2012

The fundamental equation of eddy covariance and its application in flux measurements

Lianhong Gu
Oak Ridge National Laboratory, Oak Ridge, TN

William J. Massman
Rocky Mountain Research Station, Fort Collins, CO

Ray Leuning
CSIRO Marine and Atmospheric Research, Canberra, ACT 2601, Australia

Stephen Pallardy
University of Missouri, Columbia, MO

Tilden Meyers
Atmospheric Turbulence and Diffusion Division, Air Resources Laboratory, NOAA, Oak Ridge, TN

See next page for additional authors

Follow this and additional works at: https://digitalcommons.unl.edu/usdoepub

Part of the Bioresource and Agricultural Engineering Commons

Authors

Lianhong Gu, William J. Massman, Ray Leuning, Stephen Pallardy, Tilden Meyers, Paul Hanson, Jeffery Riggs, Kevin Hosman, and Bai Yang
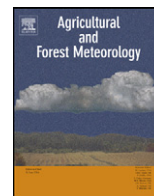
The fundamental equation of eddy covariance and its application in flux measurements☆

Lianhong Gu [a,*], William J. Massman [b], Ray Leuning [c], Stephen G. Pallardy [d], Tilden Meyers [e], Paul J. Hanson [a], Jeffery S. Riggs [a], Kevin P. Hosman [d], Bai Yang [a]

[a] Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
[b] USDA Forest Service, Rocky Mountain Research Station, 240 West Prospect, Fort Collins, CO 80526, USA
[c] CSIRO Marine and Atmospheric Research, PO Box 3023, Canberra, ACT 2601, Australia
[d] Department of Forestry, University of Missouri, Columbia, MO 65211, USA
[e] Atmospheric Turbulence and Diffusion Division, Air Resources Laboratory, NOAA, Oak Ridge, TN 37830, USA

ARTICLE INFO

ABSTRACT

A fundamental equation of eddy covariance (FQEC) is derived that allows the net ecosystem exchange (NEE) $\overline{N_s}$ of a specified atmospheric constituent s to be measured with the constraint of conservation of any other atmospheric constituent (e.g. N_2, argon, or dry air). It is shown that if the condition $\left|\overline{N_s}\right| \gg \left|\overline{\chi_s}\right| \left|\overline{N_{CO_2}}\right|$ is true, the conservation of mass can be applied with the assumption of *no net ecosystem source or sink* of dry air and the FQEC is reduced to the following equation and its approximation for horizontally homogeneous mass fluxes:

$$\overline{N_s} = \overline{c_d}\,\overline{w'\chi_s'}\Big|_h + \int_0^h \overline{c_d}(z)\frac{\overline{\partial\chi_s}}{\partial t}\,dz + \int_0^h [\overline{\chi_s}(z) - \overline{\chi_s}(h)]\frac{\overline{\partial c_d}}{\partial t}\,dz \approx \overline{c_d}(h)\left\{\overline{w'\chi_s'}\Big|_h + \int_0^h \frac{\overline{\partial\chi_s}}{\partial t}\,dz\right\}.$$

Here w is vertical velocity, c molar density, t time, h eddy flux measurement height, z vertical distance and $\chi_s = c_s/c_d$ molar mixing ratio relative to dry air. Subscripts s, d and CO_2 are for the specified constituent, dry air and carbon dioxide, respectively. Primes and overbars refer to turbulent fluctuations and time averages, respectively. This equation and its approximation are derived for non-steady state conditions that build on the steady-state theory of Webb, Pearman and Leuning (WPL; Webb et al., 1980. Quart. J. R. Meteorol. Soc. 106, 85–100), theory that is widely used to calculate the eddy fluxes of CO_2 and other trace gases. The original WPL constraint of no *vertical flux* of dry air across the EC measurement plane, which is valid only for steady-state conditions, is replaced with the requirement of no net ecosystem source or sink of dry air for non-steady state conditions. This replacement does not affect the '*eddy flux*' term $\overline{c_d w'\chi_s'}$ but requires the change in storage to be calculated as the '*effective change in storage*' as follows:

$$\int_0^h \frac{\overline{\partial c_s}}{\partial t}\,dz - \overline{\chi_s}(h)\int_0^h \frac{\overline{\partial c_d}}{\partial t}\,dz = \int_0^h \overline{c_d}(z)\frac{\overline{\partial\chi_s}}{\partial t}\,dz + \int_0^h [\overline{\chi_s}(z) - \overline{\chi_s}(h)]\frac{\overline{\partial c_d}}{\partial t}\,dz \approx \overline{c_d}(h)\int_0^h \frac{\overline{\partial\chi_s}}{\partial t}\,dz.$$

Without doing so, significant diurnal and seasonal biases may occur. We demonstrate that the effective change in storage can be estimated accurately with a properly designed profile of mixing ratio measurements made at multiple heights. However further simplification by using a single measurement at the EC instrumentation height is shown to produce substantial biases. It is emphasized that an adequately designed profile system for measuring the effective change in storage in proper units is as important as the eddy flux term for determining NEE.

© 2011 Elsevier B.V. All rights reserved.

When the EC instrumentation measures densities rather than mixing ratios, it is necessary to use:

$$\overline{N_s} \approx \overline{w'c_s'}\Big|_h + \overline{\chi_s}\left[\overline{w'c_v'} + \bar{c}\,\frac{\overline{w'T'}}{\bar{T}}\right]_h + \overline{c_d}(h)\int_0^h \frac{\partial \chi_s}{\partial t}\,dz.$$

Here T is temperature and c_v and c are the molar densities of water vapor and moist air, respectively. For some atmospheric gas species such as N_2 and O_2, the condition $\left|\overline{N_s}\right| \gg \left|\overline{\chi_s}\right|\left|\overline{N_{CO_2}}\right|$ is not satisfied and additional information is needed in order to apply the EC technique with the constraint of conservation of dry air.

1. Introduction

Flux measurements of trace gases, water vapor, and sensible heat with the eddy covariance (EC) technique play an important role in the fields of climate change, global change biology and ecology. Such measurements are routinely used for understanding ecosystem function, estimating terrestrial carbon budgets, testing ecosystem and land surface models, and predicting ecosystem responses to changes in mean and extreme climate conditions. However, the EC technique in its present state has several recognized problems. For example, it is unable to close the energy budget (e.g. Wilson et al., 2002) and apparently underestimates nighttime ecosystem respiration (e.g. Goulden et al., 1996; Gu et al., 2005). The nearly universal occurrence of these problems across flux sites with diverse vegetation and topographical characteristics requires periodic reexamination of the fundamental assumptions applied in the EC technique.

EC flux measurements of atmospheric constituents require constraints to compensate for inadequate accuracy in measured variables as well as for other issues. The principle guiding the current practice of EC measurements was laid out by Webb, Pearman and Leuning (WPL) in 1980 (Webb et al., 1980; Lee and Massman, 2011). The WPL's seminal theory assumed 'no source or sink of (dry) air at the ground' and as a result implemented a constraint of no vertical flux of dry air (defined as the mixture of all atmospheric constituents other than water vapor) across the EC measurement plane. Consequently, WPL 1980 was limited to the case of horizontally homogeneous mass fluxes under steady-state conditions (no temperature/pressure changes). Nevertheless, the theory has been applied widely even though the constraint of no vertical flux of dry air is invalid for non-steady state conditions, when changes in density associated with changes in temperature and pressure lead to a non-zero flux of dry air and other gases through the EC measurement plane. Fluxes of a specified atmospheric constituent thus consist of one component due to atmospheric dry air density changes that is not of particular interest, and another due to the net exchanges between the ecosystem and the atmosphere that we do wish to know. Flux measurements will be biased, diurnally and seasonally, if the non-zero vertical flux of dry air is not taken into consideration. These biases can be eliminated by careful examination of all terms in the mass conservation equation, which can be expressed in terms of mass densities, molar densities or mixing ratios. As shown below, the number of terms in the equation varies with the units chosen and this outcome affects how field measurements need to be analyzed to give the correct results.

Several authors have already realized the need to generalize the steady-state theory of WPL 1980 so that non-steady state conditions can be considered. Leuning (2004, 2007) developed mass balance equations for a trace quantity with the assumption of no net ecosystem source or sink of dry air. Kowalski and Serrano-Ortiz (2007) pointed out the assumption of zero dry air flux is invalid except right at the soil surface boundary. Lee and Massman (2011) applied the equation of continuity of dry air with zero source (Paw

et al., 2000) and the assumption of no dry air flux at the soil surface to derive equations for flux measurements. Note that the treatment of Lee and Massman (2011) and the assumption of Leuning (2004, 2007) are equivalent.

In the present study, we build upon these contributions. We broaden the eddy covariance theory by deriving a fundamental equation of eddy covariance that allows the net ecosystem exchange of a specified atmospheric constituent such as CO_2 and water vapor between the surface and atmosphere to be measured with the constraint of conservation of mass of any other atmospheric constituent. Candidate constituents that are suitable for use to constrain flux measurements are suggested. The application of the conservation of dry air for flux measurements is then seen as a special case of the fundamental equation of eddy covariance. We also establish the condition under which the assumption of no net ecosystem source or sink of dry air can be made without substantial errors in measured fluxes. It is shown that for some atmospheric gas species this assumption is not valid; for these species, we identify what additional information is needed in order to measure their fluxes with the EC technique. Biases caused by applying the steady-state theory for non-steady state conditions are assessed and certain unstated, simplifying assumptions in previous studies are clarified and investigated with observations from a flux site. Finally we show that measurements of change in storage through an adequately designed profile system and in proper units are as important as the eddy flux term for accurate determination of NEE.

2. The fundamental equation of eddy covariance

2.1. The derivation of the equation

Ever since WPL 1980, dry air has played a central role in eddy flux measurements of atmospheric constituents. On first thought, this sounds quite unusual: why should measuring the flux of one atmospheric constituent have anything to do with a constantly changing admixture of all non-H_2O atmospheric constituents most of which are not even measured? The answer to this question may seem obvious but its illumination is helpful to understanding the eddy covariance theory. Here it is shown that dry air comes into play only as a matter of convenience and the fundamental equation of eddy covariance (FQEC) can be formulated without invoking dry air at all. The FQEC can be derived either through the holistic mass balance approach or through the equation of continuity of an atmospheric constituent. These two approaches are equivalent. Here the FQEC for horizontally homogeneous mass fluxes is derived with the holistic mass balance approach. In Appendix A, the general FQEC for non-homogeneous mass fluxes is derived from equation of continuity.

For a layer of horizontally homogeneous air flows above the soil surface in which horizontal advection can be ignored, the conservation of mass dictates that the net ecosystem exchange (NEE) $\overline{N_s}$ (mol m^{-2} s^{-1}) of a specified atmospheric constituent s is balanced

by its total vertical flux $\overline{wc_s}$ across the EC measurement plane at height h and total change in storage with time t below that height:

$$\overline{N_s} = \overline{wc_s}\big|_h + \int_0^h \overline{\frac{\partial c_s}{\partial t}}\, dz. \tag{1}$$

Here w refers to vertical wind velocity, c_s to molar density (mol m^{-3}) of the specified constituent, and z to vertical distance from the soil surface. Overbars indicate time averages. Symbols and subscripts are listed in Appendix B. Note that $\overline{N_s}$ includes contributions from both plant canopy and soil (see Appendix A). Also Eq. (1) applies only to nonreactive gas species. For a reactive gas species, the right hand side of Eq. (1) is equal to the biochemically produced $\overline{N_s}$ plus any sink/source of the species of photo (and other)-chemical origins. Vilà-Guerau de Arellano et al. (1995) studied the flux-gradient relationships of chemically reactive species. The present study considers only nonreactive gas species. Later when the oxygen molecules (O$_2$) are discussed in the context of eddy covariance theory, their participation in photochemical reactions in the atmosphere will be ignored.

EC instrumentation measures both w and c_s. A naïve thought might be to insert the directly measured w and c_s into Eq. (1) and calculate $\overline{N_s}$ in a straightforward way. One reason for not doing so as explained in WPL 1980 is still valid for today's EC instrumentation: w cannot be measured with sufficient accuracy. Additional information is needed to constrain or condition Eq. (1). To see what additional information is needed, we apply the Reynolds decomposition rules to the total vertical flux:

$$\overline{wc_s}\big|_h = \overline{w'c_s'}\big|_h + \overline{w}\,\overline{c_s}\big|_h. \tag{2}$$

Here the rapid turbulent fluctuations (primed variables) have been separated from their corresponding means (overbarred variables). The total vertical flux now consists of two terms: a covariance term and a mean vertical advective flux term. Any additive bias errors in the measured w and c_s will not affect the covariance term which can therefore be used directly as part of the total vertical flux. However such errors will affect the mean vertical advective flux term $\overline{w}\,\overline{c_s}$ and additional information is needed to constrain or replace it.

Now suppose the NEE $\overline{N_d}$ of another atmospheric constituent, d, called the constraining constituent, is known *a priori*. Thus, we can write:

$$\overline{N_d} = \overline{wc_d}\big|_h + \int_0^h \overline{\frac{\partial c_d}{\partial t}}\, dz = \overline{w'c_d'}\big|_h + \overline{w}\,\overline{c_d}\big|_h + \int_0^h \overline{\frac{\partial c_d}{\partial t}}\, dz = \overline{w'c_d'}\big|_h$$
$$+ \overline{w}\,\overline{c_s}\frac{\overline{c_d}}{\overline{c_s}}\bigg|_h + \int_0^h \overline{\frac{\partial c_d}{\partial t}}\, dz. \tag{3}$$

Solving for the mean vertical advective flux $\overline{w}\,\overline{c_s}$ results in

$$\overline{w}\,\overline{c_s}\big|_h = \overline{\chi_s}(h)\left(-\overline{w'c_d'}\big|_h + \overline{N_d} - \int_0^h \overline{\frac{\partial c_d}{\partial t}}\, dz\right). \tag{4}$$

Here χ_s is the molar density ratio of s relative to the constraining constituent ($\chi_s = c_s/c_d$). The mean vertical advective flux of s is now expressed as the product of the molar density ratio and a term that is entirely defined by the constraining constituent. Substituting (4) into (2) yields the total vertical flux of s:

$$\overline{wc_s}\big|_h = \overline{w'c_s'}\big|_h + \overline{\chi_s}(h)\left(-\overline{w'c_d'}\big|_h + \overline{N_d} - \int_0^h \overline{\frac{\partial c_d}{\partial t}}\, dz\right). \tag{5}$$

Noting $c_s' = \overline{\chi_s}c_d' + \overline{c_d}\chi_s'$ as a result of linearization, we can rewrite (5) in the form of molar density ratio of s relative to the constraining constituent:

$$\overline{wc_s}\big|_h = \underbrace{\overline{c_d}\,\overline{w'\chi_s'}\big|_h}_{\text{I}} + \underbrace{\overline{\chi_s}(h)\overline{N_d}}_{\text{II}} - \underbrace{\overline{\chi_s}(h)\int_0^h \overline{\frac{\partial c_d}{\partial t}}\, dz}_{\text{III}}. \tag{6}$$

Eq. (6) shows that the total vertical flux of s across the EC measurement plane at h contains three parts: (I) the eddy flux – the covariance between vertical wind velocity and molar density ratio, multiplied by the molar density of the constraining constituent; (II) a correction due to the net ecosystem source/sink of the constraining constituent, which is termed 'constraining constituent source/sink correction'; and (III) a component due to the time change in storage of the constraining constituent below h, which is termed 'constraining constituent storage adjustment'. A key insight from Eq. (6) is that the eddy flux is only part of the total vertical flux across the EC measurement plane.

The NEE of s can now be expressed either as

$$\overline{N_s} = \overline{w'c_s'}\big|_h + \int_0^h \overline{\frac{\partial c_s}{\partial t}}\, dz + \overline{\chi_s}(h)\left(-\overline{w'c_d'}\big|_h + \overline{N_d} - \int_0^h \overline{\frac{\partial c_d}{\partial t}}\, dz\right), \tag{7}$$

or as

$$\overline{N_s} = \underbrace{\overline{c_d}\,\overline{w'\chi_s'}\big|_h}_{\text{I}} + \underbrace{\overline{\chi_s}(h)\overline{N_d}}_{\text{II}} + \underbrace{\int_0^h \overline{\frac{\partial c_s}{\partial t}}\, dz - \overline{\chi_s}(h)\int_0^h \overline{\frac{\partial c_d}{\partial t}}\, dz}_{\text{III}}. \tag{8}$$

The net exchange of s with the atmosphere is the sum of: (I) the eddy flux, (II) the flux of s associated with $\overline{N_d}$, and (III) the total change in mass of s stored in the air column below h minus the change in mass of s arising from heating, cooling or change in atmospheric pressure within the air column. From now on, we will call term III the 'effective change in storage' of s. The concept of effective change in storage acknowledges that part of the total change in storage of s below h and therefore part of the total vertical flux of s at h are not caused by the biological processes of the ecosystem and are not part of the NEE of s. As shown later, the physical meaning of term III will become clearer when changes in storage are expressed in terms of molar density ratios.

In the derivation above, the WPL 1980 concept of mean vertical velocity is not invoked. The use of the concept of thermal expansion velocity of Lee and Massman (2011) is also avoided. For the purpose of comparison with these previous studies, we note that both the WPL velocity and the thermal expansion velocity are inseparable part of the diagnostic mean vertical bulk velocity ($\overline{w}$). This diagnostic velocity is responsible for the mean vertical advective flux in the total vertical flux (see Eq. (2)) and given by

$$\frac{1}{\overline{c_s}(h)}\left(-\overline{w'c_s'}\big|_h + \overline{N_s} - \int_0^h \overline{\frac{\partial c_s}{\partial t}}\, dz\right) = \frac{1}{\overline{c_d}(h)}\left(-\overline{w'c_d'}\big|_h + \overline{N_d} - \int_0^h \overline{\frac{\partial c_d}{\partial t}}\, dz\right). \tag{9}$$

This identity is obtained by manipulating Eq. (7). Note that the subscripts s and d can refer to any atmospheric constituent and the two sides of the identity are symmetrical in form. Eq. (9) expresses the coupling in atmospheric transport of different atmospheric constituents. It indicates the basis upon which the flux measurements of a specified atmospheric constituent are ultimately constrained: no matter what processes are responsible for the presence of a nonzero mean vertical bulk velocity, this velocity must be identical for each and every atmospheric constituent.

Eqs. (7) and (8) are derived with a minimum number of assumptions. Either equation can be termed the fundamental equation of eddy covariance for horizontally homogeneous mass fluxes. In

Appendix A, the general FQEC for non-homogeneous mass fluxes is derived and is reproduced here:

$$\overline{N_s} = \overline{c_d}\,\overline{w'\chi_s'}\Big|_h + \overline{\chi_s}(h)\overline{N_d} + \left\{ \int_0^h \frac{\overline{\partial c_s}}{\partial t}\,dz - \overline{\chi_s}(h)\int_0^h \frac{\overline{\partial c_d}}{\partial t}\,dz \right\}$$

$$+ \underbrace{\left\{ \int_0^h \nabla_H \cdot (\overline{\mathbf{u}c_d}\,\overline{\chi_s} + \overline{c_d}\overline{\mathbf{u}'\chi_s'})\,dz - \overline{\chi_s}(h)\int_0^h \nabla_H \cdot (\overline{\mathbf{u}c_d})\,dz \right\}}_{\text{horizontal advection}} \quad (10)$$

Here $\mathbf{u}$ is the 2D horizontal velocity field and ∇_H is the 2D horizontal gradient operator. Compared with the FQEC for horizontally homogeneous mass fluxes, the general FQEC contains a term for horizontal advection.

2.2. Choices of the constraining constituent

The derivation of the FQEC in Section 2.1 and in Appendix A shows that in theory it is unnecessary to restrict the selection of the constraining constituent to dry air. The conservation of mass of any atmospheric constituent can be used to constrain flux measurements with the eddy covariance technique as long as its net ecosystem exchange with the atmosphere is known *a priori*. However, there is a practical advantage in using dry air: one does not need an extra gas analysis system besides those that measure the constituent *s* and water vapor whose net ecosystem exchanges are our interest. With an open gas analysis system for *s* and water vapor, $\overline{w'c_d'}$ in Eq. (7) is replaced with the measurable moisture covariance $\overline{w'c_v'}$ and temperature covariance $\overline{w'T'}$. This is done by using $c_d = c - c_v$ and the equation of state for moist air $c = P/RT$ (c is moist air molar density, P total atmospheric pressure, and R universal gas constant) as in WPL 1980. After some manipulation, Eq. (7) changes to

$$\overline{N_s} = \overline{w'c_s'}\Big|_h + \overline{\chi_s}\left[\overline{w'c_v'} + \bar{c}\frac{\overline{w'T'}}{\bar{T}}\right]_h + \overline{\chi_s}(h)\overline{N_d}$$

$$+ \int_0^h \frac{\overline{\partial c_s}}{\partial t}\,dz - \overline{\chi_s}(h)\int_0^h \frac{\overline{\partial c_d}}{\partial t}\,dz. \quad (11)$$

Here χ_s becomes the molar mixing ratio of *s* relative to dry air. To derive Eq. (11), the covariance between the vertical velocity and pressure *P* is neglected. Also linearization is applied to avoid additional terms related to higher order fluctuations (beyond variances and covariances) in measured quantities (Fuehrer and Friehe, 2002). Unlike Eqs. (7) and (8), Eq. (11) is valid only when the conservation of dry air is used to constrain flux measurements.

The advantage of using dry air as the constraining constituent can also be its potential weakness. Dry air contains numerous gases and its composition varies with time. There are no fast response technologies to measure its density directly. When the ideal gas law is used to compute dry air density, additional measurements in atmospheric pressure, temperature and water vapor density are needed (see Eq. (11)). Errors in these measurements propagate into the calculated dry air density and covariances and thus fluxes of the specified atmospheric constituent. Furthermore, the use of dry air necessitates repeated application of linearization, a process that neglects contribution to calculated fluxes of higher order fluctuations in measured quantities (Fuehrer and Friehe, 2002). If a single atmospheric gas is used as the constraining constituent and its density is measured directly, the FQEC Eq. (7) is applied without the need of any indirect calculation or linearization. The elimination of uncertainties associated with indirect calculation and linearization will result in more accurate flux measurements.

N_2 and argon are potentially good choices as the constraining constituent. N_2 is the most abundant constituent in the atmosphere and argon is the third. Except for O_2, the molar density ratio of any atmospheric gas species to that of N_2 or argon is far less than 1. Ecosystems exchange N_2 with the atmosphere as a result of nitrogen fixation, nitrification and denitrification. But typical net exchange rates of N_2 from all processes are only in the range of tens of nanomoles per meter square per second (Meijide et al., 2010; Welsh et al., 2000). Argon is an inert gas and no known ecosystem processes are involved in its absorption or production. Therefore when N_2 or argon is used as the constraining constituent, the constraining constituent source/sink correction term $\overline{\chi_s N_d}$ is likely very small in comparison with the flux of any specified atmospheric constituent, and thus can be ignored. This is a benefit in addition to that no indirect calculation or linearization is necessary. Research in this direction may advance the eddy covariance technique. For the present study, however, we focus on the use of dry air as the constraining constituent.

3. Approximations to the fundamental equation of eddy covariance

3.1. The constraint of no net ecosystem source/sink of dry air

No matter whether the constraint of no vertical flux of dry air or that of no net ecosystem source/sink of dry air is applied, an apparent contradiction exists. If one wants to measure the flux of a non-water vapor atmospheric constituent, which is always part of dry air, is it not already implied that the vertical flux of dry air or the net ecosystem exchange of dry air is not zero? This contradiction is resolved with an analysis of the complete ecosystem budget of dry air and its effect on flux measurements. The analysis also leads to some new insights about the eddy covariance technique when dry air is used as the constraining constituent.

Terrestrial ecosystems affect the boundary-layer budget of dry air mainly through the exchanges of CO_2 and O_2. On time scales relevant for flux measurements (minutes to hours), the exchanges of these two gases are not balanced and do not cancel their contributions to the budget of dry air. This is because several biological processes, in addition to photosynthetic assimilation, are involved in the determination of the ecosystem $O_2:CO_2$ molar exchange ratio k which can vary from 0.7 to 1.6 (Seibt et al., 2004). Besides CO_2 and O_2, ecosystems may absorb or emit trace gases such as N_2, N_2O, NO_x (Galbally et al., 2010; Meijide et al., 2010), CH_4 in wetlands (McDermitt et al., 2011; Tuzson et al., 2010), carbonyl sulfide (Campbell et al., 2008), CO (Galbally et al., 2010; King and Crosby, 2002) and isoprene (C_5H_8, Fuentes et al., 1999). $\overline{N_{CO_2}}$ and $\overline{N_{O_2}}$ are in the order of $10\,\mu\text{mol}\,\text{m}^{-2}\,\text{s}^{-1}$ whereas measured fluxes of other trace gases produced by ecosystems generally are in the order of $10\,\text{pmol}\,\text{m}^{-2}\,\text{s}^{-1}$ to $10\,\text{nmol}\,\text{m}^{-2}\,\text{s}^{-1}$. Therefore the net ecosystem exchange of dry air is likely dominated by the stoichiometric imbalance between O_2 and CO_2 exchanges with minor contributions from other trace gases. Its typical value is likely in the range of tens of micromoles per meter square per second. Therefore some error will be introduced if the conservation of mass of dry air is used as a constraint in measuring fluxes of atmospheric constituents with the assumption of no net ecosystem source/sink of dry air ($\overline{N_d} = 0$).

To assess the magnitude of error introduced by assuming $\overline{N_d} = 0$, suppose dry air consists of *n* individual gases each of which has a net exchange between the ecosystem and atmosphere.

$$\overline{N_d} = \sum_{i=1}^{n}\overline{N_i} = \overline{N_{CO_2}} + \overline{N_{O_2}} + \sum_{i=3}^{n}\overline{N_i} = (1-k)\overline{N_{CO_2}} + \sum_{i=3}^{n}\overline{N_i}.$$

Here CO_2 and O_2 are separated from other dry air components because their net exchanges are much larger than those of others

and are stoichiometrically coupled. The negative sign preceding k indicates O_2 and CO_2 exchanges are in opposing directions. Substituting $\overline{N_d}$ in Eq. (8) and collecting terms yields:

$$\overline{N_s}[1 - \overline{\chi_s}(h)] = \overline{c_d}\,\overline{w'\chi_s'}\Big|_h + \overline{\chi_s}(h)\sum_{i=1,i\neq s}^{n}\overline{N_i}$$
$$+ \int_0^h \overline{\frac{\partial c_s}{\partial t}}\,dz - \overline{\chi_s}(h)\int_0^h \overline{\frac{\partial c_d}{\partial t}}\,dz. \tag{12}$$

The constraining constituent or dry air source/sink correction term is split into two parts. The bracket in the left-hand side represents a self-correction factor of the specified constituent while the second term in the right-hand side represents a correction due to the net exchanges of the remaining dry air components. Both corrections become more important for larger mixing ratios. The significance of these corrections is best illustrated with the following special cases.

3.1.1. N_2

Suppose one is interested in measuring the net ecosystem exchange of N_2 due to nitrogen fixation or nitrification/denitrification processes. $\overline{\chi_{N_2}} \approx 0.78$. $[\overline{N_{N_2}} - \overline{N_{N_2}}(1 - 0.78)]/\overline{N_{N_2}} = 0.78$. Thus, ignoring the self-correction factor alone, a 78% error will be committed. Neglecting net exchanges of other dry air components will result in even larger errors. Since the dry air source/sink correction term is dominated by the stoichiometric imbalance between $\overline{N_{CO_2}}$ and $\overline{N_{O_2}}$, it can be approximated with $\overline{\chi_{N_2}}(1 - k)\overline{N_{CO_2}}$. Assuming $\overline{N_{CO_2}} = -30$ mmol CO_2 m^{-2} s^{-1} and $k = 1.6$, $\overline{\chi_{N_2}}(1 - k)\overline{N_{CO_2}} = 14$ mmol N_2 m^{-2} s^{-1}. This is orders of magnitude larger than ecosystem N_2 fluxes (Welsh et al., 2000). Thus, flux measurements of N_2 made with the eddy covariance technique under the assumption of no net ecosystem source/sink of dry air would be meaningless. To measure the flux of N_2, Eq. (12) must be applied.

3.1.2. CO_2

Taking the stoichiometric relationship between $\overline{N_{CO_2}}$ and $\overline{N_{O_2}}$ into consideration and ignoring contributions from other dry air components, Eq. (8) can be rewritten as

$$\overline{N_{CO_2}}[1 - \overline{\chi_{CO_2}}(h)(1 - k)] = \overline{c_d}\,\overline{w'\chi_{CO_2}'}\Big|_h + \int_0^h \overline{\frac{\partial c_{CO_2}}{\partial t}}\,dz - \overline{\chi_{CO_2}}(h)\int_0^h \overline{\frac{\partial c_d}{\partial t}}\,dz.$$

Assuming $\overline{\chi_{CO_2}}(h) = 4 \times 10^{-4}$ (400 ppm) and $k = 1.6$, $1 - \overline{\chi_{CO_2}}(h)(1 - k) = 1.00024 \approx 1$. Thus when measuring CO_2 fluxes, the error caused by assuming *a priori* there is no net ecosystem source or sink of dry air does not exceed 0.024%.

3.1.3. $^{13}CO_2$

Let $R_{13CO_2}^N = \overline{N_{13CO_2}}/\overline{N_{CO_2}}$, the carbon-13 fraction in the mean NEE of CO_2. The ecosystem budget equation of $^{13}CO_2$ can be approximated as

$$\overline{N_{13CO_2}}\left[1 - \frac{\overline{\chi_{13CO_2}}(h)(1 - k)}{R_{13CO_2}^N}\right] = \overline{c_d}\,\overline{w'\chi_{13CO_2}'}\Big|_h + \int_0^h \overline{\frac{\partial c_{13CO_2}}{\partial t}}\,dz$$
$$- \overline{\chi_{13CO_2}}(h)\int_0^h \overline{\frac{\partial c_d}{\partial t}}\,dz.$$

$\overline{\chi_{13CO_2}} \approx \overline{c_{13CO_2}}/\overline{c_{12CO_2}} \times \overline{\chi_{CO_2}} = 0.011145 \times 4 \times 10^{-4} \approx 4 \times 10^{-6}$, where 0.011145 is the current atmospheric ^{13}C to ^{12}C molar ratio (Keeling et al., 2010). Information on $R_{13CO_2}^N$ is very limited. But if it is assumed that the stable isotopic composition of soil respiration has a $\delta^{13}C$ of $-30‰$ (Kammer et al., 2011),

then $R_{13CO_2}^N \approx (1 - 0.03) \times 0.01124 \approx 0.01$, where 0.01124 is the standard carbon isotopic molar ratio in the Pee Dee Belemnite (PDB; Craig, 1957). If only photosynthesis and C3 plants are considered, $R_{13CO_2}^N = 0.011145/(1 + 0.02) \approx 0.01$, where 0.02 is a typical photosynthetic discrimination for C3 plants ($\Delta = 20‰$, Farquhar et al., 1989). Therefore, one might assume that ecosystems have a typical $R_{13CO_2}^N$ on the order of 0.01, and $1 - \overline{\chi_{13CO_2}}(h)(1 - k)/R_{13CO_2}^N \approx 1.00024 \approx 1$. Thus we can conclude that the assumption of no net ecosystem source or sink of dry air is also valid for measuring carbon isotopic fluxes.

3.1.4. O_2

An interesting situation arises when one attempts to measure O_2 flux instead of CO_2 flux. Using $\overline{N_d} \approx (1 - (1/k))\overline{N_{O_2}}$, Eq. (8) becomes

$$\overline{N_{O_2}}\left[1 - \overline{\chi_{O_2}}(h)\left(1 - \frac{1}{k}\right)\right] = \overline{c_d}\,\overline{w'\chi_{O_2}'}\Big|_h + \int_0^h \overline{\frac{\partial c_{O_2}}{\partial t}}\,dz - \overline{\chi_{O_2}}(h)\int_0^h \overline{\frac{\partial c_d}{\partial t}}\,dz.$$

$\overline{\chi_{O_2}} \approx 0.21$. For $k = 1.6$, $1 - \overline{\chi_{O_2}}(1 - (1/k)) \approx 0.9$. Thus, a 10% error will be introduced by setting $\overline{N_d} = 0$. To measure the flux of O_2, the value of k is needed.

3.1.5. H_2O

The dry air source/sink correction term for water vapor flux is approximately given by $\overline{\chi_{H_2O}}(1 - k)\overline{N_{CO_2}}$. For a relative humidity of 100% at an air temperature of 25 °C, $\overline{\chi_{H_2O}} \approx 0.03$. Assuming a peak daytime $\overline{N_{CO_2}} = -30$ mmol CO_2 m^{-2} s^{-1} and $k = 1.6$, the correction is about 0.54 µmol H_2O m^{-2} s^{-1} = 0.00054 mmol H_2O m^{-2} s^{-1}. Typical water vapor flux is on the order of 1 mmol H_2O m^{-2} s^{-1}. Thus, assuming $\overline{N_d} = 0$ causes errors <0.05% for water vapor flux measurements.

An important insight from these special case analyses is that, with the information typically available, the contemporary eddy covariance technique cannot measure the flux of every atmospheric constituent even when a fast response gas analyzer with sufficient accuracy is available. For example, it cannot be used to determine fluxes of N_2 and O_2 unless the fluxes of other non-water vapor gases are known and the ecosystem O_2:CO_2 molar exchange ratio is given. As a general rule, the assumption of no net ecosystem source or sink of dry air can be made for measuring fluxes of an atmospheric constituent s only if the following condition is true:

$$\left|\overline{N_s}\right| \gg \left|\overline{\chi_s}\right|\left|\overline{N_{CO_2}}\right|. \tag{13}$$

When this condition holds, the NEE of s for horizontally homogeneous air flows can be calculated with

$$\overline{N_s} = \overline{c_d}\,\overline{w'\chi_s'}\Big|_h + \int_0^h \overline{\frac{\partial c_s}{\partial t}}\,dz - \overline{\chi_s}(h)\int_0^h \overline{\frac{\partial c_d}{\partial t}}\,dz, \tag{14}$$

for a closed-path system, or with

$$\overline{N_s} = \overline{w'c_s'}\Big|_h + \overline{\chi_s}\left[\overline{w'c_v'} + \bar{c}\,\frac{\overline{w'T'}}{\overline{T}}\right]_h + \int_0^h \overline{\frac{\partial c_s}{\partial t}}\,dz - \overline{\chi_s}(h)\int_0^h \overline{\frac{\partial c_d}{\partial t}}\,dz, \tag{15}$$

for an open-path system. These two equations are identical to those in Leuning (2004, 2007) and Lee and Massman (2011) who for their purpose of discussion assumed *a priori* there is no net ecosystem source or sink of dry air.

3.2. The assumption of steady-state conditions of WPL 1980

A central concept in WPL 1980 was that 'there is no source or sink of (dry) air at the ground'. This concept was implemented by making the vertical flux of dry air at the EC measurement plane to be zero (Eqn. (11) in WPL 1980). The WPL 1980 treatment is only valid

for steady-state conditions. For non-steady state conditions, it will be necessary to modify the term for the change in storage in order to avoid biases in the estimated NEE. Note that the *eddy flux* term derived by WPL 1980 is still correct for non-steady state conditions (Leuning, 2007; also see Appendix A). Horizontally homogenous, non-steady flows have been addressed in Leuning (2004, 2007), Kowalski and Serrano-Ortiz (2007) and Lee and Massman (2011). Later, we will use measurements to demonstrate the magnitude of the change in storage term when the steady-state theory is replaced with the more general non-steady state theory.

3.3. Approximations to the effective change in storage

To compute the effective change in storage

$$\int_0^h \overline{\frac{\partial c_s}{\partial t}}\, dz - \overline{\chi_s}(h) \int_0^h \overline{\frac{\partial c_d}{\partial t}}\, dz, \tag{16}$$

the molar density profiles of both s and dry air must be known. Trace gas profiles are typically measured by sampling air at multiple levels, drying the air and then passing it through a closed-path gas analyzer. Mixing ratios are conserved when temperatures (T) and pressures (P) at the air sampling height differ from those in the gas analyzer but the same is not true when measuring densities. Measurement of density profiles thus requires additional knowledge of T and P at each sampling height, whereas both density and mixing ratio measurements require knowledge of T and P in the gas analyzer itself. Therefore it will be convenient if the effective change in storage can be calculated directly from mixing ratio profiles.

The total change in storage of s can be expressed in mixing ratio through linearization:

$$\int_0^h \overline{\frac{\partial c_s}{\partial t}}\, dz = \int_0^h \overline{\frac{\partial \chi_s c_d}{\partial t}}\, dz = \int_0^h \overline{\chi_s}(z) \overline{\frac{\partial c_d}{\partial t}}\, dz + \int_0^h \overline{c_d}(z) \overline{\frac{\partial \chi_s}{\partial t}}\, dz, \tag{17}$$

which leads to an equivalent expression for the effective change in storage

$$\int_0^h \overline{\frac{\partial c_s}{\partial t}}\, dz - \overline{\chi_s}(h) \int_0^h \overline{\frac{\partial c_d}{\partial t}}\, dz = \int_0^h \overline{c_d}(z) \overline{\frac{\partial \chi_s}{\partial t}}\, dz + \int_0^h [\overline{\chi_s}(z) - \overline{\chi_s}(h)] \overline{\frac{\partial c_d}{\partial t}}\, dz. \tag{18}$$

Both $\overline{\partial \chi_s}/\partial t$ and $\overline{\partial c_d}/\partial t$ are functions of height. Note that the second term in the right-hand side of Eq. (18) depends on the difference in mixing ratio at heights z and h and it becomes negligible for well mixed conditions, irrespective of the magnitude of $\overline{\partial c_d}/\partial t$.

Leuning (2007) simplified Eq. (18) by implicitly introducing the following approximations:

$$\int_0^h \overline{c_d}(z) \overline{\frac{\partial \chi_s}{\partial t}}\, dz \approx \overline{c_d}(h) \int_0^h \overline{\frac{\partial \chi_s}{\partial t}}\, dz, \tag{19}$$

and

$$\int_0^h \overline{\chi_s}(z) \overline{\frac{\partial c_d}{\partial t}}\, dz \approx \overline{\chi_s}(h) \int_0^h \overline{\frac{\partial c_d}{\partial t}}\, dz, \tag{20}$$

to yield

$$\int_0^h \overline{\frac{\partial c_s}{\partial t}}\, dz - \overline{\chi_s}(h) \int_0^h \overline{\frac{\partial c_d}{\partial t}}\, dz \approx \overline{c_d}(h) \int_0^h \overline{\frac{\partial \chi_s}{\partial t}}\, dz. \tag{21}$$

Consequently $\overline{N_s}$ is reduced, elegantly, to

$$\overline{N_s} \approx \overline{c_d}(h) \left(\overline{w'\chi_s'}\big|_h + \int_0^h \overline{\frac{\partial \chi_s}{\partial t}}\, dz \right). \tag{22}$$

Eq. (22) is simply the conservation equation for the quantity 'mixing ratio' with the mean molar density of dry air at h as a conversion factor. This result arises because part of the total vertical flux of s at h is equal and opposite to a change in storage that is not caused by ecosystem exchange but by air expansion and contraction below h as a result of changes in T and P. Under fully mixed conditions, these two components in the effective change in storage term cancel each other and do not appear in the χ_s-based expression of $\overline{N_s}$ because χ_s is conserved to varying T and P.

Eq. (22) still requires a vertical profile of χ_s. It is worthy to investigate whether it can be simplified further by assuming the mean change in time of χ_s does not depend on height, which results in

$$\overline{N_s} \approx \overline{c_d} \left(\overline{w'\chi_s'} + \overline{\frac{\partial \chi_s}{\partial t}} h \right) \bigg|_h. \tag{23}$$

With Eq. (23), only a single-height mixing ratio measurement is needed. The simple method of estimating changes in storage from single-height, most frequently, tower-top measurements has been used widely by the flux community (Amiro, 2001; Carrara et al., 2003; Greco and Baldocchi, 1996; Hollinger et al., 1994; Kolari et al., 2004; Pilegaard et al., 2001).

When the eddy covariance instrumentation measures densities rather than mixing ratios, the WPL equivalents of Eqs. (22) and (23) are, respectively:

$$\overline{N_s} \approx \overline{w'c_s'}\big|_h + \overline{\chi_s} \left[\overline{w'c_v'} + \bar{c} \overline{\frac{w'T'}{T}} \right]_h + \overline{c_d}(h) \int_0^h \overline{\frac{\partial \chi_s}{\partial t}}\, dz, \tag{24}$$

and

$$\overline{N_s} \approx \overline{w'c_s'}\big|_h + \overline{\chi_s} \left[\overline{w'c_v'} + \bar{c} \overline{\frac{w'T'}{T}} \right]_h + \overline{c_d} \overline{\frac{\partial \chi_s}{\partial t}}\bigg|_h h. \tag{25}$$

In Section 4, we will show that Eqs. (22) and (24) are highly accurate while Eqs. (23) and (25) can cause considerable error. This indicates that the operators of time derivative and vertical integration on mixing ratio are not commutable.

3.4. The approximation to horizontal advection in the case of non-homogeneous mass fluxes

In Appendix A, it is shown that the horizontal advection term in the case of non-homogeneous mass fluxes can be potentially simplified by introducing 3D versions of the approximations Eqs. (19) and (20). The simplified horizontal advection term is

$$\int_0^h \nabla_H \cdot (\overline{\mathbf{u}c_d}\, \overline{\chi_s} + \overline{c_d}\overline{\mathbf{u}'\chi_s'})\, dz - \overline{\chi_s}(h) \int_0^h \nabla_H \cdot (\overline{\mathbf{u}c_d})\, dz \approx \overline{c_d}(z) \int_0^h \nabla_H \cdot (\overline{\mathbf{u}'\chi_s'})\, dz. \tag{26}$$

Combining this approximation with the approximated effective change in storage (Eq. (21)) and the assumption of no net ecosystem source/sink of dry air, the general FQEC Eq. (10) is reduced to

$$\overline{N_s} \approx \overline{c_d}(h) \left\{ \overline{w'\chi_s'}\big|_h + \int_0^h \nabla_H \cdot (\overline{\mathbf{u}'\chi_s'})\, dz + \int_0^h \overline{\frac{\partial \chi_s}{\partial t}}\, dz \right\}. \tag{27}$$

We do not intend to evaluate the accuracy of Eq. (27) in this current study. It is presented here as something of interest for future investigation.

4. Observational evaluation of approximations to the fundamental equation of eddy covariance for horizontally homogeneous mass fluxes

4.1. Tasks of evaluation and assumptions adopted

We used observations to assess errors introduced by approximations to the FQEC for horizontally homogeneous mass fluxes. Two tasks were performed. First, we determined the magnitude of the dry air storage adjustment term $-\overline{\chi_s}(h) \int_0^h (\overline{\partial c_d}/\partial t)\,dz$. Second, we evaluated the relative errors caused by estimating the effective change in storage term (Eq. (16)) with the approximation of Eq. (21) using a measured mixing ratio profile or with the approximation of Eq. (23) using a single measurement at the height of the EC instrumentation. The relative errors were given by

$$\varepsilon_1 = 100 \times \frac{\int_0^h [\overline{c_d}(z) - \overline{c_d}(h)](\overline{\partial \chi_s}/\partial t)\,dz + \int_0^h [\overline{\chi_s}(z) - \overline{\chi_s}(h)](\overline{\partial c_d}/\partial t)\,dz}{\int_0^h \overline{c_d}(z)(\overline{\partial \chi_s}/\partial t)\,dz + \int_0^h [\overline{\chi_s}(z) - \overline{\chi_s}(h)](\overline{\partial c_d}/\partial t)\,dz} \qquad (28)$$

for profile, and

$$\varepsilon_2 = 100 \times \frac{\int_0^h \overline{c_d}(z)(\overline{\partial \chi_s}/\partial t)\,dz - \overline{c_d}(h)(\overline{\partial \chi_s}/\partial t)(h)h + \int_0^h [\overline{\chi_s}(z) - \overline{\chi_s}(h)](\overline{\partial c_d}/\partial t)\,dz}{\int_0^h \overline{c_d}(z)(\overline{\partial \chi_s}/\partial t)\,dz + \int_0^h [\overline{\chi_s}(z) - \overline{\chi_s}(h)](\overline{\partial c_d}/\partial t)\,dz} \qquad (29)$$

for single measurement. The fluxes were computed by assuming no net ecosystem exchange of dry air (i.e., $\overline{N_d} = 0$) and no horizontal advection.

4.2. Study site and measurements

Measurements in 2007 from the Missouri Ozark AmeriFlux (MOFLUX) site were used. The MOFLUX site is located within the University of Missouri's Baskett Wildlife Research and Education Area (BREA) in central Missouri, USA ($38°40'$N, $92°12'$W). The site is occupied by a mixed forest of mostly deciduous species dominated by oaks (*Quercus* spp.) with the evergreen species eastern red cedar (*Juniperus virginiana* L.) as a minor component. The canopy height is about 20 m. Detailed site information can be found elsewhere (Pallardy et al., 1988; Gu et al., 2006). Under unstressed conditions during mid growing season, CO_2 fluxes generally fall into the range of -30 to $5\,\mu mol\,m^{-2}\,s^{-1}$ (uptake negative, emission positive) and water vapor fluxes $0–10\,mmol\,m^{-2}\,s^{-1}$ (Gu et al., 2006, 2007; Yang et al., 2010). In addition to typical EC and meteorological instrumentation, MOFLUX is equipped with a CO_2/H_2O mole fraction profile system (Table 1) and an air temperature/humidity profile system which are attached to the 32 m flux tower (Yang et al., 2007). The CO_2/H_2O profile system measures CO_2 and H_2O mole fractions at 12 levels (0.15, 0.30, 0.61, 0.91, 1.52, 3.05, 6.10, 9.14, 12.19, 16.76, 22.86, and 30.48 m) with a single LI-7000 CO_2/H_2O gas analyzer (LI-COR, Inc., Lincoln, Nebraska, USA). Air is drawn sequentially from the 12 heights through Teflon tubing to the analyzer housed in a shelter near the base of the flux tower. One measurement cycle lasts 12 min. The temperature/humidity profile system measures air temperature and humidity at 8 levels (0.61, 1.52, 6.10, 9.14, 12.19, 16.76, 22.86, and 30.48 m) with 8 Vaisala HMP45 C temperature/RH probes. Data from these two profiles plus barometric pressure measurements at the top of the tower allow the calculation of ambient molar densities of dry air, CO_2 and H_2O and gas mixing ratio relative to dry air at different heights.

Because the CO_2/H_2O profile and the temperature/RH profile did not match each other exactly in measurement time and height, a bivariate mesh grid cubic spline with a moving window of one day was used to interpolate temperatures from the temperature/RH profile to the desired heights and times of the CO_2/H_2O profile. The interpolated temperatures were then used to convert CO_2 and
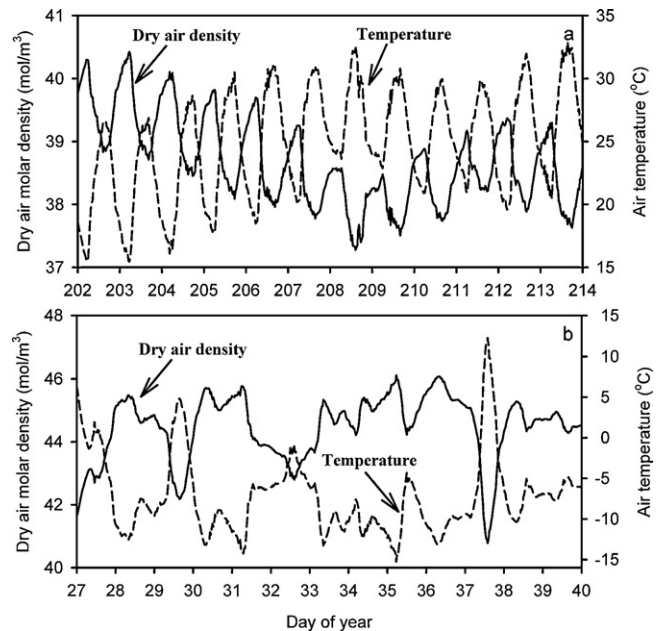
Fig. 1. Diurnal variations in the dry air molar density and air temperature during a summer period (a) and a winter period (b) of 2007 at the Missouri Ozark AmeriFlux site.

H_2O mole fractions to ambient molar densities using the ideal gas law. The ideal gas law was applied again to calculate dry air molar densities from the converted H_2O molar densities, interpolated temperatures, and atmospheric pressure. The atmospheric pressure was interpolated from measurements at the top of the tower to any desired height with the hydrostatic equation. A cubic spline similar to that for temperature was then used to interpolate dry air molar densities and CO_2 and H_2O molar densities and mixing ratios to regular half-hourly time intervals to match with eddy flux measurements. Rates of change in storage of dry air, CO_2 and H_2O were calculated by integrating the obtained profiles of dry air, CO_2 and H_2O molar densities, respectively. Finally, the dry air storage adjustment, the effective change in storage and its approximations were calculated for fluxes of CO_2 and H_2O.

4.3. Results of observational evaluation

4.3.1. The magnitude of the dry air storage adjustment term

The dry air density showed clear diurnal variations, implying systematic positive and negative fluxes of dry air through the EC measurement plane, depending on the sign of $\partial c_d/\partial t$ (Eq. (16)). Typical temporal patterns were demonstrated for a summer period (Fig. 1a) and a winter period (Fig. 1b) at the top profile measurement height of about 30 m (2 m below the EC measurement level). The magnitude of diurnal variation was nearly $2\,mol\,m^{-3}$ during summer and more than twice as much during winter. In the morning as the surface heating began, the dry air density decreased steadily, reached a minimum at the temperature maximum and then increased afterwards. It peaked around the daily temperature minimum. The dry air density also varied beyond the diurnal time scales with the daily cycles superimposed on the longer trends.

As could be inferred from the diurnal variations in dry air densities, the total mass of dry air below the EC measurement plane in a column of unit ground area (storage in dry air) was not constant. Fig. 2a and b showed the time series of the rate of change in storage of dry air for the corresponding periods in Fig. 1a and b, respectively. The rate of change in storage of dry air ranged from $-5\,mmol\,m^{-2}\,s^{-1}$ during the day to $5\,mmol\,m^{-2}\,s^{-1}$ at night for the summer period (Fig. 2a) and from -6 to $6\,mmol\,m^{-2}\,s^{-1}$ for the

Table 1
A comparison of profile design for estimating change in storage between this and some previous studies.

References	Canopy height (m)	EC height (m)	Profile levels (below EC)
Anthoni et al. (1999)	33	47	4 (1, 8, 31, and 46 m)
Hollinger et al. (1994)	30	36	4 (2, 17, 23, and 30 m)
Knohl et al. (2003)	33	44	9 (0.1, 0.3, 1, 2, 5, 10, 20, 30, and 40 m)
Priante-Filho et al. (2004)	29	42	5 (1, 4, 12, 20, and 28 m)
Vourlitis et al. (2001)	29	42	5 (1, 4, 12, 20, and 28 m)
Yang et al. (1999)	22	40	8 (0.8, 2.3, 9.5, 15.7, 18.8, 21.9, 25, and 34.2 m)
This study	20	32	12 (0.15, 0.3, 0.61, 0.91, 1.52, 3.05, 6.1, 9.14, 12.19, 16.76, 22.86 and 30.48 m)

winter period (Fig. 2b). Assuming no horizontal advection, a negative change in storage of dry air implied a positive flux of dry air (upwards) across the EC measurement plane while a positive change in storage indicated downwards flow of dry air.

The dry air storage term of s that accounts for positive or negative fluxes of dry air (the dry air storage adjustment) was shown in Fig. 3 for the flux of CO_2 and Fig. 4 for water vapor. Also shown in these two figures were the percentages of the dry air storage adjustments relative to the corresponding eddy fluxes.

The dry air storage adjustment tended to be positive during the day and negative at night and larger in the morning than in the afternoon for both CO_2 and water vapor (Figs. 3 and 4). For CO_2, the adjustment generally fell into the range of -2 to $2\ \mu mol\ m^{-2}\ s^{-1}$ although values exceeding this range were observed, particularly during winter time. Around midday during summer when the eddy flux was large, the dry air storage adjustment for the flux of CO_2 was about 10% of the eddy flux (CO_2 eddy flux was about $-20\ \mu mol\ m^{-2}\ s^{-1}$ during a typical summer day, data not shown). However, at night and during day–night transitional periods, the adjustment was occasionally much larger than the eddy flux itself (Fig. 3a). In winter (Fig. 3b), the adjustment was of similar or larger magnitude than that of the eddy flux and at times dominated over the eddy flux at night or during transitional periods.

The temporal pattern of the dry air storage adjustment for flux of water vapor was the same as that of CO_2 as both are proportional to the rate of change in storage of dry air below the EC measurement
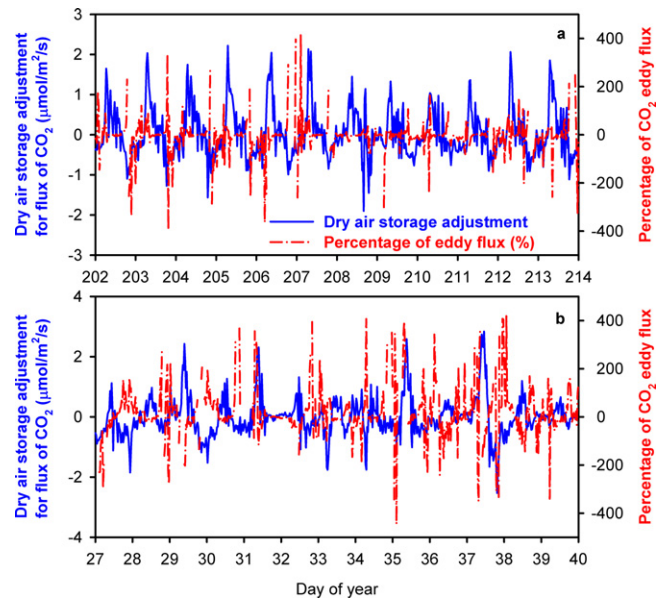
Fig. 3. Diurnal variations in the dry air storage adjustment for flux (solid blue curves) and the adjustment as a percentage of the eddy flux (dash-dot red curves) of CO_2 during a summer period (a) and a winter period (b) of 2007 at the Missouri Ozark AmeriFlux site. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)
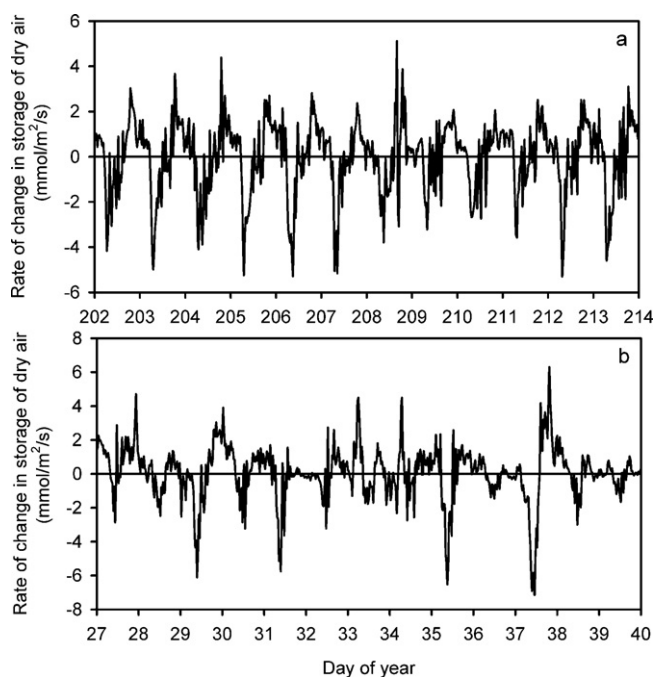
Fig. 2. Diurnal variations in the rate of change in storage of dry air below the eddy covariance measurement plane during a summer period (a) and a winter period (b) of 2007 at the Missouri Ozark AmeriFlux site.
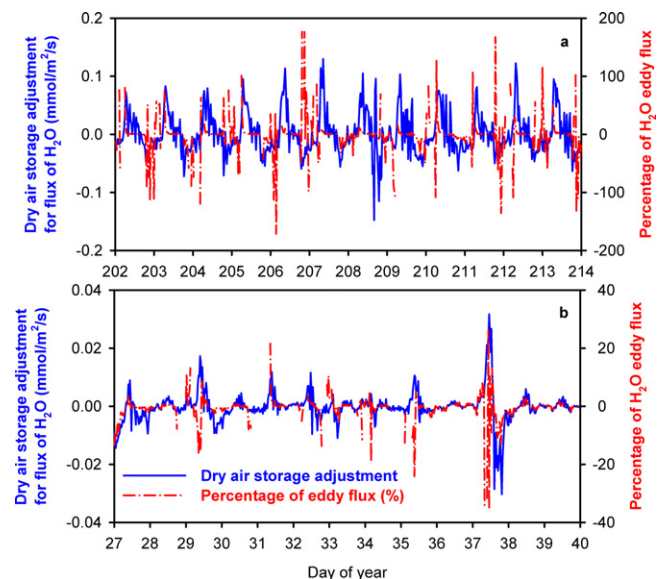

Fig. 4. Diurnal variations in the dry air storage adjustment for flux (solid blue curves) and the adjustment as a percentage of the eddy flux (dash-dot red curves) of water vapor during a summer period (a) and a winter period (b) of 2007 at the Missouri Ozark AmeriFlux site. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)
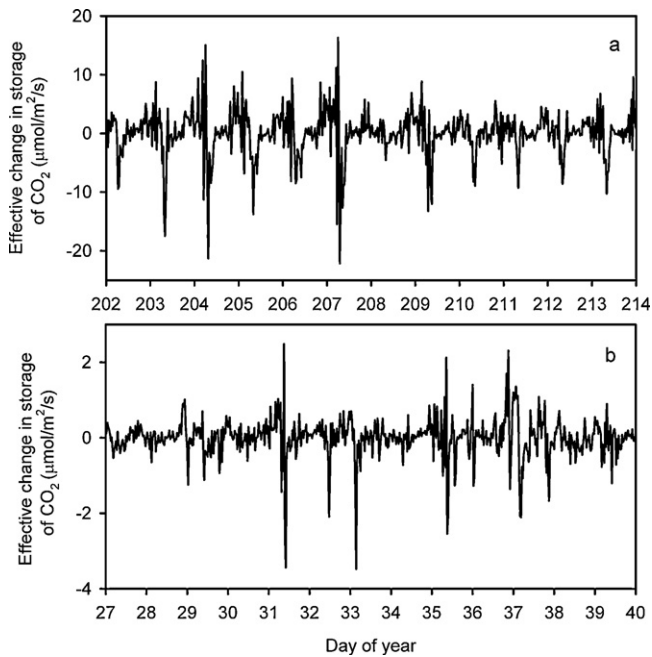
Fig. 5. Temporal variations in the exactly-computed effective change in storage of CO_2 during a summer period (a) and a winter period (b) of 2007 at the Missouri Ozark AmeriFlux site.

plane. The adjustment ranged from -0.15 to $0.15\,\mathrm{mmol\,m^{-2}\,s^{-1}}$ during summer (Fig. 4a) and from -0.03 to $0.03\,\mathrm{mmol\,m^{-2}\,s^{-1}}$ during winter (Fig. 4b). This magnitude of adjustment was about 2% of the vertical eddy flux of water vapor during peak transpiration periods. But at night or during transitional periods, the adjustment was comparable to or even larger than the eddy flux. Because it was positive during the day, the adjustment should increase the measured evapotranspiration and latent heat flux somewhat.

4.3.2. The magnitude of the effective change in storage computed exactly

The effective change in storage (Eq. (16)) computed exactly from the vertical profile systems at MOFLUX was shown in Fig. 5 for CO_2 and Fig. 6 for water vapor for selected representative periods. The effective change in storage of CO_2 varied diurnally with a range from -20 to $20\,\mathrm{\mu mol\,m^{-2}\,s^{-1}}$ in summer (Fig. 5a) and from -3 to $3\,\mathrm{\mu mol\,m^{-2}\,s^{-1}}$ in winter (Fig. 5b). The effective change in storage of water vapor also showed diurnal variations with a range from -2 to $2\,\mathrm{mmol\,m^{-2}\,s^{-1}}$ in summer (Fig. 6a) and from -0.6 to $0.6\,\mathrm{mmol\,m^{-2}\,s^{-1}}$ in winter (Fig. 6b). These large ranges had the same magnitudes as the vertical eddy fluxes in corresponding time periods. Thus clearly it was important to account for the effective change in storage in flux measurements.

4.3.3. The errors of the approximations to the effective change in storage

Fig. 7 showed the probability density distributions of the relative errors of approximating the effective change in storage of CO_2 and water vapor with a multi-height mixing ratio profile (ε_1, a and b) or with a single tower-top mixing ratio measurement (ε_2, c and d). When the 12-height mixing ratio profile was used, the distributions were symmetrical with 97% of the values of the estimated effective change in storage of CO_2 having a relative error between -5% and $+5\%$ (Fig. 7a) and 94% for water vapor (Fig. 7b). Thus Eq. (21) provides an excellent approximation to the effective change in storage (Eq. (16)) when measurements at multiple heights are used to characterize the mixing ratio profile. In contrast, when a single mixing ratio at the tower top was used to estimate the storage term,
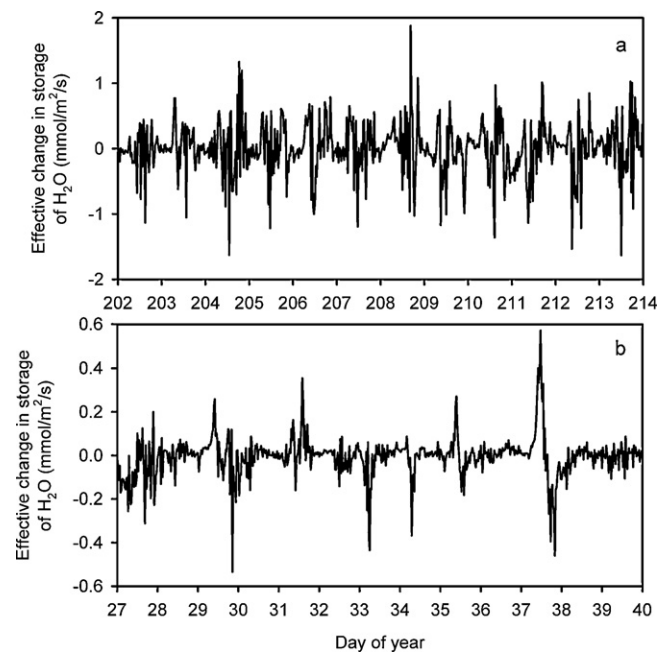

Fig. 6. Temporal variations in the exactly-computed effective change in storage of water vapor during a summer period (a) and a winter period (b) of 2007 at the Missouri Ozark AmeriFlux site.

the distributions were strongly positively skewed (Fig. 7c and d), indicating the tower-top approximation underestimated changes in storage. Furthermore, only 5% (6%) of the values had a relative error between -5% and $+5\%$ for CO_2 (water vapor).

We note that previous researchers have compared (Carrara et al., 2003; Hollinger et al., 1994; Knohl et al., 2003; Vourlitis et al., 2001; Yang et al., 1999) or used interchangeably (Anthoni et al., 1999; Knohl et al., 2003; Priante-Filho et al., 2004; Vourlitis et al., 2001) estimates of change in storage based on tower-top and profile measurements. Profile designs varied considerably in these studies (Table 1). An earlier investigation from MOFLUX found that an adequately designed profile for change in storage should consider both the number and configuration of measurement heights (Yang et al., 2007). At the MOFLUX site, change in storage tended to be dominated by variations near the ground, particularly when the atmosphere was stratified, and therefore the lower section was measured densely (Table 1). If a profile is not designed adequately, particularly if the sections near sources or sinks are not sampled with sufficient density, it may give an estimate of change in storage that is not much different from that based on tower-top measurements. Difference in profile design (Table 1) may explain why our finding was inconsistent with that of some previous studies with respect to the adequacy in using single tower-top measurements for estimating change in storage.

5. Discussion

Using the conservation of mass of dry air as a constraint in flux measurements is an important feature of the contemporary eddy covariance technique. However, the eddy covariance theory itself can be formulated independent of dry air. A fundamental equation of eddy covariance has been derived that allows the net ecosystem exchange of a specified atmospheric constituent to be measured with the constraint of the conservation of mass of any other atmospheric constituent. The basis upon which the flux measurements are ultimately constrained is that the mean bulk velocity must be identical for each and every atmospheric constituent, no matter what processes cause this velocity. It is neither necessary nor
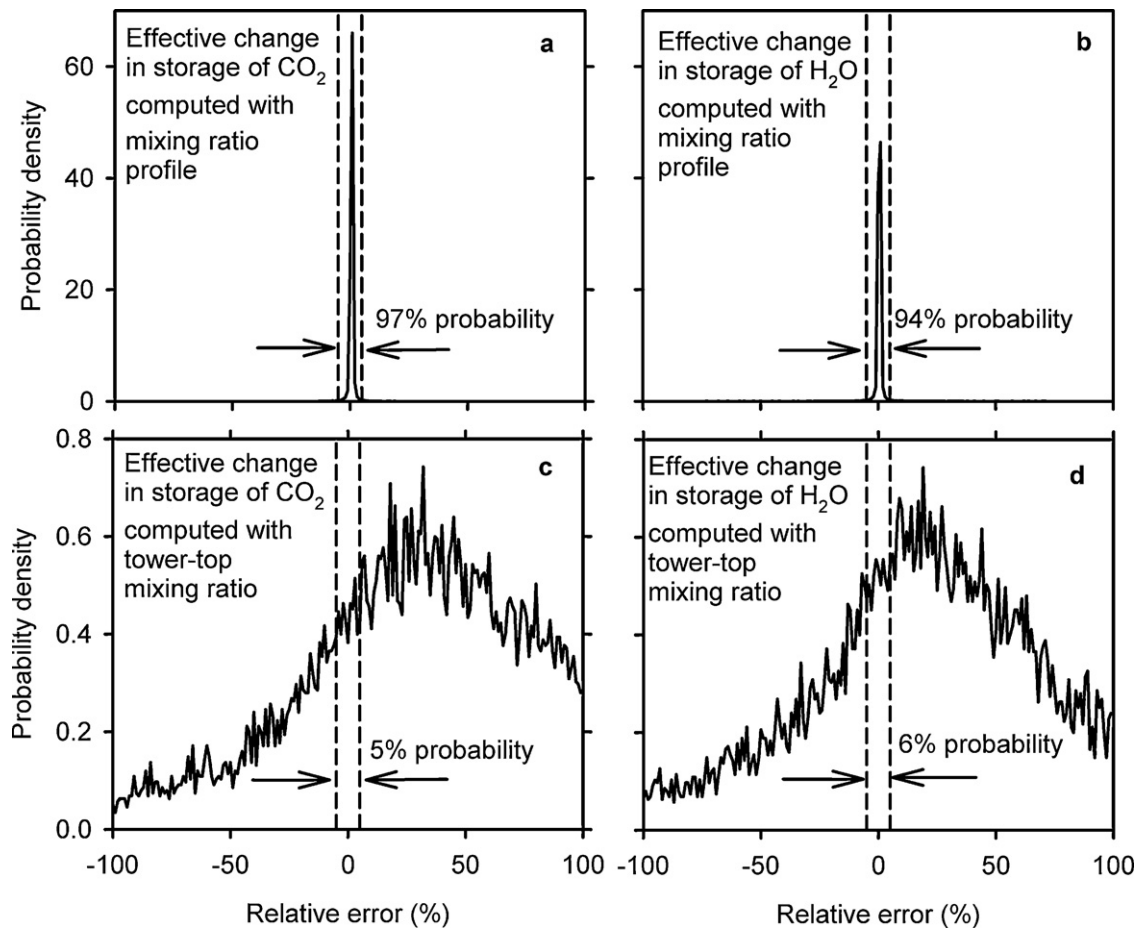
Fig. 7. Probability density distributions for the relative error in the effective change in storage calculated with measurements of a mixing ratio profile (a and b) or with a single-height (tower-top) mixing ratio measurement (c and d). a and c are for the effective change in storage of CO_2 and b and d are for water vapor. The two vertical dash lines in each plot represent −5% and +5% errors respectively. Data are from the whole year of 2007 at the Missouri Ozark AmeriFlux site.

feasible to separate the mean bulk velocity into components that result from individual processes. The application of the conservation of dry air is a special case of the fundamental equation of eddy covariance and is convenient from an instrumentation point of view. However N_2 or argon may also be used.

When the conservation of mass of dry air is used as a constraint, the net ecosystem exchange of a specified atmospheric constituent s for horizontally homogeneous mass fluxes can be measured using any of the following equations:

$$\overline{N_s} = \overline{c_d}\,\overline{w'\chi_s'}\Big|_h + \int_0^h \overline{c_d}(z)\frac{\overline{\partial\chi_s}}{\partial t}\,dz + \int_0^h [\overline{\chi_s}(z) - \overline{\chi_s}(h)]\frac{\overline{\partial c_d}}{\partial t}\,dz, \quad (14)$$

$$\overline{N_s} = \overline{w'c_s'}\Big|_h + \overline{\chi_s}\left[\overline{w'c_v'} + \bar{c}\frac{\overline{w'T'}}{\bar{T}}\right]_h + \int_0^h \frac{\overline{\partial c_s}}{\partial t}\,dz - \overline{\chi_s}(h)\int_0^h \frac{\overline{\partial c_d}}{\partial t}dz, \quad (15)$$

and

$$\overline{N_s} \approx \overline{c_d}(h)\left(\overline{w'\chi_s'}\Big|_h + \int_0^h \frac{\overline{\partial\chi_s}}{\partial t}\,dz\right), \quad (22)$$

if $|\overline{N_s}| \gg |\overline{\chi_s}|\,|\overline{N_{CO_2}}|$. Note that Eq. (14) listed above uses an equivalent expression for the effective change in storage as shown in Eq. (18).

With the information typically available, the contemporary eddy covariance technique cannot measure the flux of every atmospheric constituent even when a fast response gas analyzer with

sufficient accuracy is available. The condition $|\overline{N_s}| \gg |\overline{\chi_s}|\,|\overline{N_{CO_2}}|$ is required because Eqs. (14), (15) and (22) are derived with the assumption that there is no net ecosystem source or sink of dry air ($\overline{N_d} = 0$). N_2 and O_2 are two examples of gas species whose fluxes cannot be measured with the contemporary eddy covariance technique unless the fluxes of other non-water vapor gases are known and the ecosystem O_2:CO_2 molar exchange ratio is given.

Eq. (22) approximates $\overline{N_s}$ by the product of dry air density at the eddy covariance measurement height and the net ecosystem exchange of the quantity 'mixing ratio' $\overline{w'\chi_s'}\big|_h + \int_0^h (\overline{\partial\chi_s}/\partial t)\,dz$. Some error may occur if it is used. However, measurements made at the Missouri Ozark AmeriFlux site indicated that the error in the effective change in storage term was less than 5% for 95% of the time (Fig. 7), a finding consistent with theoretical expectations. The convenience in the application of Eq. (22) thus outweighs its small error. Further simplification by using a single measurement at tower-top with the implicit assumption that there is no vertical gradient in mixing ratio can cause substantial biases and this method should be avoided. We emphasize that an adequately designed profile system for measuring the effective change in storage in proper units is as important as the eddy flux term for determining NEE.

Eqs. (14), (15) and (22) are valid for mass fluxes in horizontally homogeneous air flows under non-steady state conditions. In contrast, the theory of Webb, Pearman and Leuning (1980) applied for horizontally homogeneous mass fluxes under steady-state conditions and hinged upon the governing constraint of zero mean vertical flux of dry air across the eddy covariance measurement

plane. Leuning (2007) showed that the vertical *eddy flux* term does not differ between the steady- and non-steady state conditions. However, it is necessary to account for positive or negative fluxes of dry air across the eddy covariance measurement plane under non-steady state conditions which arise when temperature and pressure change or when a meteorological front passes over the site. Without doing so, measurements of net ecosystem exchange can be biased, diurnally and seasonally. Thus in support of previous researchers (Leuning, 2004, 2007; Kowalski and Serrano-Ortiz, 2007; Lee and Massman, 2011), we recommend that the flux community adopt the non-steady state theory and Eqs. (14), (15) or (22) for horizontally homogeneous mass fluxes.

For non-homogeneous mass fluxes, the general fundamental equation of eddy covariance is

$$
\overline{N_s} = \overline{c_d}\overline{w'\chi_s'}\Big|_h + \overline{\chi_s}(h)\overline{N_d} + \left\{ \int_0^h \overline{\frac{\partial c_s}{\partial t}}\, dz - \overline{\chi_s}(h) \int_0^h \overline{\frac{\partial c_d}{\partial t}}\, dz \right\}
$$
$$
+ \left\{ \int_0^h \nabla_H \cdot (\overline{\mathbf{u}c_d}\,\overline{\chi_s} + \overline{c_d}\overline{\mathbf{u}'\chi_s'})\, dz - \overline{\chi_s}(h) \int_0^h \nabla_H \cdot (\overline{\mathbf{u}c_d})\, dz \right\}
$$
$$
\tag{10}
$$

It is possible to approximate the general fundamental equation of eddy covariance with

$$
\overline{N_s} \approx \overline{c_d}(h) \left\{ \overline{w'\chi_s'}\Big|_h + \int_0^h \nabla_H \cdot (\overline{\mathbf{u}'\chi_s'})\, dz + \int_0^h \overline{\frac{\partial \chi_s}{\partial t}}\, dz \right\}. \tag{27}
$$

However, further investigation is needed to ascertain the accuracy of this approximation.

Acknowledgements

Appendix A. The fundamental equation of eddy covariance (FQEC)

Begin with the equation of continuity of a specified atmospheric constituent *s*.

$$
\frac{\partial c_s}{\partial t} + \nabla \cdot (\mathbf{v}c_d\chi_s + \mathbf{J}_s) = S_s.
$$

where **v** is the ambient 3D velocity field; $\mathbf{J}_s$ is the 3D diffusional flux (mol m^{-2} s^{-1}), which for the present discussion will consist only of a vertical component [i.e., $\mathbf{J}_s = (0, 0, J_s)$]; and S_s is the source/sink intensity of *s* (mol m^{-3} s^{-1}). Molecular transport is usually ignored when discussing atmospheric transport, but this term is useful and germane to the present discussion and so it will be included here. Applying Reynolds averaging to this equation yields (to a high degree of accuracy)

$$
\overline{\frac{\partial c_s}{\partial t}} + \nabla_H \cdot (\overline{\mathbf{u}c_d}\,\overline{\chi_s} + \overline{c_d}\overline{\mathbf{u}'\chi_s'}) + \frac{\partial}{\partial z}(\overline{wc_d}\,\overline{\chi_s} + \overline{c_d}\overline{w'\chi_s'} + \overline{J_s}) = \overline{S_s}. \tag{A1}
$$

Here we have separated the horizontal and vertical components, so that **u** is the 2D horizontal velocity and ∇_H is the 2D horizontal gradient operator. Next integrate this equation vertically from the soil surface to some arbitrary height, *h* (which can be, but is not necessarily, above the canopy top). This yields

$$
\int_0^h \overline{\frac{\partial c_s}{\partial t}}\, dz + \int_0^h \nabla_H \cdot (\overline{\mathbf{u}c_d}\,\overline{\chi_s} + \overline{c_d}\overline{\mathbf{u}'\chi_s'})\, dz
$$
$$
+ (\overline{wc_d}\,\overline{\chi_s} + \overline{c_d}\overline{w'\chi_s'} + \overline{J_s})\Big|_0^h = \int_0^h \overline{S_s}\, dz. \tag{A2}
$$

At this point it is fair to say the term $\overline{c_d}(h)\overline{w'\chi_s'}(h)$ is the measured eddy covariance flux (or the turbulent dry air mixing ratio flux). It inherently includes the density terms, which WPL 1980 (and some previous and subsequent researchers) have identified and argued as necessary for a complete description of the turbulent trace gas surface exchange flux. The dilemma that WPL 1980 (and again subsequent researchers) have had to face is what to do with the 'quasi-advective term', $\overline{wc_d}(h)\overline{\chi_s}(h)$. In WPL 1980, this term was zero as a consequence of their assumptions. Realizing the limitation of WPL 1980, Leuning (2004) and Lee and Massman (2011) provided a different approach for dealing with it. The present discussion takes a similar, but more transparent, approach to this term. Specifically, we show here that it can be eliminated from Eq. (A2) rather simply by employing the conservation of mass of dry air with a strategy that is a dynamic equivalence to what is used in Section 2 of the main text.

First, begin with Reynolds averaging the equation of continuity for dry air. This yields

$$
\overline{\frac{\partial c_d}{\partial t}} + \nabla_H \cdot (\overline{\mathbf{u}c_d}) + \frac{\partial}{\partial z}(\overline{wc_d} + \overline{J_d}) = \overline{S_d}. \tag{A3}
$$

Next, integrate this last equation from 0 to *h* and then multiply the resulting equation by $\overline{\chi_s}(h)$. This yields

$$
\overline{\chi_s}(h) \int_0^h \overline{\frac{\partial c_d}{\partial t}}\, dz + \overline{\chi_s}(h) \int_0^h \nabla_H \cdot (\overline{\mathbf{u}c_d})\, dz + \overline{\chi_s}(h)(\overline{wc_d} + \overline{J_d})\Big|_0^h
$$
$$
= \overline{\chi_s}(h) \int_0^h \overline{S_d}\, dz. \tag{A4}
$$

Finally, subtract Eq. (A4) from Eq. (A2) and assume that molecular transport (diffusion) within the free atmosphere is always small enough to ignore (i.e., $\overline{J_s}(h) \approx 0$ and $\overline{J_d}(h) \approx 0$ for $h \gg 0$]. After some simple manipulations, we obtain

$$
\left\{ \int_0^h \overline{\frac{\partial c_s}{\partial t}}\, dz - \overline{\chi_s}(h) \int_0^h \overline{\frac{\partial c_d}{\partial t}}\, dz \right\} + \left\{ \int_0^h \nabla_H \cdot (\overline{\mathbf{u}c_d}\,\overline{\chi_s} + \overline{c_d}\overline{\mathbf{u}'\chi_s'})\, dz \right.
$$
$$
- \left. \overline{\chi_s}(h) \int_0^h \nabla_H \cdot (\overline{\mathbf{u}c_d})\, dz \right\} + \overline{c_d}\overline{w'\chi_s'}\Big|_h + \overline{\chi_s}(h) \left\{ \int_0^h \overline{S_d}\, dz \right.
$$
$$
+ \left. \overline{wc_d}(0) + \overline{J_d}(0) \right\} = \int_0^h \overline{S_s}\, dz + \overline{wc_s}(0) + \overline{J_s}(0). \tag{A5}
$$

Several flux terms at the lower boundary now appear in Eq. (A5). $\overline{J_s}(0)$ is the flux of *s* at the soil surface due to molecular diffusion and may be identified as soil efflux measured with a soil chamber while $\overline{wc_s}(0)$ may be regarded as an enhanced soil diffusion term due to any pressure pumping effect. Similar interpretations can be made to $\overline{J_d}(0)$ and $\overline{wc_d}(0)$. Thus,

$$
\overline{N_d} = \int_0^h \overline{S_d}\, dz + \overline{wc_d}(0) + \overline{J_d}(0),
$$
$$
\overline{N_s} = \int_0^h \overline{S_s}\, dz + \overline{wc_s}(0) + \overline{J_s}(0).
$$

This leads to

$$\left\{\int_0^h \overline{\frac{\partial c_s}{\partial t}}\, dz - \overline{\chi_s}(h) \int_0^h \overline{\frac{\partial c_d}{\partial t}}\, dz\right\} + \left\{\int_0^h \nabla_H \cdot (\overline{\mathbf{u}c_d}\,\overline{\chi_s} + \overline{c_d}\,\overline{\mathbf{u}'\chi_s'})\, dz - \overline{\chi_s}(h) \int_0^h \nabla_H \cdot (\overline{\mathbf{u}c_d})\, dz\right\} + \underbrace{\overline{c_d w'\chi_s'}\Big|_h}_{\text{eddy flux}} + \underbrace{\overline{\chi_s}(h)\overline{N_d}}_{\text{dry air source/sink correction}} = \overline{N_s}.$$

$$\underbrace{\phantom{\int_0^h \overline{\frac{\partial c_s}{\partial t}}\, dz - \overline{\chi_s}(h) \int_0^h \overline{\frac{\partial c_d}{\partial t}}\, dz}}_{\text{effective change in storage}} \quad \underbrace{\phantom{\int_0^h \nabla_H \cdot (\overline{\mathbf{u}c_d}\,\overline{\chi_s} + \overline{c_d}\,\overline{\mathbf{u}'\chi_s'})\, dz - \overline{\chi_s}(h) \int_0^h \nabla_H \cdot (\overline{\mathbf{u}c_d})\, dz}}_{\text{horizontal advection}}$$

$$\text{(A6)}$$

Eq. (A6) is identical to Eq. (8) in the main text except for the additional horizontal advection term. Although the conservation of mass of dry air is used explicitly in the derivation, any atmospheric constituent can be used to constrain flux measurements with the eddy covariance technique as long as its net ecosystem exchange with the atmosphere is known *a priori*. Eq. (A6) is still valid after relevant variables of dry air in it are replaced with corresponding variables of the new constraining constituent. We term Eq. (A6) the fundamental equation of eddy covariance (FQEC).

In the main text, we showed that by introducing the following two approximations:

$$\int_0^h \overline{c_d}(z) \overline{\frac{\partial \chi_s}{\partial t}}\, dz \approx \overline{c_d}(h) \int_0^h \overline{\frac{\partial \chi_s}{\partial t}}\, dz, \tag{A7}$$

and

$$\int_0^h \overline{\chi_s}(z) \overline{\frac{\partial c_d}{\partial t}}\, dz \approx \overline{\chi_s}(h) \int_0^h \overline{\frac{\partial c_d}{\partial t}}\, dz, \tag{A8}$$

the effective change in storage can be simplified into

$$\int_0^h \overline{\frac{\partial c_s}{\partial t}}\, dz - \overline{\chi_s}(h) \int_0^h \overline{\frac{\partial c_d}{\partial t}}\, dz \approx \overline{c_d}(h) \int_0^h \overline{\frac{\partial \chi_s}{\partial t}}\, dz, \tag{A9}$$

without losing much accuracy. The horizontal advection term can also be simplified in a similar way.

$$\int_0^h \nabla_H \cdot (\overline{\mathbf{u}c_d}\,\overline{\chi_s} + \overline{c_d}\,\overline{\mathbf{u}'\chi_s'})\, dz - \overline{\chi_s}(h) \int_0^h \nabla_H \cdot (\overline{\mathbf{u}c_d})\, dz = \int_0^h [\overline{\chi_s}(z)$$

$$- \overline{\chi_s}(h)] \nabla_H \cdot (\overline{\mathbf{u}c_d})\, dz + \int_0^h \nabla_H \cdot (\overline{c_d}\,\overline{\mathbf{u}'\chi_s'})\, dz + \int_0^h \nabla_H \overline{\chi_s}(z)$$

$$\cdot (\overline{\mathbf{u}c_d})\, dz. \tag{A10}$$

If the following three approximations:

$$\int_0^h \nabla_H \cdot [\overline{c_d}(x,y,z) \overline{\mathbf{u}'\chi_s'}]\, dz \approx \overline{c_d}(h) \int_0^h \nabla_H \cdot (\overline{\mathbf{u}'\chi_s'})\, dz, \tag{A11}$$

$$\int_0^h \overline{\chi_s}(x,y,z) \nabla_H \cdot (\overline{\mathbf{u}c_d})\, dz \approx \overline{\chi_s}(h) \int_0^h \nabla_H \cdot (\overline{\mathbf{u}c_d})\, dz, \tag{A12}$$

and,

$$\int_0^h \nabla_H \overline{\chi_s}(x,y,z) \cdot (\overline{\mathbf{u}c_d})\, dz \approx 0, \tag{A13}$$

can be made, the horizontal advection term can be reduced to

$$\int_0^h \nabla_H \cdot (\overline{\mathbf{u}c_d}\,\overline{\chi_s} + \overline{c_d}\,\overline{\mathbf{u}'\chi_s'})\, dz - \overline{\chi_s}(h) \int_0^h \nabla_H \cdot (\overline{\mathbf{u}c_d})\, dz \approx \overline{c_d}(z)$$

$$\int_0^h \nabla_H \cdot (\overline{\mathbf{u}'\chi_s'})\, dz. \tag{A14}$$

Substituting the approximations (A9) and (A14) into the FQEC (A6) and applying the condition of no dry air source/sink ($\overline{N_d} = 0$) leads to

$$\overline{c_d}(h) \left\{\int_0^h \overline{\frac{\partial \chi_s}{\partial t}}\, dz + \int_0^h \nabla_H \cdot (\overline{\mathbf{u}'\chi_s'})\, dz + \overline{w'\chi_s'}\Big|_h\right\} \approx \overline{N_s}. \tag{A15}$$

The approximations (A11)–(A13) are generalizations of the approximations of (A7) and (A8). They are likely to have reasonable accuracy if the 3D air flows are well-mixed not only vertically but also horizontally even when source/sink distributions of the specified atmospheric constituent are not homogeneous horizontally. However the data presented in this current study neither support nor refute (A11)–(A13). Further studies are needed to investigate how accurate Eq. (A15) is.

In summary, the FQEC and its derivation provide the most transparent method to date for discussing the nature of the approximations and governing constraints that have historically been and are continuing to be imposed on either the FQEC or some of the terms that comprise the FQEC. The following points can be made:

(A) The expression for the 'effective change in storage' results solely from the equations of continuity of dry air and the atmospheric constituent and Reynolds averaging. It is completely independent of any other assumptions.
(B) Exactly the same is true of 'horizontal advection'.
(C) The only requirement for deriving the 'eddy flux' term is Reynolds averaging and the identification of the need to express this flux term in a form that accounts for (or removes) the effects of atmospheric expansion and contraction on measurements of c_s'. But WPL 1980 essentially made this issue synonymous with the assumptions of steady-state horizontally homogeneous air flows that had no dry-air exchange with the soil (i.e., $\overline{wc_d} \equiv 0$). As this study shows, this identification is not necessary. Nevertheless, WPL's 1980 basic result on the *eddy flux* term is sound for non-steady state conditions (Leuning, 2007) because the development and manipulation of these concepts and equations are mathematically linear in nature and to a certain extent also independent of one another.
(D) The basic intent behind the development of the FQEC, which is really just another statement of the conservation of mass of an atmospheric constituent, is to define all the other measurements required to estimate 'NEE' by summing (adding and subtracting) the measured terms. Therefore, NEE is not directly measured, but inferred indirectly as a combination of other terms.
(E) Here we propose that the term $\overline{wc_s}(0)$ be interpreted as the interaction of the near-surface atmospheric processes with the soil. In the case of CO_2 one might then expect this term to be related to (horizontal and vertical) advective flows induced in soils that would enhance the fluxes of CO_2 from soils, i.e., to pressure pumping effects. Under most conditions, it is expected to be a relatively small part of $\overline{J_s}(0)$ and is included here primarily for the sake of completeness.
(F) WPL 1980 made the condition of no (dry) air exchange at the surface (i.e., $\overline{wc_d}(0) \equiv 0$) central to their arguments about the eddy flux term. Although we certainly concur that this zero dry air flux boundary condition is a reasonable and supportable assumption for steady-state conditions, under the assumptions of non-steady state, horizontally inhomogeneous conditions, the present discussion shows that it is unnecessary to and independent of 'the effective change in storage term', 'the eddy flux', and 'the dry air source/sink correction term'. It is only under steady-state, horizontally homogeneous conditions that

this assumption plays an important role because it basically defines the equation of continuity of dry air, which for this one exceptional case can be expressed as $\overline{wc_d}(h) \equiv 0$. This, of course, is ultimately WPL's 1980 original governing constraint, which they expressed in terms of a mean (but unmeasurable) dry air drift velocity. The present discussion shows that there is no need to invoke this drift velocity at all.

Appendix B. List of symbols and subscripts

Symbols

c	Molar density
h	Eddy flux measurement height
$\mathbf{J}$	The vector of the molecular diffusional flux
k	The ecosystem O_2 to CO_2 molar exchange ratio
N	Net ecosystem exchange
n	The total number of gas components in dry air
P	Atmospheric pressure
R	Universal gas constant
S	Source/sink intensity of an atmospheric constituent
t	Time
T	Temperature
$\mathbf{u}$	Horizontal (2D) wind velocity field
$\mathbf{v}$	3D wind velocity field
w	Vertical velocity
z	Vertical distance from soil surface
χ	The molar density ratio of the specified atmospheric constituent to the constraining constituent; molar mixing ratio when dry air is the constraining constituent

Subscripts

s	The specified atmospheric constituent whose flux is to be measured
d	The constraining atmospheric constituent or dry air
v	Water vapor

References

Amiro, B.D., 2001. Paired-tower measurements of carbon and energy fluxes following disturbance in the boreal forest. Global Change Biol. 7, 253–268.

Anthoni, P.M., Law, B.E., Unsworth, M.H., 1999. Carbon and water exchange of an open canopied ponderosa pine ecosystem. Agric. Forest Meteorol. 95, 151–168.

Campbell, J.E., Carmichael, G.R., Chai, T., Mena-Carrasco, M., Tang, Y., Blake, Y.D., Blake, N.J., Vay, S.A., Collatz, G.J., Baker, I., Berry, J.A., Montzka, S.A., Sweeney, C., Schnoor, J.L., Stanier, C.O., 2008. Photosynthetic control of atmospheric carbonyl sulfide during the growing season. Science 322, 1085–1088.

Carrara, A., Kowalski, A.S., Neirynck, J., Janssens, I.A., Yuste, J.C., Ceulemans, R., 2003. Net ecosystem CO_2 exchange of mixed forest in Belgium over 5 years. Agric. Forest Meteorol. 119, 209–227.

Craig, H., 1957. Isotopic standards for carbon and oxygen and correction factors for mass spectrometric analysis of carbon dioxide. Geochim. Cosmochim. Acta 12, 133–149.

Farquhar, G.D., Ehleringer, J.R., Hubick, K.T., 1989. Carbon isotope discrimination and photosynthesis. Annu. Rev. Plant Physiol. Plant Mol. Biol. 40, 503–537.

Fuentes, J.D., Wang, D., Gu, L., 1999. Seasonal variations in isoprene emissions from a boreal aspen forest. J. Appl. Meteorol. 38, 855–869.

Fuehrer, P.L., Friehe, C.A., 2002. Flux corrections revisited. Bound.-Layer Meteorol. 102, 415–457.

Galbally, I., Meyer, C.P., Wang, Y.P., Kirstine, W., 2010. Soil-atmosphere exchange of CH_4, CO, N_2O and NO_x and the effects of land-use change in the semiarid Mallee system in Southeastern Australia. Global Change Biol. 16, 2407–2419.

Goulden, M.L., Munger, J.W., Fan, S.M., Daube, B.C., Wofsy, S.C., 1996. Measurements of carbon sequestration by long-term eddy covariance: methods and a critical evaluation of accuracy. Global Change Biol. 2, 169–182.

Greco, S., Baldocchi, D.D., 1996. Seasonal variations of CO_2 and water vapour exchange rates over a temperate deciduous forest. Global Change Biol. 2, 183–197.

Gu, L., Meyers, T., Pallardy, S.G., Hanson, P.J., Yang, B., Heuer, M., Hosman, K.P., Liu, Q., Riggs, J.S., Sluss, D., Wullschleger, S.D., 2007. Influences of biomass heat and biochemical energy storages on the land surface fluxes and radiative temperature. J. Geophys. Res. 112, D02107, doi:10.1029/2006JD007425.

Gu, L., Meyers, T., Pallardy, S.G., Hanson, P.J., Yang, B., Heuer, M., Hosman, K.P., Riggs, J.S., Sluss, D., Wullschleger, S.D., 2006. Direct and indirect effects of

atmospheric conditions and soil moisture on surface energy partitioning revealed by a prolonged drought at a temperate forest site. J. Geophys. Res., D16102, doi:10.1029/2006JD007161.

Gu, L., Falge, E.M., Boden, T., Baldocchi, D.D., Black, T.A., Saleska, S.R., Suni, T., Verma, S.B., Vesala, T., Wofsy, S.C., Xu, L., 2005. Objective threshold determination for nighttime eddy flux filtering. Agric. Forest Meteorol. 128, 179–197.

Hollinger, D.Y., Kelliher, F.M., Byers, J.N., Hunt, J.E., McSeveny, T.M., Weir, P.L., 1994. Carbon dioxide exchange between an undisturbed old growth temperate forest and the atmosphere. Ecology 71, 134–150.

Kammer, A., Tuzson, B., Emmenegger, L., Knohl, A., Mohn, J., Hagedorn, F., 2011. Application of a quantum cascade laser-based spectrometer in a closed chamber system for real-time $\delta^{13}C$ and $\delta^{18}O$ measurements of soil-respired CO_2. Agric. Forest Meteorol. 151, 39–48.

Keeling, R.F., Piper, S.C., Bollenbacher, A.F., Walker, S.J., 2010. Monthly Atmospheric $^{13}C/^{12}C$ Isotopic Ratios for 11 SIO Stations, Trends: A Compendium of Data on Global Change. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, TN, USA.

King, G.M., Crosby, H., 2002. Impacts of plant roots on soil CO cycling and soil-atmosphere CO exchange. Global Change Biol. 8, 1085–1093.

Knohl, A., Schulze, E.-D., Kolle, O., Buchmann, N., 2003. Large carbon uptake by an unmanaged 250-year-old deciduous forest in Central Germany. Agric. Forest Meteorol. 118, 151–167.

Kolari, P., Pumpanen, J., Rannik, Ü., Ilvesniemi, H., Hari, P., Berninger, F., 2004. Carbon balance of different aged Scots pine forests in Southern Finland. Global Change Biol. 10, 1–14.

Kowalski, A.S., Serrano-Ortiz, P., 2007. On the relationship between the eddy covariance, the turbulent flux, and surface exchange for a trace gas such as CO_2. Bound.-Layer Meteorol. 124, 129–141.

Lee, X., Massman, W.J., 2011. A perspective on thirty years of the Webb, Pearman and Leuning density corrections. Bound.-Layer Meteorol. 139, 37–59.

Leuning, R., 2004. Measurements of trace gas fluxes in the atmosphere using eddy covariance: WPL corrections revisited. In: Lee, X., Massman, W., Law, B. (Eds.), Handbook of Micrometeorology: A Guide for Surface Flux Measurements and Analysis. Kluwer Academic Publishers, Dordrecht, Netherlands, pp. 119–132.

Leuning, R., 2007. The correct form of the Webb, Pearman and Leuning equation for eddy fluxes of trace gases in steady and non-steady state, horizontally homogeneous flows. Bound.-Layer Meteorol. 123, 263–267.

McDermitt, D., Burba, G., Xu, L., Anderson, T., Komissarov, A., Riensche, B., Schedlbauer, J., Starr, G., Zona, D., Oechel, W., Oberbauer, S., Hastings, S., 2011. A new low-power, open-path instrument for measuring methane flux by eddy covariance. Appl. Phys. B-Lasers Opt. 102, 391–405.

Meijide, A., Cardenas, L.M., Bol, R., Bergstermann, A., Goulding, K., Well, R., Vallejoa, A., Scholefield, D., 2010. Dual isotope and isotopomer measurements for the understanding of N_2O production and consumption during denitrification in an arable soil. Eur. J. Soil Sci. 61, 364–374.

Pallardy, S.G., Nigh, T.A., Garrett, H.E., 1988. Changes in forest composition in central Missouri: 1968–1982. Am. Midland Nat. 120, 380–390.

Paw, U.K.T., Baldocchi, D.D., Meyers, T.P., Wilson, K.B., 2000. Correction of eddy-covariance measurements incorporating both advective effects and density fluxes. Bound.-Layer Meteorol. 97, 487–511.

Pilegaard, K., Hummelshøj, P., Jensen, N.O., Chen, Z., 2001. Two years of continuous CO_2 eddy-flux measurements over a Danish beech forest. Agric. Forest Meteorol. 107, 29–41.

Priante-Filho, N., Vourlitis, G.L., Hayashi, M.M.S., Nogueira, J.D., Campelo, J.H., Nunes, P.C., Souza, L.S.E., Couto, E.G., Hoeger, W., Raiter, F., Trienweiler, J.L., Miranda, E.J., Priante, P.C., Fritzen, C.L., Lacerda, M., Pereira, L.C., Biudes, M.S., Suli, G.S., Shiraiwa, S., Do Paulo, S.R., Silveira, M., 2004. Comparison of the mass and energy exchange of a pasture and a mature transitional tropical forest of the southern Amazon Basin during a seasonal transition. Global Change Biol. 10, 863–876.

Seibt, U., Brand, W.A., Heimann, M., Lloyd, J., Severinghaus, J.P., Wingate, L., 2004. Observations of O_2:CO_2 exchange ratios during ecosystem gas exchange. Global Biogeochem. Cycles 18 (Article Number: GB4024).

Tuzson, B., Hiller, R.V., Zeyer, K., Eugster, W., Neftel, A., Ammann, C., Emmenegger, L., 2010. Field intercomparison of two optical analyzers for CH_4 eddy covariance flux measurements. Atmos. Meas. Tech. 3, 1519–1531.

Vilà-Guerau de Arellano, J.V., Duynkerke, P.G., Zeller, K.F., 1995. Atmospheric surface layer similarity theory applied to chemically reactive species. J. Geophys. Res. 100 (D1), 1397–1408.

Vourlitis, G.L., Priante-Filho, N., Hayashi, M.M.S., Nogueira, J.D., Caseiro, F.T., Campelo Jr., J.H., 2001. Seasonal variations in the net ecosystem CO_2 exchange of a mature Amazonian transitional tropical forest (cerradão). Funct. Ecol. 15, 388–395.

Webb, E.K., Pearman, G.I., Leuning, R., 1980. Correction of flux measurements for density effects due to heat and water vapor transfer. Quart. J. R. Meteorol. Soc. 106, 85–100.

Welsh, D.T., Bartoli, M., Nizzoli, D., Castaldelli, G., Riou, S.A., Viaroli, P., 2000. Denitrification, nitrogen fixation, community primary productivity and inorganic-N and oxygen fluxes in an intertidal *Zostera noltii* meadow. Mar. Ecol.-Prog. Ser. 208, 65–77.

Wilson, K., Goldstein, A., Falge, E., Aubinet, M., Baldocchi, D., Berbigier, P., Bernhofer, C., Ceulemans, R., Dolman, H., Field, C., Grelle, A., Ibrom, A., Law, B.E., Kowalski, A., Meyers, T., Moncrieff, J., Monson, R., Oechel, W., Tenhunen, J., Valentini, R., Verma, S., 2002. Energy balance closure at FLUXNET sites. Agric. Forest Meteorol. 113, 223–243.

Yang, B., Hanson, P.J., Riggs, J.S., Pallardy, S.G., Heuer, M., Hosman, K.P., Meyers, T.P., Wullschleger, S.D., Gu, L., 2007. Biases of CO_2 storage in eddy flux measurements in a forest pertinent to vertical configurations of a profile system and CO_2 density averaging. J. Geophys. Res. 112, D20123, doi:10.1029/2006JD008243.

Yang, B., Pallardy, S.G., Meyers, T.P., Gu, L., Hanson, P.J., Wullschleger, S.D., Heuer, M., Hosman, K.P., Riggs, J.S., Sluss, D.W., 2010. Environmental controls on water use efficiency during severe drought in an Ozark forest in Missouri, USA. Global Change Biol. 16, 2252–2271.

Yang, P.C., Black, T.A., Neumann, H.H., Novak, M.D., Blanken, P.D., 1999. Spatial and temporal variability of CO_2 concentration and flux in a boreal aspen forest. J. Geophys. Res. 104 (D22), 27653–27661.