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A Perspective on Thirty Years of the Webb, Pearman and Leuning Density Corrections

Xuhui Lee · William J. Massman

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Abstract The density correction theory of Webb et al. (1980, Q J Roy Meteorol Soc 106: 85–100, hereafter WPL) is a principle underpinning the experimental investigation of surface fluxes of energy and masses in the atmospheric boundary layer. It has a long-lasting influence in boundary-layer meteorology and micrometeorology, and the year 2010 marks the 30th anniversary of the publication of the WPL theory. We provide here a critique of the theory and review the research it has spurred over the last 30 years. In the authors' opinion, the assumption of zero air source at the surface is a fundamental novelty that gives the WPL theory its enduring vitality. Considerations of mass conservation show that, in a non-steady state, the WPL mean vertical velocity and the thermal expansion velocity are two distinctly different quantities of the flow. Furthermore, the integrated flux will suffer a systematic bias if the expansion velocity is omitted or if the storage term is computed from time changes in the CO₂ density. A discussion is provided on recent efforts to address several important practical issues omitted by the original theory, including pressure correction, unintentional alternation of the sampled air, and error propagation. These refinement efforts are motivated by the need for an unbiased assessment of the annual carbon budget in terrestrial ecosystems in the global eddy flux network (FluxNet).

Keywords Density corrections · Eddy covariance · Mass conservation

List of Symbols

T Temperature
 p Atmospheric pressure

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S	Source term
W	Total mean vertical velocity
z	Measurement height
χ	Molar mixing ratio
μ	Ratio of molecular mass relative to dry air
ω	Mass mixing ratio
ρ	Mass density
ϱ	Molar density

Subscripts

a	Moist air
c	CO ₂
d	Dry air or density term
o	Oxygen
v	Water vapour

1 Introduction

Boundary-layer meteorology is concerned with flow patterns and processes in the atmospheric boundary layer (ABL), many of which are controlled by the fluxes of energy, water and trace gases at the earth's surface. The density correction theory of [Webb et al. \(1980\)](#), hereafter WPL, after the authors Webb, Pearman and Leuning) is a principle underpinning the experimental investigation of these fluxes. The theory states that density fluctuations associated with heat and water vapour diffusion must be taken into account when determining the true surface–air exchange from the measured turbulent fluxes.

The WPL theory has had a large influence in boundary-layer meteorology and micrometeorology, as evidenced by the exponential growth of its citation counts shown in [Fig. 1](#). Also shown in [Fig. 1](#) are citation statistics for two other landmark papers in physical meteorology. These three articles deal with very different subjects: [Sellers et al. \(1986\)](#) presented a theoretical framework, the simple biospheric model or SiB, for how to couple the biosphere with the atmosphere in a global circulation model. [Craig \(1961\)](#) reported the discovery of a robust relationship between oxygen and hydrogen isotopic abundance in precipitation, a relationship now widely known as the Global Meteoric Water Line or GMWL. [Webb et al. \(1980\)](#) presented a theory indispensable for the measurement of surface–air gaseous exchanges. All three, even though engaged in different problems, share a common attribute in that they have opened a new channel of scientific pursuit. As with SiB and GMWL, WPL is an abbreviation that has become part of our scientific language. Some people may argue that methodological articles are less important than articles aiming at understanding natural phenomena. Yet examples abound in the history of science to show that often it is methodological breakthroughs that inject rigour into, and supply new research questions, for a particular discipline ([Kuhn 1962](#)). It is safe to say that, without the density correction theory, the expansion of FluxNet research ([Baldocchi 2008](#)) would not have been possible.

The atmospheric transport of heat and water vapour and the transport of carbon dioxide are governed by the same aerodynamic principles. The former has been a central focus of boundary-layer meteorology, and the latter a subject of great interest to ecologists and climate scientists. WPL removed a systematic bias in the application to CO₂ of the micrometeorological methods originally designed for measuring the heat and water vapour fluxes. The

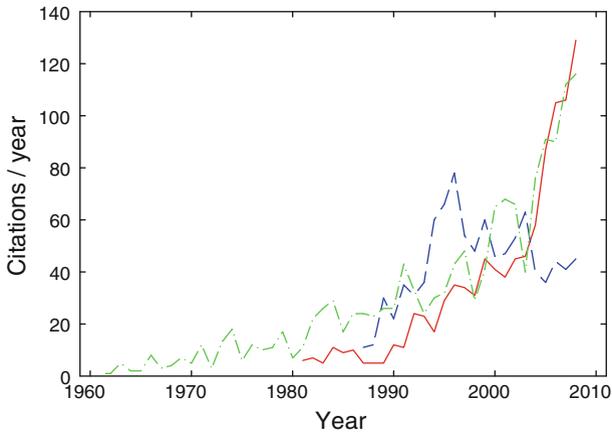


Fig. 1 Citation statistics according to the Web of Science database: *solid line* Webb et al. (1980); *dash-dotted line* Craig (1961); *dashed line* Sellers et al. (1986)

theory is among several factors that have contributed to the acceptance by ecologists of the eddy-covariance (EC) method as a powerful tool to investigate ecosystem metabolism (e.g., Chapin et al. 2004; Schlesinger 2004). [Other factors include improved hardware and computing power and a series of synthesis articles aimed at the ecological community (e.g., Baldocchi et al. 1988; Dabberdt et al. 1993).] That roughly 25% of the 1000-plus articles that cite WPL were published in ecological journals attests to its growing role in ecological research.

The year 2010 marks the 30th anniversary of the publication of the WPL theory. The goal of this perspective paper is to provide a critique of the theory and review the research it has spurred over the last 30 years. The WPL paper is an example of tight logical reasoning. An anecdote about the article's authorship, recounted in Sect. 2, also offers a useful lesson on the importance of idea-sharing in the modern scientific enterprise. Placing it in a historical context, Sect. 3 attempts to answer the question of why the article has long-lasting vitality while other similar studies are largely forgotten. Section 4 is a discussion of two contrasting experimental strategies in dealing with the density corrections, and Sect. 5 presents a brief summary of the WPL theory extended to non-steady state conditions. The progress to date in the refinement of the density correction theory is summarised in Sect. 6. These refinement efforts are motivated by the need for an unbiased determination of the net ecosystem carbon exchange in the global tower flux network (FluxNet). The relevant mathematical details are given in Appendices A–C.

Our paper compliments other rigorous discussions of the WPL theory published in recent years. Fuehrer and Friehe (2002) presented a complete density correction formulation that includes the terms omitted by WPL, while Paw U et al. (2000), Massman and Lee (2002) and Leuning (2004, 2007) extended the WPL theory to non-steady state and three-dimensional flows.

2 The Guelph Connection and Beyond

In a graduate course on research methods that one of us (XL) taught at Yale University, the students were presented with this scenario:

You received a letter from a colleague just before you are about to submit for publication your work on an important problem. The letter shows that you offer only a partial solution to the problem and suggests a way for a more complete analysis. What should you do?

This scenario is constructed, as part of a discussion on authorship and credit attribution, from an account of the events leading to the publication of the WPL paper. An earlier version of the article, authored by Webb and Pearman, considered only the correction for water vapour. After seeing a preprint of the paper, Leuning sent Webb his derivation on the temperature correction. Leuning's derivation however contained an error in using absolute zero as the reference temperature, rather than a more vaguely defined base temperature in the WPL paper (Ray Leuning, personal communication, 2010). Despite this error, Webb and Pearman added Leuning to the author list and thus the WPL theory was formed.

In ignorance of this history, the class was divided in their opinions. Some students believed that the work would be strengthened if the authors collaborate with the letter writer, and others countered that doing so would give him too much credit. Anyone who has read the WPL paper knows that a theory without the temperature correction would be much weaker than the WPL theory. WPL seemed to have the foresight of avoiding the peril of fragmented publication. Imagine that Webb and Pearman went alone with the water vapour correction, followed by a Leuning article that corrects Webb and Pearman's correction and someone else correcting Leuning's correction. Such a theory of triple corrections would have been extremely confusing to say the least, and most likely would have set back the experimental research on surface–air fluxes. The case of WPL argues for researchers to unite and strengthen, not to divide (into the least publishable units) and weaken, their work.

A Guelph connection also speaks to the value of idea-sharing. At the time, Leuning was a postdoctoral scientist working with George Thurtell at the University of Guelph. It was Thurtell who brought the temperature effect to Leuning's attention and encouraged him to work on it. Thurtell's role is not known to the general public. A curious reader may ask where Thurtell's insights came from. Baffled by the lack of energy balance in EC measurements, a challenge that confronts micrometeorologists to this day (e.g., [Foken 2008](#); [Mahrt 2010](#)), he had been contemplating all the possible places, perhaps including the density effects, where eddy covariance could go wrong. It was also possible that he was first exposed to the problem when serving on the doctoral advisory committee of Ray Desjardins, who was working at Cornell University at that time on the relaxed eddy-accumulation method for CO₂ flux measurement ([Desjardins 1972](#)). Desjardins proposed an unpublished solution to the density effect due to temperature by assigning a weighting factor to the measured CO₂ density in proportion to the inverse of air temperature (Ray Desjardins, personal communication, 2010). This list of possibilities can go on, but as with any idea exchange, the discussion at Guelph was a complex thought process that cannot be fully disentangled with words. Nevertheless, this anecdote is a reminder that “research is not about ownership, but about sharing” ([Day 2006](#); [Friedland and Folt 2009](#)).

3 Novelties of the WPL Theory

The assumption of zero dry air source is a fundamental novelty of the WPL theory. Several essential elements of the theory had already been published by other researchers. The correction algorithm of [Jones and Smith \(1977\)](#) for the sensible heat flux is identical to WPL's formulation in dry air and accurate to within 4% in moist air. [Bakan \(1978\)](#) argued that the

covariance between the vertical velocity and the mass mixing ratio is the true surface flux, which is a key conclusion reached by WPL. Several authors showed how the ideal gas law should be manipulated to obtain the mean vertical velocity arising from air density fluctuations (Priestley and Swinbank 1947; Brook 1978; Jones and Smith 1978; Smith and Jones 1979). These studies, however, suffer from assumptions that are either incomplete or incorrect (Leuning and Legg 1982; Webb 1982). For example, Brook (1978) assumed that the turbulent flux of moist air is zero at the surface, and from there on his analysis went astray. He concluded incorrectly that “changes in density, due to water vapour fluctuations, do not contribute to any significant extent to turbulent fluxes.” WPL’s assumption is free of these defects. Perhaps more importantly, their results have the power of generality: the theory is now shown after modifications to be valid for both steady and non-steady state (Leuning 2007) and for both homogeneous and heterogeneous flows (Paw U et al. 2000; Massman and Lee 2002; Leuning 2004).

The atmospheric modelling community has long been using the mass mixing ratio as a model variable (Appendix A). In his large-eddy simulation study published 6 years before the WPL paper, Deardorff (1974) expressed the conservation of atmospheric vapour in the form of specific humidity.¹ The same vapour conservation equation is used in mesoscale models (Pielke 2001). Similarly, the conservation equation for CO₂ is developed in terms of its mass mixing ratio in the investigation of large-scale atmospheric transport (Bolin and Keeling 1963; Fung et al. 1983), its diffusion in the atmospheric boundary layer (Chen et al. 2004; Górska et al. 2008) and in large-eddy simulations of its EC-based surface flux (Huang et al. 2008). The mass mixing ratio has two important properties that the density quantity does not have: (i) it is a conserved variable during thermal expansion and contraction (Appendix A), and (ii) only a non-zero source or sink in the flow field can give rise to its spatial gradient (Kowalski and Serrano-Ortiz 2007). So it is advantageous to use the mixing ratio quantity to diagnose the influence of surface exchange on the ABL. Using the gas density would create an artificial diffusion flux in the model domain (Kowalski and Serrano-Ortiz 2007). Although not the intent at the time, by formulating the surface flux with the mass mixing ratio, WPL effectively brought the flux measurement into compliance with these tested modelling principles.

In the era prior to infrared technology, specific humidity was used in the measurement of water vapour flux involving eddy covariance (Dyer and Maher 1965), gradient-diffusion (Swinbank 1951; Dyer 1967) and the surface-layer mass conservation (Dyer and Pruitt 1962). The concept of Bowen ratio was originally formulated with the vertical gradient of the vapour pressure (Bowen 1926). So were the first applications of the Bowen ratio/energy balance method in the terrestrial environment (Tanner 1960), although there was confusion as to whether the vapour density or vapour pressure gradient is the driver of the water vapour flux in the surface layer (Andy Black, personal communication, 2010). Because the change in atmospheric pressure spanning the measurement heights is very small, the difference between the use of the vapour pressure and that of specific humidity should be negligible. These studies are not susceptible to the density effect due to the sensible heat flux. The choice of specific humidity or the vapour pressure over the vapour density appears to be a matter of convenience, not an intentional effort to avoid the density effect. The fast-responding psychrometer of Dyer and Maher (1965) and the reversal Bowen ratio apparatus of Tanner (1960) and Black and McNaughton (1971) all measured directly the vapour pressure, not the vapour density. Even if the vapour density were used, the error due to the density effect would probably have gone

¹ Specific humidity—the ratio of the mass of water vapour to the mass of moist air—is a conserved quantity. The mass ratio of a trace gas, if expressed relative to moist air, is however not conserved because it is influenced by the diffusion of water vapour.

unnoticed since people were preoccupied with concerns about much larger sources of error, such as the inequality of the eddy diffusivity for water vapour and sensible heat (Verma et al. 1978). In the case of the Bowen ratio/energy balance method, the density error would have been further masked by forcing energy balance closure (McNaughton and Laubach 1998; Lee et al. 2004a). Only when infrared gas analysers became available for the measurement of CO₂ did the error turn into an anomaly. Surely a negative CO₂ flux makes no sense over a landscape void of photosynthetic activities (Leuning et al. 1982). WPL were among the first to recognise this anomaly.

4 Two Experimental Strategies

The manner in which WPL presented their arguments also deserves some attention. They relied on the logic of deduction, rather than the inductive inference favoured by experimentalists, to gain insights. They based their reasoning on the simple premise that there is no net source or sink of dry air at the surface. In their deductions, the reader finds guidance for two contrasting strategies in micrometeorological experimentation. One strategy deals with measurement errors numerically either online or in the post-field data analysis. The other removes the problem in the pre-field hardware preparatory phase. A brief discuss of each follows.

The mean vertical velocity due to the density fluctuations (\overline{w}_d) is typically less than 1 mm s^{-1} . WPL argued that such a small \overline{w}_d cannot be measured reliably and hence numerical corrections are a necessity. They derived for this purpose a simple expression for the corrections using the statistics measured over some pre-set averaging intervals. (In Appendices B and C we show that the same expression can be derived from the principle of mass conservation without invoking the WPL mean velocity.) According to their reasoning, if air temperature and humidity are measured simultaneously with, and at the same frequency as, the density of the trace gas in question, the corrections can also be made online by a point-by-point method whereby the trace gas density is converted to its mixing ratio and its true flux is computed from the covariance between the mixing ratio and the vertical velocity (Leuning 2004; Ibrom et al. 2007a; Miller et al. 2010). For open-path eddy covariance, the density effects cannot be avoided through optimisation of hardware or its field installation. Other unavoidable sources of error include tilted instruments and inadequate instrument response to turbulent fluctuations. These errors are also dealt with numerically in post-field analysis. It is now recognized that the correction sequence matters. Several studies have shown that frequency corrections should precede the WPL corrections (Massman 2004; Liu et al. 2006). Similarly, corrections for instrument tilt should be made before the WPL corrections, otherwise errors in the sensible and latent heat fluxes propagate to the trace gas flux through the WPL term.

Unlike these other corrections, a large WPL term should not be automatically taken as indication of a poor measurement system. The physics underlying the WPL correction is unambiguous; it is essentially an application of the ideal gas law to the conversion from gas density to gas mixing ratio. The same, however, is not true for frequency corrections as they involve either the assumption of spectral similarity (Goulden et al. 1996; Marandino et al. 2007) or the use of an idealised cospectrum model (Moore 1986; Massman 2000). Likewise, tilt corrections are dependent upon the choice of reference frame used for coordinate rotation and so are not completely objective (Finnigan 2004; Lee et al. 2004b).

The second experimental strategy emphasises hardware design prior to field deployment. A carefully constructed system should greatly reduce or even eliminate the need for post-field

corrections. WPL reasoned that, in a flux-gradient application, the density effects can be avoided by drying the air sample and bringing it to a common temperature before the gas density is measured. Such an intentional modification of the sampling air is now standard practice in the gradient measurement of trace gases including CO₂ (Denmead and Bradley 1985; Price and Black 1990), methane (e.g., Simpson et al. 1995) and nitrous oxide (e.g. Wagner-Riddle et al. 2007).

The same reasoning can be extended to the EC method. A chief advantage of the closed-path eddy covariance over the open-path technique is that the former eliminates the density effect due to the sensible heat flux (Leuning and Judd 1996). A sampling tube as short as 5 m is enough to remove temperature fluctuations in the sampled air (Rannik et al. 1997; Sahlée and Drennan 2009). A post-field correction to the latent heat flux is still necessary but its magnitude is typically an order smaller than the correction due to the sensible heat flux.

The magnitude of the WPL term often exceeds that of the flux itself. In the early 1980s, people doubted that the EC method could ever be successfully used in the marine environment where the CO₂ flux signal is weak (Shashi Verma, personal communication, 2010). Errors in the WPL term arising from errors in the latent heat flux overwhelm the true CO₂ flux for roughly 40% of the global ocean surface (Miller et al. 2010). Error propagation is also serious in the correction for the sensible heat flux involving open-path analysers (Liu et al. 2006). In a recent ship-borne campaign, Miller et al. (2010) used closed-path eddy covariance to avoid the density effect due to the sensible heat flux. They further eliminated 97% of the density correction due to the latent heat flux by drying the air sample. This configuration enabled them to resolve a small sea–air CO₂ flux on the order of $-0.1 \mu\text{mol m}^{-2} \text{s}^{-1}$ in the North Atlantic. Marandino et al. (2007) found that pre-drying reduces the WPL term to 4% of the true dimethyl sulphide flux over the North Pacific Ocean.

Obviously, hardware considerations are not limited to the density effects. WPL did not believe that the closed-path EC technique would have fast enough response to be feasible. Since then, considerable progress has been made in limiting tube attenuation on signal fluctuations. The response of an EC system is improved if flow in the tube is maintained turbulent rather than laminar (Lenschow and Raupach 1991; Massman 1991). Heating (Ibrom et al. 2007b), careful choice of tube material (Gramann 1995) and use of short tubes (Lee et al. 1996) also bring improvement.

Miller et al. (2010) and the tube attenuation studies cited above placed a higher priority on hardware configuration over post-field numerical corrections. A measurement system should be prepared so as to eliminate bias errors as much as possible prior to field deployment. Confidence in data quality is high if only a small portion of the errors is left to post-field corrections.

5 Extension to Non-Steady State

The WPL theory, originally formulated for horizontally homogeneous flow and steady state conditions, has been extended to non-steady state and inhomogeneous flow. Appendix B provides a synthesis of the insights obtained from Paw U et al. (2000), Massman and Lee (2002), Leuning (2004, 2007), Liu (2005), Massman and Tuovinen (2006), Kowalski and Serrano-Ortiz (2007), and Finnigan (2009). A key element of these studies is the deployment of the conservation of mass of atmospheric CO₂ and mass of dry air to constrain the WPL density terms. In non-steady state and horizontally homogeneous conditions, the conservation of CO₂ can be written as

$$\int_0^z \frac{\partial \bar{\rho}_c}{\partial t} dz' - \bar{\chi}_c(z) \int_0^z \frac{\partial \bar{\rho}_d}{\partial t} dz' + \left[\bar{\rho}_d \overline{w' \chi'_c} \right] (z) = \int_0^z \frac{\bar{S}_c}{m_c} dz' \quad (1)$$

(Eq. 5, [Leuning 2007](#); Appendix B). The reader is referred to the symbol list for symbol definitions. The integration spans the air column between the surface and the height of the eddy-covariance measurements. In Eq. 1, the term on the right represents the true net ecosystem exchange (NEE), the first two terms on the left are storage terms related to changes in the molar density of CO₂ and dry air, and the third term on the left is the familiar eddy-covariance term.

Equation 1 defines a number of important properties regarding eddy-covariance flux measurements. The non-steady state conditions are represented by the time change terms (first and second term on the left). In the special case of steady state, this equation states that the mixing ratio flux is equivalent to the true NEE, a key conclusion of WPL. But because there is no instrument that measures the mixing ratio directly, we must consider how to account for the extrinsic density effects. In Appendix C, we have expressed the flux in terms of the CO₂ density, by employing the ideal gas law, Dalton's law of partial pressures, and the Reynolds decomposition ([Leuning 2004, 2007](#)). In this derivation, no appeal to an "unmeasurable" vertical velocity or to the "conservation" of dry air flux is required. This is somewhat different than the original WPL formulation because they specifically made such an appeal.

In non-steady state, the total mean vertical velocity is the sum of two components

$$W = -\frac{1}{\bar{\rho}_d} \overline{w' \rho'_d} - \frac{1}{\bar{\rho}_d} \int_0^z \frac{\partial \bar{\rho}_d}{\partial t} dz' \quad (2)$$

(Eq. 32, Appendix B), where the first term on the right-hand side is the WPL velocity, and the second term is the expansion velocity of the air column below the measurement height,

$$\bar{w}_e = -\frac{1}{\bar{\rho}_d} \int_0^z \frac{\partial \bar{\rho}_d}{\partial t} dz'. \quad (3)$$

These two velocities describe two different properties of the flow even though both are related to surface fluxes of heat and water vapour. The main cause of \bar{w}_e is the surface sensible heat flux. [Finnigan \(2009\)](#) presents an expanded form of \bar{w}_e that includes other contributions from the temporal changes in vapour density and in atmospheric pressure. Some of these changes are caused by air-mass movement at the synoptic scale unrelated to surface processes.

The second term on the left-hand side of Eq. 1 arises from the expansion and contraction of the air column below the measurement height, and can be rewritten as

$$-\bar{\chi}_c(z) \int_0^z \frac{\partial \bar{\rho}_d}{\partial t} dz' = \bar{\rho}_c(z) \bar{w}_e(z). \quad (4)$$

Omission of the column expansion term will bias the NEE calculation if the storage is computed only from the temporal changes in the CO₂ density. The column expansion term is usually much smaller than the eddy-covariance term except during morning and evening transitions over land. Over the course of a day, a negative correlation exists between $\bar{\rho}_c$ and \bar{w}_e : in daylight hours $\bar{\rho}_c$ is lower than average and \bar{w}_e is positive, and vice versa at night. So the bias error is systematic for flux measurements integrated over periods longer than 24 h.

Leuning (2007) and Kowalski (2008) recommend that the mixing ratio instead of the density be used to compute the storage term. According to Leuning (2007), the storage term is expressed as

$$\bar{\rho}_d(z) \int_0^z \frac{\partial \bar{\chi}_c}{\partial t} dz'$$

and this method should eliminate most of the error associated with column expansion. The residual error is determined by the shape factor of the dry air and CO₂ density profiles, $\bar{\rho}_d(z)/\bar{\rho}_d$ and $\bar{\rho}_c(z)/\bar{\rho}_c$, as

$$\begin{aligned} & \int_0^z \frac{\partial \bar{\rho}_c}{\partial t} dz' - \bar{\chi}_c(z) \int_0^z \frac{\partial \bar{\rho}_d}{\partial t} dz' - \bar{\rho}_d(z) \int_0^z \frac{\partial \bar{\chi}_c}{\partial t} dz' \\ &= \int_0^z \left(1 - \frac{\bar{\rho}_d(z)}{\bar{\rho}_d}\right) \frac{\partial \bar{\rho}_c}{\partial t} dz' - \bar{\chi}_c(z) \int_0^z \left(1 - \frac{\bar{\rho}_d^2(z)}{\bar{\rho}_d^2} \frac{\bar{\rho}_c}{\bar{\rho}_c(z)}\right) \frac{\partial \bar{\rho}_d}{\partial t} dz'. \end{aligned} \tag{5}$$

A numerical assessment of Eq. 5, although beyond the scope of this review, is achievable if measurements of air temperature and CO₂ profiles are available.

The column expansion term is related to a quasi-advective term identified by Massman and Lee (2002; see also Eq. 31 in Appendix B). In differential form, it appears as $w' \rho'_d (\partial \bar{\chi}_c / \partial z)$ in the CO₂ mass conservation. The same term also appears in the derivation of Paw U et al. (2000, their Eq. 18) and Leuning (2004, his Eq. 9). Integrating the conservation equation and imposing the lower boundary condition on the dry air flux, we show that there may be some compensation to the quasi-advective term in the storage flux term (Appendix B).

6 Further Refinement of the Density Correction Theory

The density correction theory has been undergoing continuous refinement in ecosystem carbon balance studies. The two largest terms retained by WPL in the Taylor expansion of the fluctuations of air density are a good approximation for short-term field campaigns. In the interest of obtaining an accurate annual NEE measurement, it is important that we clarify the roles of the smaller terms in the expansion. The complete density correction for an open-path EC system consists of five components (Fuehrer and Friehe 2002), arranged here in the order of importance, as

$$F_d (= \bar{w}_d \bar{\rho}_c) = F_{d,T} + F_{d,v} + F_{d,p} + F_{d,c} + F_{d,h} \tag{6}$$

where subscript *T* denotes the correction due to fluctuations in temperature, *v* in water vapour, *p* in atmospheric pressure (*p*), *c* in carbon dioxide, and the *h* correction due to higher-order covariances. Their exact expressions are

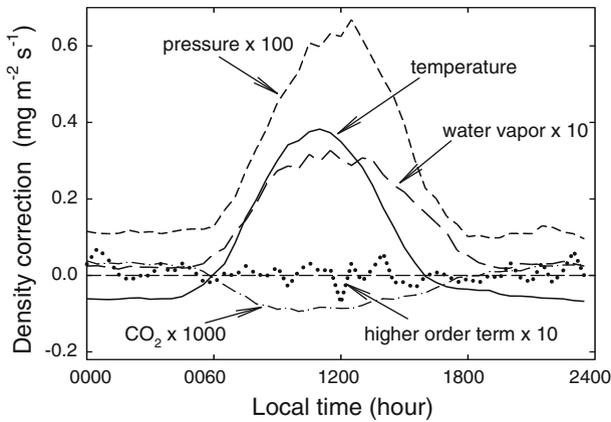


Fig. 2 Diurnal composites of the density corrections for a mixed forest in north-east China, averaged over an annual cycle (Zhang et al. 2011): temperature correction (Eq. 7), water vapour correction (Eq. 8, multiplied by 10), pressure correction (Eq. 9, multiplied by 100), CO₂ self-dilution correction (Eq. 10, multiplied by 1000), and correction due to the higher order temperature term (Eq. 11, multiplied by 10)

$$F_{d,T} = (1 + \mu_v \bar{w}_v) \frac{\overline{w'T'}}{T} \bar{\rho}_c, \quad (7)$$

$$F_{d,v} = \mu_v \frac{\overline{w'\rho'_v}}{\bar{\rho}_d} \bar{\rho}_c, \quad (8)$$

$$F_{d,p} = -(1 + \mu_v \bar{w}_v) \frac{\overline{w'p'}}{\bar{p}} \bar{\rho}_c, \quad (9)$$

$$F_{d,c} = \mu_c \frac{\overline{w'\rho'_c}}{\bar{\rho}_d} \bar{\rho}_c, \quad (10)$$

$$F_{d,h} = -(1 + \mu_v \bar{w}_v) \frac{1}{T} \left(\frac{\overline{w'T'^2}}{T} \right) \bar{\rho}_c. \quad (11)$$

The temperature and water vapour terms (Eqs. 7 and 8) are considered by WPL. The pressure correction term (Eq. 9) is always positive regardless of the time of the day and season (Massman and Lee 2002; Zhang et al. 2011). The term $F_{d,c}$ represents a self-dilution effect on CO₂ (Eq. 10). In Eq. (11), the higher-order terms involving the pressure fluctuations are omitted.

Here we use a dataset obtained during an experiment in a mixed forest in north-east China (Zhang et al. 2011) to gain an appreciation of the relative importance of each of these terms. A unique feature of the experiment is that static pressure fluctuations were measured continuously over one full year. The results are summarised as diurnal composites in Fig. 2 and annual sums in Table 1. The higher-order term ($F_{d,h}$) appears random and can be omitted. The CO₂ self-dilution term ($F_{d,c}$) is negative in the day and positive at night; its annual sum is also negligible. Without the pressure correction ($F_{d,p}$), the open-path EC system would bias the nighttime ecosystem respiration to lower values and the daytime photosynthetic carbon uptake to higher values. The annual cumulative pressure correction is 40 g C m⁻² s⁻¹ or roughly 20% of the annual NEE of this forest, so clearly the pressure term should not be omitted for open-path EC systems.

Table 1 Density corrections to the annual net ecosystem carbon exchange at a mixed forest in north-east China (Zhang et al. 2011)

Term	$F_{d,T}$	$F_{d,v}$	$F_{d,p}$	$F_{d,c}$	$F_{d,h}$
Annual sum	552	88	40	5	-0.1

All correction terms are in $\text{g C m}^{-2} \text{ year}^{-1}$

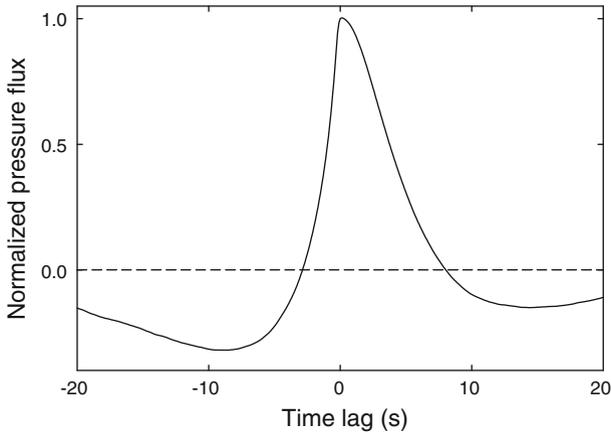


Fig. 3 Normalized pressure flux as a function of time lag. The pressure flux at time lag τ is calculated as the covariance between $w(t)$ and $p(t + \tau)$ and is normalized by the flux at zero lag. The data represents the composite of the observations at 30-min intervals over a 10-day period in July 2007

The dataset can also be used to obtain an assessment of the pressure correction for closed-path systems. We suggest that the static pressure fluctuations should propagate through the sampling tube at the speed of sound with virtually no time delay and with minimum amplitude damping. New pressure fluctuations generated by the measurement system should occur at frequencies too high to affect the $\overline{w'\rho'_c}$ covariance (Massman 2004), except in ship-borne observations where hydrostatic pressure fluctuations due to ship motion may be correlated with air turbulence (Miller et al. 2010). Since the CO_2 flux is computed with the CO_2 time series that is lagged by the time delay of the analyser, to correct for the pressure effect one should also delay the static pressure oscillations in the in-situ air by the same amount in the computation of the $w-p$ covariance in Eq. (9). The observations at the forest show that with a delay of 1 s the covariance $\overline{w'p'}$ decreases to 90% of the value with zero lag, and with a delay of 20 s, the covariance decreases to 10% and with the opposite sign (Fig. 3). So the pressure correction is not negligible if the closed-path system has a short sampling tube. A crude correction can be obtained with a two-step procedure. First, the in-situ pressure flux $\overline{w'p'}$ can be estimated from a non-dimensional relationship that describes its dependence on friction velocity and air stability (Zhang et al. 2011). Next, the in-situ flux is reduced by an appropriate amount according to Fig. 3 to account for the time lag.

WPL made an implicit assumption that all the quantities in the density correction relation are measured accurately. In practice, inadequate sensor response at high eddy frequencies is inevitable. For open-path systems, spectral corrections to the fluxes of sensible heat and water vapour should be applied before the WPL correction is made, or else the propagation of errors will bias evaluation of the trace gas flux (Leuning and Moncrieff 1990; Leuning

and King 1992; Massman 2004; Liu et al. 2006). In the example given in Table 1, if these fluxes had been underestimated by 2% due to the high frequency loss, a 2% upward adjustment would have increased the temperature correction by $11 \text{ g C m}^{-2} \text{ year}^{-1}$ and the water vapour correction by $2 \text{ g C m}^{-2} \text{ year}^{-1}$. Errors also occur if other variables in Eqs. (7)–(11) are not measured accurately. A 5% underestimation in $\bar{\rho}_c$ due to lens soiling implies an overestimation by 13% of the photosynthetic uptake in an ecosystem in a semi-arid climate (Serrano-Oriz et al. 2007). The WPL correction errors due to different CO_2 and H_2O time lags in a closed-path system result in a 7% error in the annual net CO_2 exchange above a beech forest (Ibrom et al. 2007a,b).

Addressing the commutability of the density and spectral corrections, Massman (2004) made a distinction between active and passive sensors. Closed-path systems always contain physical elements, such as the sampling tube, that actively alter the air sample. Open-path systems are mostly passive as they do not physically alter the sample, except in situations where the analyser itself is a source of heat that can modify the temperature of the air in its optical path (Grelle and Burba 2007). The artificial density fluctuations caused by sensor self-heating produce an apparent (and sometimes substantial) carbon uptake in the cold season unrelated to the true NEE (Goulden et al. 2006; Ono et al. 2008; Burba et al. 2008). Spectral corrections associated with passive sampling should be made to the covariance terms in Eqs. (7)–(11), but those with active sampling only to the covariance $\overline{w'\rho'_c}$. In the case of active sampling, over-corrections occur if the $\overline{w'\rho'_v}$ covariance, either corrected for amplitude damping of the sampling tube or computed at a lag time for $\overline{w'\rho'_v}$ instead of that for $\overline{w'\rho'_c}$, is used (Massman 2004; Ibrom et al. 2007a). Converting raw data point-by-point to the CO_2 mixing ratio avoids these over-corrections.

Massman's reasoning can be extended to two other measurement problems. First, flow distortion caused by the measurement platform is an active form of alternation affecting both open-path and closed-path systems. The associated flux reduction can be as much as 20% for sensible heat (Lee and Hu 2002) and 8% for water vapour (Griessbaum and Schmidt 2009). No correction for the interference should be made to these fluxes prior to the density corrections to the CO_2 flux.

The second problem is related to energy balance closure in micrometeorological experiments. An incomplete closure of 80% or less is common (e.g., Wilson et al. 2002; Foken 2008; Mahrt 2010). In some modelling studies, the measured sensible and latent heat fluxes are adjusted proportionally to force energy balance (Aranibar et al. 2006; Xiao et al. 2010). It is, however, incorrect to use the adjusted fluxes in the above density correction procedure. The lack of energy balance is caused by both instrument errors and meteorological factors. The instrument errors may be associated with both active and passive sampling, and should be dealt with according to Massman (2004). The meteorological factors contributing to the imbalance include advection (Mahrt 2010), stationary convective eddies (Lee 1998; Kanda et al. 2004), and entrainment of free air into the ABL (Huang et al. 2008). They exist even if the CO_2 mixing ratio is perfectly measured (and according to WPL, no density corrections are required).

Considerations of the density effects are not limited to eddy-covariance and flux-gradient measurements. Density corrections are necessary in some relaxed eddy-accumulation applications (Pattay et al. 1992). The flux measured with a chamber is influenced by water vapour dilution if evaporation occurs inside the chamber (Licor 1997; Lee 2000; Pape et al. 2009). Water vapour dilution also affects the mass mixing ratio measurement involving a mass-flow controller (Lee 2000).

It is now feasible to measure the isotopic fluxes of CO_2 and water vapour using the EC method (Griffis et al. 2008, 2010). As with the mass mixing ratio quantity, the abundance

of the isotopic species of water vapour or CO₂ is a conserved quantity when expressed in the delta notation. EC measurements of the delta flux (or isoforcing) do not require density corrections (Lee et al. 2009).

7 Closing Remarks

In the authors' opinion, the WPL paper has gained its prominent status for three main reasons. The inclusion of the density effects due to both temperature and water vapour significantly strengthens the density correction theory. The assumption of zero dry air source is a fundamental novelty that gives the theory its enduring vitality. The concrete guidance on flux measurements deduced from tight logical reasoning explains why the theory is widely accepted by experimentalists.

Recent discussions have clarified the meaning of the WPL dry air constraint. Central to these discussions is the use of the mass conservation equations. In non-steady state, the WPL velocity and the velocity of air column expansion are two distinctly different quantities of the flow field. More generally, the mean vertical velocity is the sum of the WPL velocity, the column expansion velocity and the vertical velocity associated with horizontal flow convergence (Eq. 38, Appendix B). These developments confirm the validity of WPL's conclusion that there is no density effect if the flux is formulated with the mass mixing ratio.

WPL omitted several practical issues in long-term EC experiments. Neglect of the static pressure fluctuations can cause a non-negligible bias in the estimate of the annual net ecosystem carbon exchange with open-path systems. Errors can also propagate through the density correction procedure if the variables used in the corrections are not measured accurately. Some of these errors can be eliminated by pre-field hardware design and others require post-field numerical corrections.

Finally, we have shed new light on the quasi-advective term, which has been and continues to be overlooked in ecosystem carbon budget studies. This term appears in the derivation of the density corrections on the basis of mass conservation. More traditional approaches are unable to produce this term. Use of the CO₂ mixing ratio to compute the storage term should eliminate most of the bias associated with the quasi-advective influence.

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Appendix A: Conservation of the Mass Mixing Ratio

Atmospheric models often start with the equation of mixing ratio conservation,

$$\frac{d\omega_c}{dt} = S_c/\rho_d. \quad (12)$$

Using the relationship

$$d/dt = \partial/\partial t + \mathbf{v} \bullet \nabla \quad (13)$$

where ∇ is the spatial gradient operator and \mathbf{v} the velocity, Eq. (12) can be written in partial derivative form, as

$$\frac{\partial\omega_c}{\partial t} + \mathbf{v} \bullet \nabla\omega_c = S_c/\rho_d. \quad (14)$$

In this Appendix, we show that Eq. (12) can be derived from the principle of mass conservation.

In the texts on fluid flows, the principle of mass conservation is expressed with the mass density. The conservation equations of dry air and CO₂ are

$$\frac{\partial \rho_d}{\partial t} + \nabla \cdot (\mathbf{v} \rho_d) = S_d, \quad (15)$$

$$\frac{\partial \rho_c}{\partial t} + \nabla \cdot (\mathbf{v} \rho_c) = S_c. \quad (16)$$

Using Eq. (13) we can rewrite Eqs. (15) and (16) as

$$\frac{d\rho_d}{dt} + \rho_d \nabla \cdot \mathbf{v} = S_d, \quad (17)$$

$$\frac{d\rho_c}{dt} + \rho_c \nabla \cdot \mathbf{v} = S_c. \quad (18)$$

Noting that $\omega_c = \rho_c / \rho_d$ and applying the chain rule of differentiation, we obtain

$$\frac{d\omega_c}{dt} = \frac{1}{\rho_d} \left(\frac{d\rho_c}{dt} - \frac{\rho_c}{\rho_d} \frac{d\rho_d}{dt} \right). \quad (19)$$

Substituting Eqs. (17) and (18) into Eq. (19) and ignoring the dry air source term S_d (Appendix B), we obtain Eq. (12).

Equations (12), (17) and (18) state that in the air layer free of sources and sinks, ω_c of an air parcel is conserved (that is, $d\omega_c/dt = 0$), but ρ_c and ρ_d are not unless the flow is incompressible.

Appendix B: WPL Theory in Non-Steady State and in Inhomogeneous Flows

Mass Conservation

WPL state that without “some kind of governing constraint” the theory of micrometeorological flux measurements made in a turbulent atmosphere would be “indeterminate”. Central to their solution to this indeterminacy problem was the zero vertical flux of dry air and the resulting vertical velocity. Since flux measurements are practically synonymous with micrometeorology, understanding the fundamentals of this problem is not only enlightening, but a requisite as well. This discussion examines the dry-air flux condition, the WPL vertical velocity, their relationship to the conservation of mass of dry air, and their consequences to the form of the equation of mass conservation for trace gases.

Physically the need for the WPL density terms arises from the need to separate the dynamic density effects that originate within the atmosphere (expansion/compression/dilution) from effects exclusive to the surface exchange, which result solely from the addition or removal of mass by sources or sinks below the level of the measurements. Unfortunately, measurements made by any instrument designed to detect the density of an atmospheric constituent will include all of these effects. Of course, this is essentially all micrometeorological instruments because they are almost universally designed to detect the number of molecules (or number density) of a particular gas within some sample volume. It is, therefore, of fundamental importance to micrometeorological flux measurements to be able to separate the rate at which molecules are released into or removed from the atmosphere by a [net] source or sink of a gas located below the height of the instrument from any extrinsic effects associated with,

(i) the thermal (temperature) and mechanical (pressure) expansion and compression that are inherent to a turbulent atmosphere, and (ii) elution/dilution caused by sources or sinks of other gases below the level of measurement. Consequently, the ideal measure of the “true” surface exchange flux should be proportional to the mixing ratio flux, where the mixing ratio is relative to dry air (Massman and Tuovinen 2006), because such a flux is insensitive to (or more precisely accounts for) these other external effects.

These ideas are now formalised with the introduction of the three-dimensional conservation of mass (equation of continuity) of atmospheric CO₂ (Eq. 16). Since the molecular mass of CO₂, m_c , is constant, Eq. (16) can be expressed in terms of molar density, $\varrho_c = \rho_c/m_c$, with no loss of generality, as

$$\frac{\partial(\varrho_d \chi_c)}{\partial t} + \nabla \bullet (v \varrho_d \chi_c) = S_c/m_c \tag{20}$$

where ϱ_d is the molar density of dry air [mol m⁻³] and $\chi_c = \varrho_c/\varrho_d$ is the CO₂ molar (or volume) mixing ratio [mol mol⁻¹, often expressed as ppmV].

Expressing this last equation in terms more meaningful to micrometeorology requires first performing the Reynolds decomposition into mean and fluctuating parts, then taking the time average of the result, and lastly neglecting several small terms (as discussed in Leuning 2004). Employing fully standard notation, the result is

$$\overline{\varrho_d} \frac{\partial \overline{\chi_c}}{\partial t} + (\overline{v} \overline{\varrho_d} + \overline{v' \varrho_d'}) \bullet \nabla \overline{\chi_c} + \nabla \bullet (\overline{\varrho_d} \overline{v' \chi_c'}) = \frac{\overline{S_c}}{m_c} - \overline{\chi_c} \left[\frac{\partial \overline{\varrho_d}}{\partial t} + \nabla \bullet (\overline{v} \overline{\varrho_d}) \right] \tag{21}$$

where, by employing the equation of continuity for dry air, the expression inside the brackets on the right-hand side can be replaced by $\overline{S_d}/m_d$ with $\overline{S_d}$ as the time-averaged source term of dry air and m_d as the dry-air molecular mass (Eq. 15). Massman and Lee (2002) noted that, in general, $\overline{S_d} \neq 0$ because it is related to S_c (or $\overline{S_c}$) through photosynthesis and respiration and N₂ production by bacteria in the soil. Nevertheless, this dry-air source will not be considered here because it is relatively small (i.e., $\overline{\chi_c} [\overline{S_d}/m_d] \ll \overline{S_c}/m_c$) and is not important to the present study (Leuning 2004, 2007). Thus we have the following two mass conservation equations:

$$\frac{\partial \overline{\varrho_d}}{\partial t} + \nabla \bullet (\overline{v} \overline{\varrho_d}) = 0, \tag{22}$$

and

$$\overline{\varrho_d} \frac{\partial \overline{\chi_c}}{\partial t} + (\overline{v} \overline{\varrho_d} + \overline{v' \varrho_d'}) \bullet \nabla \overline{\chi_c} + \nabla \bullet (\overline{\varrho_d} \overline{v' \chi_c'}) = \frac{\overline{S_c}}{m_c}. \tag{23}$$

The remainder of the present discussion develops three scenarios of increasing complexity in order to illuminate the nature of WPL’s insights and to extend and refocus their original WPL formulation to the mass conservation.

Steady State Conditions and Homogeneous Flow

We begin by assuming conditions that are both steady state and horizontally homogeneous. Equations (22) and (23) then reduce to

$$\frac{\partial}{\partial z} [W \overline{\varrho_d} + \overline{w' \varrho_d'}] = 0, \tag{24}$$

and

$$\left[W\bar{\varrho}_d + \overline{w'\varrho'_d} \right] \frac{\partial \bar{\chi}_c}{\partial z} + \frac{\partial \left(\bar{\varrho}_d \overline{w'\chi'_c} \right)}{\partial z} = \frac{\bar{S}_c}{m_c}, \quad (25)$$

where the mean vertical velocity is denoted by W . Integrating Eq. (24) from the soil surface ($z = 0$) to the measurement height z , we obtain

$$\left[W\bar{\varrho}_d + \overline{w'\varrho'_d} \right] (z) = \left[W\bar{\varrho}_d + \overline{w'\varrho'_d} \right] (0), \quad (26)$$

where the zero dry-air flux condition at the soil surface is $\left[W\bar{\varrho}_d + \overline{w'\varrho'_d} \right] (0) = 0$, which in turn yields the original WPL governing constraint, i.e., $W\bar{\varrho}_d + \overline{w'\varrho'_d} = 0$ and the resulting WPL vertical velocity, i.e., $W = -\overline{w'\varrho'_d}/\bar{\varrho}_d$ specific to the conditions of steady state and homogeneous flow. So Eq. (25) simplifies to

$$\frac{\partial \left(\bar{\varrho}_d \overline{w'\chi'_c} \right)}{\partial z} = \frac{\bar{S}_c}{m_c}. \quad (27)$$

These results demonstrate that the utility of the zero dry-air flux condition is the simplification of the conservation of mass for a trace gas.

Non-Steady State Conditions

For horizontally homogeneous non-steady state conditions Eqs. (22) and (23) can be written (after some trivial mathematical manipulation) as

$$\frac{\partial}{\partial z} \left[W\bar{\varrho}_d + \overline{w'\varrho'_d} \right] = -\frac{\partial \bar{\varrho}_d}{\partial t}, \quad (28)$$

and

$$\bar{\varrho}_d \frac{\partial \bar{\chi}_c}{\partial t} + \frac{\partial \left[W\bar{\varrho}_d + \overline{w'\varrho'_d} \right] \bar{\chi}_c}{\partial z} - \bar{\chi}_c \frac{\partial}{\partial z} \left[W\bar{\varrho}_d + \overline{w'\varrho'_d} \right] + \frac{\partial \left(\bar{\varrho}_d \overline{w'\chi'_c} \right)}{\partial z} = \frac{\bar{S}_c}{m_c}. \quad (29)$$

Substituting Eq. (28) into the third term of the left of Eq. (29) yields

$$\frac{\partial \bar{\varrho}_c}{\partial t} + \frac{\partial \left[W\bar{\varrho}_d + \overline{w'\varrho'_d} \right] \bar{\chi}_c}{\partial z} + \frac{\partial \left(\bar{\varrho}_d \overline{w'\chi'_c} \right)}{\partial z} = \frac{\bar{S}_c}{m_c}, \quad (30)$$

where we have combined the resulting first and third terms (the storage terms) on the left-hand side of Eq. (29) to yield the final storage term $\partial \bar{\varrho}_c / \partial t$ in Eq. (30). Next, integrating Eq. (30) and imposing the lower boundary condition on the dry-air flux yields the following conservation of CO₂ in non-steady state

$$\int_0^z \frac{\partial \bar{\varrho}_c}{\partial t} dz' + \bar{\chi}_c(z) \left[W\bar{\varrho}_d + \overline{w'\varrho'_d} \right] (z) + \left[\bar{\varrho}_d \overline{w'\chi'_c} \right] (z) = \int_0^z \frac{\bar{S}_c}{m_c} dz'. \quad (31)$$

In Eq. (31), the first term on the left-hand side is the ‘storage flux’ associated with changes in $\bar{\varrho}_c$. The second term is the advective term, which includes the quasi-advective term, $\bar{\chi}_c \overline{w'\varrho'_d}$, and the third term is the eddy-covariance term, for which the WPL density effects are implicit. Finally, the term on the right-hand side is the net ecosystem exchange. [Massman](#)

and Lee (2002) suggest that the quasi-advective term may be non-negligible in annual carbon balance estimates, but to our knowledge no measurements of this term have been reported.

Equation (31) can be further simplified into Eq. (1) in the main text by combining with the integral form of Eq. (28). Equation 1 suggests that there may be some compensation to the quasi-advective term contained in the storage flux term.

Equation (28) can be used to shed light on the mean vertical velocity in non-steady state. Integrating Eq. (28) and rearranging the terms, we obtain

$$W = -\frac{1}{\bar{\varrho}_d} \overline{w'\varrho'_d} - \frac{1}{\bar{\varrho}_d} \int_0^z \frac{\partial \bar{\varrho}_d}{\partial t} dz'. \tag{32}$$

So W is the sum of the WPL velocity (first term on the right-hand side) and the expansion velocity of the air column below the measurement height,

$$\bar{w}_e = -\frac{1}{\bar{\varrho}_d} \int_0^z \frac{\partial \bar{\varrho}_d}{\partial t} dz'. \tag{33}$$

An expanded form of \bar{w}_e is given by Finnigan (2009). By deploying the conservation equations of heat and water vapour, it can be shown that, if the expansion is caused only by the surface sensible heat and water vapour fluxes, W is invariant with measurement height.

Non-Steady State, Horizontally Inhomogeneous Conditions

So far this discussion has focused on rather special cases and we note that the dry-air flux condition varies with the assumptions that are made about the type of motion being considered. It is no different when assuming conditions that are non-steady state and horizontally inhomogeneous. We begin by re-writing Eqs. (22) and (23) in a manner that separates the horizontal and vertical flux components. This yields

$$\frac{\partial \bar{\varrho}_d}{\partial t} + \nabla_{\mathbf{H}} \bullet (\bar{\mathbf{u}} \bar{\varrho}_d) + \frac{\partial}{\partial z} [W \bar{\varrho}_d + \overline{w'\varrho'_d}] = 0 \tag{34}$$

and

$$\begin{aligned} &\bar{\varrho}_d \frac{\partial \bar{\chi}_c}{\partial t} + (\bar{\mathbf{u}} \bar{\varrho}_d) \bullet \nabla_{\mathbf{H}} \bar{\chi}_c + \nabla_{\mathbf{H}} \bullet (\bar{\varrho}_d \bar{\mathbf{u}}' \chi'_c) \\ &+ [W \bar{\varrho}_d + \overline{w'\varrho'_d}] \frac{\partial \bar{\chi}_c}{\partial z} + \frac{\partial (\bar{\varrho}_d \overline{w'\chi'_c})}{\partial z} = \frac{\bar{S}_c}{m_c}, \end{aligned} \tag{35}$$

where \mathbf{u} is the horizontal velocity vector and $\nabla_{\mathbf{H}}$ is the two-dimensional horizontal gradient operator. As in the last section we will use Eq. (34), mass conservation for dry air, in both the differential and vertically integrated forms, which are

$$\frac{\partial}{\partial z} [W \bar{\varrho}_d + \overline{w'\varrho'_d}] = -\frac{\partial \bar{\varrho}_d}{\partial t} - \nabla_{\mathbf{H}} \bullet (\bar{\mathbf{u}} \bar{\varrho}_d) \tag{36}$$

and

$$[W \bar{\varrho}_d + \overline{w'\varrho'_d}](z) = -\int_0^z \frac{\partial \bar{\varrho}_d}{\partial t} dz' - \int_0^z \nabla_{\mathbf{H}} \bullet (\bar{\mathbf{u}} \bar{\varrho}_d) dz'. \tag{37}$$

Rearranging Eq. (37) shows that the mean vertical velocity now consists of three components, the WPL velocity, the column expansion velocity and the velocity resulting from horizontal flow convergence:

$$W = -\frac{1}{\bar{\varrho}_d} \overline{w' \varrho'_d} - \frac{1}{\bar{\varrho}_d} \int_0^z \frac{\partial \bar{\varrho}_d}{\partial t} dz' - \frac{1}{\bar{\varrho}_d} \int_0^z \nabla_{\mathbf{H}} \bullet (\bar{u} \bar{\varrho}_d) dz'. \quad (38)$$

Equation 35 can now be written as

$$\frac{\partial \bar{\varrho}_c}{\partial t} + \nabla_{\mathbf{H}} \bullet (\bar{u} \bar{\varrho}_d \bar{\chi}_c + \bar{\varrho}_d \bar{u}' \chi'_c) + \frac{\partial [W \bar{\varrho}_d + \overline{w' \varrho'_d}] \bar{\chi}_c}{\partial z} + \frac{\partial (\bar{\varrho}_d \overline{w' \chi'_c})}{\partial z} = \frac{\bar{S}_c}{m_c}, \quad (39)$$

which upon integration and after imposing the zero dry-air flux lower boundary condition yields

$$\int_0^z \frac{\partial \bar{\varrho}_c}{\partial t} dz' + \int_0^z \nabla_{\mathbf{H}} \bullet (\bar{u} \bar{\varrho}_d \bar{\chi}_c + \bar{\varrho}_d \bar{u}' \chi'_c) dz' + \bar{\chi}_c(z) [W \bar{\varrho}_d + \overline{w' \varrho'_d}] (z) + [\bar{\varrho}_d \overline{w' \chi'_c}] (z) = \int_0^z \frac{\bar{S}_c}{m_c} dz' \quad (40)$$

and using Eq. (37) to eliminate the vertical advective term, $W \bar{\varrho}_d + \overline{w' \varrho'_d}$, then yields

$$\int_0^z \frac{\partial \bar{\varrho}_c}{\partial t} dz' - \bar{\chi}_c(z) \int_0^z \frac{\partial \bar{\varrho}_d}{\partial t} dz' + \int_0^z \nabla_{\mathbf{H}} \bullet (\bar{u} \bar{\varrho}_d \bar{\chi}_c + \bar{\varrho}_d \bar{u}' \chi'_c) - \bar{\chi}_c(z) \int_0^z \nabla_{\mathbf{H}} \bullet (\bar{u} \bar{\varrho}_d) dz' + [\bar{\varrho}_d \overline{w' \chi'_c}] (z) = \int_0^z \frac{\bar{S}_c}{m_c} dz'. \quad (41)$$

These last two relations demonstrate that the zero flux lower boundary condition eliminates the need to directly measure the trace gas vertical advective terms associated with the mass flux of dry air, but at a cost of much more complexity in the storage terms and the horizontal advective terms. In the spirit of Massman and Lee (2002), either of Eqs. (40) and (41) can be considered the fundamental equation of eddy covariance.

Appendix C: Measuring the Surface Flux of a Trace Gas

As previously mentioned, the (dry-air) CO₂ mixing ratio flux, $\overline{w' \chi'_c}$, is the ideal measure of the surface flux, but there is no instrument that measures χ_c or χ'_c directly. If such an instrument did exist, then no formal WPL corrections would be necessary. Failing the availability of the ideal technology, we must consider how to account for the extrinsic density effects.

Reynolds decomposition of χ_c yields

$$\chi_c = \bar{\chi}_c + \chi'_c = \frac{\bar{\varrho}_c + \varrho'_c}{\bar{\varrho}_d + \varrho'_d} \quad (42)$$

which to first-order produces

$$\bar{\chi}_c = \frac{\bar{\varrho}_c}{\bar{\varrho}_d} \tag{43}$$

and

$$\bar{\varrho}_d \chi'_c = \varrho'_c - \bar{\chi}_c \varrho'_d. \tag{44}$$

This last expression is the one we seek. Here the fluctuation in atmospheric CO₂ density associated with the surface source or sink is the left-hand term $\bar{\varrho}_d \chi'_c$. Here ϱ'_c is the fluctuation in ambient atmospheric CO₂ as measured by any density-sensing instrument, while $\bar{\chi}_c \varrho'_d$ accounts for the extrinsic effects. Formally connecting the last result to the WPL density terms, requires an expression for ϱ'_d . This can be found by employing the ideal gas law, Dalton’s law of partial pressures, and Reynolds decomposition, yielding

$$\varrho_d = \bar{\varrho}_d + \varrho'_d = \frac{\bar{p}_a + p'_a}{R(\bar{T}_a + T'_a)} - (\bar{\varrho}_v + \varrho'_v) \tag{45}$$

where R is the universal gas constant, T_a is the ambient (moist) air temperature, p_a is the ambient atmospheric pressure, and ϱ_v is the molar concentration of atmospheric water vapour. Again to first order this last relation yields

$$\bar{\varrho}_d = \bar{\varrho}_a - \bar{\varrho}_v \tag{46}$$

and

$$\varrho'_d = -\bar{\varrho}_d(1 + \bar{\chi}_v) \left[\frac{T'_a}{\bar{T}_a} - \frac{p'_a}{\bar{p}_a} \right] - \varrho'_v \tag{47}$$

where χ_v is the water vapour mixing ratio [mol mol⁻¹]. Therefore the surface exchange flux [mol m⁻² s⁻¹] is expressed as

$$\bar{\varrho}_d \overline{w' \chi'_c} = \overline{w' \varrho'_c} + \bar{\varrho}_c(1 + \bar{\chi}_v) \left[\overline{\frac{w' T'_a}{\bar{T}_a}} - \overline{\frac{w' p'_a}{\bar{p}_a}} \right] + \bar{\chi}_c \overline{w' \varrho'_v} \tag{48}$$

or [in terms of kg m⁻² s⁻¹] as

$$\bar{\rho}_d \overline{w' \omega'_c} = \overline{w' \rho'_c} + \bar{\rho}_c(1 + \bar{\chi}_v) \left[\overline{\frac{w' T'_a}{\bar{T}_a}} - \overline{\frac{w' p'_a}{\bar{p}_a}} \right] + \bar{\omega}_c \mu_v \overline{w' \rho'_v} \tag{49}$$

where ω_c is the mass mixing ratio of CO₂ [kg kg⁻¹] and $\mu_v = m_d/m_v$ with m_v as the molecular mass of water vapour. The above equation does not consider the higher order terms of Fuehrer and Friehe (2002) but retains the three terms of practical significance (Table 1).

At this point no appeal to an ‘unmeasurable’ vertical velocity or to the ‘conservation’ of dry air flux is required for this result. This is somewhat different to the original WPL (1980) formulation because they specifically made such an appeal. The only fundamental constraints required for the present result (as applied to a minor constituent of the atmosphere, of course) are basically the identification of dry-air mixing ratio, χ_c or ω_c , as the appropriate measure of CO₂ density and the mass conservation of dry air, Eq. (22). In our opinion this is the main insight of Paw U et al. (2000).

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