1d).

A more quantitative measurement of such an effect is given in Fig. 2, which shows the bin-averaged values of the response times for CO2 and H2O ($t_{\text{CO2}}$ and $t_{\text{H2O}}$) as a function of relative humidity for different years. When the tube was new (2002), $t_{\text{H2O}}$ showed a very small dependence on RH, slightly increasing from 0.25 s [the same value as that estimated by Keronen et al. (2003) using data from summer 2002] for low-RH conditions to about 0.4 s at high RH. This small variation in $t_{\text{H2O}}$ gives an almost negligible difference in the flux correction factor (less than 1%). However, already in 2003, when the sampling tube was 1 yr old, the relative humidity started to have a significant effect on $t_{\text{H2O}}$, which increases from 0.25 s to about 0.8 s at 90% relative humidity (Fig. 2c). This effect became more pronounced in the following years (Fig. 2d). Similar behavior was observed in 2001 (Fig. 2a), before the sampling line was replaced. The increasing rate of $t_{\text{H2O}}$ as a function of RH shows a clear dependence on the tube age and then on the potential contamination of the tube walls by particulate matter. On the contrary, the low-pass filtering of the CO2 fluctuations did not change with time and/or ambient conditions, and the observed value of 0.15 s is consistent with the one reported by Rannik et al. (2004) for the same EC system. The observed variability of $t_{\text{H2O}}$ with the relative humidity is well characterized by Eq. (7). Such a simple curve explains well (for the fitting statistics see Table 1) the dependence between $t_{\text{H2O}}$ and RH for each year. In short, the apparent frequency response of water vapor deteriorated year by year, while no deterioration was observed for the CO2 signal. Since the analyzer was calibrated frequently and all physical characteristics of the EC setup were held constant during the years, we are confident that this change in $t_{\text{H2O}}$ was caused only by the ageing–inside dirtiness of the sampling tube.
b. The attenuation factors for CO2 and water vapor fluxes

Attenuation factors \( F_a \) for CO2 and water vapor fluxes are estimated by numerical integration of Eq. (2), where the empirical cospectral models for the unstable and stable thermal stratification [Eqs. (3) and (4), respectively] and the experimentally derived transfer functions \( H_{ws}(n) \) have been used.

For CO2 flux, given the height \( z - d = 12.8 \text{ m} \) and the response time \( \tau_{CO2} = 0.15 \text{ s} \), the attenuation factor \( F_a \) depends on the atmospheric stability and the mean wind speed (Fig. 3, top). For H2O flux, the attenuation factor changes also as a function of the effective response time, given by Eq. (7).

In Fig. 3 (bottom) we show \( F_a \) for water vapor as a function of dimensionless response time \( [\tau_{H2O} U(z - d)] \) for the same period (summer 2006). In this case the magnitude of the attenuation factor is larger with respect to the one calculated for CO2, mainly because of longer response times for water vapor. The corrected EC flux \( ws \) may be simply calculated by using the estimated \( F_a \) and the measured (attenuated) flux \( (ws)_m \) in Eq. (1).

The corrected latent heat (LE) fluxes are calculated by using both a constant response time \( \tau_{H2O} \) equal to 0.25 s (Keronen et al. 2003) and a variable RH-dependent \( \tau_{H2O} \). For the year 2002, when the sampling tube was new, the relative humidity effect on \( \tau_{H2O} \) was very small, the averaged relative difference between the two corrected fluxes is less than 1%, and the cospectral attenuation amounts on average to 7% (Figs. 4a,b).

A relevant departure between the two corrected fluxes was found for the year 2006 (Figs. 4c,d), when the effect of the relative humidity on \( \tau_{H2O} \) was much larger. Using a constant response time \( \tau_{H2O} = 0.25 \text{ s} \), the corrected LE fluxes were on average only 6% larger than the measured fluxes (Fig. 4c).

The view strongly changes if the fluxes are corrected using the effective response time, taking into account the relative humidity dependence of \( \tau_{H2O} \) (Fig. 4d). Here the scatter between the uncorrected and corrected fluxes is amplified, and the correction becomes very large mainly

\[ \text{Table 1. Empirical coefficients estimated for each year by using the non-linear fitting curve [see Eq. (7)], where } \tau_{H2O} \text{ is the response time for water vapour in seconds and RH is the relative humidity in percentage.} \]

<table>
<thead>
<tr>
<th>Period</th>
<th>( a )</th>
<th>( b )</th>
<th>( c )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2001</td>
<td>0.3</td>
<td>5.99</td>
<td>5.21</td>
<td>0.999</td>
</tr>
<tr>
<td>2002 new tube</td>
<td>0.246</td>
<td>0.24</td>
<td>2.942</td>
<td>0.97</td>
</tr>
<tr>
<td>2003</td>
<td>0.24</td>
<td>1.31</td>
<td>7.404</td>
<td>0.993</td>
</tr>
<tr>
<td>2004</td>
<td>0.23</td>
<td>1.87</td>
<td>4.05</td>
<td>0.93</td>
</tr>
<tr>
<td>2005</td>
<td>0.18</td>
<td>5.4</td>
<td>4.6</td>
<td>0.987</td>
</tr>
<tr>
<td>2006</td>
<td>0.22</td>
<td>3.77</td>
<td>4.847</td>
<td>0.987</td>
</tr>
</tbody>
</table>

Fig. 2. Relationship between the response time for water vapor and the relative humidity (expressed as a fraction of 1) estimated for several years (triangles). The solid line represents the empirical model, where the fitting curve coefficients are reported in Table 1. The response time for CO2 (circles) is also plotted, showing no dependence on relative humidity.
when the absolute value of the LE flux is small (e.g., during nighttime, when the relative humidity is high). For further analysis we use weekly average fluxes in order to quantify the amount of the new correction for different seasons.

Figure 5a shows the seasonal pattern of the relative difference between the measured and the corrected weekly averaged LE flux values for 2006. Using a constant response time equal to 0.25 s, the corrected LE fluxes were on average 6% larger than the measured ones. If the LE fluxes are corrected with the effective response time, the measured relative difference clearly increases, ranging from 10%–15% in summertime to 30%–40% during the winter, when high-RH conditions dominate and the magnitude of the fluxes is lower (Fig. 5b).

c. Effect on energy and water balance

In addition to these main results, here we briefly present the implications of the new water vapor flux correction for the energy and water balance at our site.

The surface energy balance closure for 2006 (old tube) is shown in Fig. 6, where the vertical axis represents the turbulent energy transfer, that is, the sum of the sensible ($H$) and latent heat fluxes (LE), and the horizontal axis the available energy. The net radiation ($R_n$) and ground heat flux ($G$) were directly measured, and the storage terms $\Sigma S$ (changes in the biomass heat storage and the sensible and latent heat storages into the air column below the EC measurement height) were estimated from profile measurements using methods similar to that of Oncley et al. (2007). The energy balance closure was calculated as a linear fit to the 30-min measurements. The closure estimated from all available 2006 data was 0.86 (intercept $\pm 0.2 W m^{-2}$) when the latent heat flux was corrected using the constant $\tau_{H2O}$ (Fig. 6a). When the effect of RH was taken into account in $\tau_{H2O}$ (Fig. 6b), the average energy balance closure improved slightly (0.87 with intercept $\pm 2 W m^{-2}$). When only $70\% < RH < 80\%$ conditions (Fig. 6c,d) were considered, the improvement of the closure was larger (+4%).

Although the effect on the energy balance closure at this Scots pine site was rather conservative, the new correction both reduced the intercept and improved the slope. Because the relative difference between the two corrections [constant $\tau_{H2O}$ and $\tau_{H2O} = f(RH)$] is largest when the fluxes are low (high RH), the absolute difference is rather constant across the whole range of LE (and available energy). Therefore, other factors, which were not considered here and are widely discussed in other studies (Cava et al. 2007; Foken 2008), can determine the lack of energy balance closure.
Figure 7 shows the annual cumulative curves of evapotranspiration fluxes (ET, in millimeters) for 2006, calculated using the two response times. The measured annual sum of ET corrected with a constant (=0.25 s) and a variable [=/f(RH)] response time. The dashed lines mark the 1:1 line, and the solid lines represent the linear regression functions: (a) \( y = 0.93x + 0.06, R^2 = 0.999 \); (b) \( y = 0.925x - 0.03, R^2 = 0.999 \); (c) \( y = 0.94x + 0.05, R^2 = 0.999 \); and (d) \( y = 0.89x - 1.06, R^2 = 0.989 \).

6. Discussion

a. Relative humidity effect on the high-frequency attenuation of water vapor flux

In this study we investigated the low-pass-filtering effect for CO\(_2\) and H\(_2\)O signals measured by a closed-path eddy covariance system. The cospectral transfer function method was used for estimating the high-frequency attenuation factor for CO\(_2\) and H\(_2\)O fluxes. The main finding of this study is that the tubing age and the ambient relative humidity are relevant factors to consider when we want to estimate the high-frequency spectral attenuation of water vapor fluxes. In particular, we found that when the sampling tube was new and clean inside, the dependence of the water vapor response time on RH was very small (almost negligible in terms of flux attenuation). In this case the heating of the tube was efficient enough to prevent (or to minimize) the water absorption on the tube wall. The presence of dust, salt, and small particles inside the tube may increase with the age of the tube (even if it includes an inlet filter). Then the tube wall surfaces are contaminated with a variety of atmospheric aerosols and condensation nuclei. In this case, our results show that the damping of water vapor fluctuations strongly depends on relative humidity, and this dependence increases with the age (dirtiness) of the tube. One possible qualitative explanation of such a time-dependent phenomenon is that the heating of the contaminated tube wall is less efficient and the surface temperature is likely not uniform along the tube, because of the presence of randomly distributed particulate matter, which act as sites for water vapor condensation. In addition, microscale mechanisms that depend on the hygroscopic and chemical properties of pollutants (the nature and relative amount of which are generally unknown) could occur inside the tube.

These effects are not taken into account in traditional corrections nor do theoretical transfer functions exist dealing with it [except in a recent study by Massman and Ibrom (2008)]. At present, assuming a basic maintenance and standard setup of the closed-path EC system (constant flow rate, turbulent flow in the tube, changing
filters periodically, etc.), extra maintenance of the sampling tube (cleaning or changing it) and/or frequent empirical estimations of $\tau_{H2O}$ are the only solutions to account for these effects in the closed-path EC systems. If none of these actions is performed periodically, there is a notable risk that the relationship between $\tau_{H2O}$ and relative humidity is not adequately considered and, therefore, that the water vapor fluxes are systematically underestimated. In this study we proposed a simple method, which can be used for investigating such effect in other long-term experimental eddy-covariance sites.

b. Comparison with other observations

Leuning and Judd (1996) showed that the high-frequency attenuation for water vapor by an aged and dirty sampling tube is much larger than that by a new and clean tube. They compared transfer functions for a sampling tube before and after cleaning it and observed a degradation of $\tau_{H2O}$ for the dirty sampling tube. They emphasized that the rates of physical absorption and desorption of water vapor to and from the walls of the gas tubing and filters could change, because of the presence of dust, pollen, and salt crystals in the walls of the dirty tube (Leuning and Judd 1996).

A degradation of the empirically derived $\tau_{H2O}$ values with the aging of the tube was also reported by Su et al. (2004) for closed-path EC systems at two sites. Their Table VII shows the $\tau_{H2O}$ values calculated on a monthly basis during the summer season for both sites. They did not investigate possible relative humidity effect on $\tau_{H2O}$. However, our results indicate a strong correlation between the age of the tube and the relative humidity effect. That is, without performing such analysis for different relative humidity classes, the calculated $\tau_{H2O}$ and $F_a$ values could probably be overestimated under low-RH conditions and underestimated under high-RH periods. Their daytime attenuation for water vapor fluxes ranged on average between 10% and 20%, depending on the aging of the sampling tubes.

Recently, Ibrom et al. (2007) disclosed a strong relationship between $\tau_{H2O}$ and relative humidity in two closed-path EC systems. Accounting for this unintended filtering, they estimated that the attenuation of water vapor flux in their setup of a LI-COR 6262 Infrared Gas Analyzer (IRGA) and a nonheated 50-m-long PTFE sampling tube was quite large (on average 42% of the measured flux), while for CO$_2$ the high-frequency flux attenuation was only to 4% and independent of RH. Whereas the attenuation for CO$_2$ fluxes was of similar magnitude to those we found for our dataset, the average attenuation for H$_2$O was much larger than in our case. One possible reason for this difference is that their sampling tube was significantly longer and not heated, so the condensation effect might be more important, strongly enhancing the damping of water vapor fluctuations. Moreover, the age of the tube was not taken into account in their study.

Finally, we would like to acknowledge a recent study by Massman and Ibrom (2008), who develop a semiempirical
model dealing with the water vapor absorption–desorption at the interior surface of a closed-path EC system tube wall. Massman and Ibrom’s model seems to capture the Reynolds number dependency, as well as the ambient relative humidity dependency of water vapor attenuation. However, they concluded that more experimental data are needed, and at the moment the physical basis of such a phenomenon is unknown.

7. Conclusions

To assure the reliability and comparability of the long-term flux measurements between different years and across ecological gradients, frequent calibrations and maintenance of the eddy covariance measurement setups are required. In addition, the corrections one applies on the measured raw fluxes should reflect the present state of the measurement setup as accurately as possible. In this paper, we showed that the response of a closed-path EC setup to water flux measurements is strongly deteriorated by high ambient relative humidity, and its influence increases as the sampling tube is aging. The effective response time for H2O ($\tau_{\text{H2O}}$) of a closed-path EC setup with the LI-COR 6262 IRGA and a heated 7-m-long sampling tube was almost insensitive on the RH when the tube was new, but already 1 yr later high
relative humidity started to have a significant effect. For a 4-year-old tube the underestimation of the water flux could reach 40% when the relative humidity was high (wintertime and nighttime). On the contrary, response times for CO$_2$ were not affected by either relative humidity or tube age. The new correction scheme developed in this study slightly improved the energy balance closure and annual stand water balance. The annual evapotranspiration increased by 10% relative to the value corrected by the constant $\tau_{\text{H}_2\text{O}}$.

Although the effect of the improved parameterization of $\tau_{\text{H}_2\text{O}}$ as a function of RH was rather conservative on this particular Scots pine site, where the water vapor fluxes are generally low when RH is high, the effects can be more dramatic and important in ecosystems experiencing more humid climates, such as tropical forests and wetlands. Moreover, if the influence of relative humidity is not taken into account, the water vapor fluxes are systematically underestimated, and thus the errors in cumulative values can be large.

However, it can in practice be difficult to change or clean the sampling tube of a closed-path EC setup every year. Therefore, we suggest that the procedure developed in this paper is used to analyze the effect of ambient conditions on the response of the closed-path eddy covariance setup. If found necessary, the method can be applied to correct the flux values also for earlier years.

Finally, the observational results presented in this study can be used for further improvements of turbulent flow models dealing with the attenuation effect of nonpassive scalars.

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