

On the relationship between the eddy covariance, the turbulent flux, and surface exchange for a trace gas such as CO₂

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Received: 20 November 2006 / Accepted: 12 February 2007 / Published online: 13 March 2007
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Abstract In the context of CO₂ surface exchange estimation, an analysis combining the basic principles of diffusion and scalar conservation shows that the mixing ratio is the appropriate variable both for defining the (eddy covariance) turbulent flux and also for expressing the relationship between the turbulent flux and surface exchange in boundary-layer budget equations. Other scalar intensity variables sometimes chosen, both the CO₂ density and molar fraction, are susceptible to the influence of surface exchange of heat and water vapour. The application of a hypsometric analysis to the boundary-layer “control volume” below the tower measurement height reveals flaws in previously applied approaches: (a) incompressibility cannot be assumed to simplify mass conservation (the budget in terms of CO₂ density); (b) compressibility alone makes the analysis of mass conservation vulnerable to uncertainties associated with resultant non-zero vertical velocities too small to measure or model over real terrain; and (c) the WPL (Webb et al. (1980) *Quart J Roy Meteorol Soc* 106:85–100) “zero dry air flux” assumption is invalidated except at the surface boundary. Nevertheless, the definition and removal of the WPL terms do not hinge upon this last assumption, and so the turbulent CO₂ flux can be accurately determined by eddy covariance using gas analysers of either open- or closed-path design. An appendix discusses the necessary assumptions and appropriate interpretations for deriving the WPL terms.

Keywords Conservative scalars · Eddy covariance · Mixing ratio · Net ecosystem exchange · Turbulent flux

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1 Introduction

Eddy covariance has emerged as a global-scale environmental research tool despite certain unresolved issues of fundamental methodology in the determination of surface exchange. Surface exchange data from eddy-covariance CO₂ “flux towers” describe ecosystem functioning, and long-term applications allow identification of sources and sinks of this greenhouse gas. With proliferation to hundreds of towers forming a worldwide network (Baldocchi et al. 2001) many flux towers are now managed by ecological researchers with little expertise in micrometeorology. Yet even boundary-layer experts applying this intricate technique have yet to arrive at a consensus on the appropriate means of interpreting surface exchange in terms of a calculated covariance.

For decades, the literature has abounded with ambiguity, controversy, and contradictions about the relationship between eddy covariance and surface-atmosphere exchange. The greatest unresolved issues for CO₂ exchange have to do with two inter-related matters: the so-called “density corrections” and the importance of a non-zero, mean vertical velocity. In the former case, significant work occurred around 1980 as the issue was debated (see review by Fuehrer and Friehe 2002). For some time, Webb et al. (1980, hereafter WPL) appeared to have achieved eminence and the debate lay dormant, only to erupt again recently with the widespread use of open-path gas analysers. A key uncertainty surrounds the WPL “zero dry air flux” assumption and resultant mean vertical velocity estimate (Liu 2005, Massman and Tuovinen 2006). The upsurge in flux tower measurements also has motivated interest in boundary-layer budget equations (Finnigan et al. 2003) including the role played by the mean vertical velocity in the context of mesoscale transport or advection. In general, scientists have struggled to reconcile apparently conflicting approaches to the same problem of estimating surface exchange (Paw U et al. 2000).

The lack of a rigorous definition of the CO₂ quantity being diffused by turbulence — the scalar whose covariance is proportional to the turbulent flux of interest — has contributed greatly to the confusion. This definition has been presented variously as CO₂ concentration (Wofsy et al. 1993), mixing ratio (Baldocchi 2003), density (Aubinet et al. 2000, Paw U et al. 2000), or often enough as “the scalar *c*” (Lee 1998, Yi et al. 2000). Such ambiguity can be found even within a single publication, with the turbulent flux described as the product of velocity fluctuations with those of constituent density *or* mixing ratio (e.g., Dabberdt et al. 1993). Yet the distinctions between these definitions are not trivial, and a re-examination of the fundamental principals of diffusive transport in fluids is required to identify unequivocally the appropriate covariance and define the turbulent CO₂ flux.

In this theoretical examination of the effects of atmospheric and surface exchange processes on CO₂ variables, we explore the differences between scalar variables in the context of diffusion-related fluctuations, and attempt to clarify the relationship between the eddy covariance, the turbulent CO₂ flux, and surface exchange. Basic principals of diffusive transport and conservation are applied to the problem at hand, demonstrating clearly that the mixing ratio is the preferred variable for framing the analysis (and eddy covariance). Similarly, it is shown that the budget equation for a flux-tower “control volume” is best expressed in terms of the mixing ratio when the goal is the estimation of surface exchange. Application of the hypsometric equation to the control volume makes this clear, discredits the WPL vertical velocity derived from the “zero dry air flux” assumption, and reveals errors in some previously

Table 1 Scalar intensity variables describing atmospheric CO₂, and their conservation properties as a function of atmospheric diffusion processes

Intensity variable	CO ₂ density (ρ_c)	Molar Fraction	Mixing ratio (c)
Definition	CO ₂ mass per unit air volume	Molar ratio: CO ₂ to total molecules	Mass ratio: CO ₂ to “dry air” molecules
Units (SI)	kg m ⁻³	mol mol ⁻¹	kg kg ⁻¹
<i>Atmospheric processes</i>		<i>Conservation properties</i>	
Heat conduction, expansion, compression	Non-conservative	Conservative	Conservative
Evaporation, water vapour diffusion	Non-conservative	Non-conservative	Conservative

published frameworks expressing the budget in terms of CO₂ density. Finally, an appendix explains the most appropriate means of defining the WPL terms.

2 Definitions

In this section, we examine the definition of diffusion and its meaning in an eddy covariance context, with particular attention to the scalar quantity being diffused. With a typical overall aim of characterising source/sink processes at the land surface, eddy covariance is generally used to quantify turbulent fluxes via simultaneous measurements of fluctuations in the scalar quantity and the fluid velocity. The choice of the scalar quantity of interest can depend on the physical processes that we wish to characterise, and by examining various possibilities in the case of CO₂ we shall see that there are different types of diffusion that can bring about CO₂ transport. Before addressing diffusion, we introduce several fundamental definitions for scalar variables that describe CO₂.

Various measures of intensity can describe trace components of a fluid mixture, and here we define those most frequently used for atmospheric CO₂. For convenience, the fluid is treated here as a mixture of gases; by neglecting atmospheric water in liquid and solid phases, we thus limit phase change to the surface. The chemical term “concentration” lacks a specific definition, and is best avoided. The CO₂ density (ρ_c) is the mass of CO₂ per unit air volume. The molar fraction, for a given population of molecules, is the ratio of the number of CO₂ molecules to total molecules and this is conserved through expansion/compression processes. Similarly, the mixing ratio (c) is the ratio of the mass of CO₂ to that of all molecules qualifying as “dry air” (i.e., excluding water vapour); this variable is conserved during expansion/compression, and also through all hydrological processes including phase change and water vapour diffusion. Table 1 provides an overview of these scalar intensities and their atmospheric conservation properties. Understanding the effects of atmospheric processes, including diffusion, on these three scalar intensities is critical to defining the relationship between eddy covariance, turbulent flux, and surface exchange for a trace gas such as CO₂.

2.1 Diffusion

Diffusion generally can be viewed as the random redistribution of fluid elements towards a state that is well-mixed in terms of variables that are otherwise conserved during simple movements within the fluid. Strictly speaking, it is a molecular process, but the analogy for mixing by more efficient turbulent motions (high Péclet number) is appropriate for the atmospheric boundary layer. The advantage of considering conservative variables in the definition becomes apparent when we examine the atmospheric case of adiabatic expansion/compression acting on the vertical distribution of the temperature, a non-conserved variable. When applied to such non-conserved variables, the description of diffusion is complicated by the necessary addition of atmospheric source/sink terms (Khvorostyanov and Curry 1999) that may be quite difficult to characterise. Thus atmospheric diffusion is easiest to model when applied to variables that are conserved through other atmospheric processes that occur concurrently.

In the case of the diffusion of matter, the appropriate scalar to be considered is the “proportion of marked molecules in a fluid mixture” and not the density as intuition might suggest (Batchelor 1967). Thus, here we explicitly define CO₂ diffusion as the net effect of many random motions (as may be quantified directly by eddy covariance) mixing against gradients in the molar fraction. Only material sources/sinks of gas by surface exchange cause gradients in the CO₂ molar fraction against which diffusion can effect transport. However, whether relevant to sources/sinks of CO₂ or not, transport and even diffusion of CO₂ can occur due to gradients in other quantities, as we will now see by examining two simple cases of random redistribution against gradients imposed by source/sink processes unrelated to CO₂. In the examples presented below, for simplicity we neglect the effects of gravity and assume no convection in the sense of large-scale, organised motions.

2.1.1 Heat conduction

First we will see that, as a result of sources/sinks of heat, diffusive heat transfer in one direction can imply a net, non-diffusive flow of gases (including CO₂) in the opposite direction. As in the approach of Leuning and Legg (1982) let us begin by considering two chambers separated by a membrane, but containing gas mixtures that are identical in constituent partial pressures according to standard atmospheric (dry) composition, and differ in temperature (and therefore density). When the membrane is removed, conduction of heat from the warm to the cold chamber will occur until a new equilibrium state is reached. This diffusive heat exchange also involves a movement of the centre of mass within the chambers: there is a net mass flow from the cold (dense) chamber to the warm (less dense) chamber until thermodynamic equilibrium is achieved, and part of this mass flow is a net CO₂ flux caused by random redistribution. However, because this “incidental” CO₂ flux comes about in the absence of gradients in the CO₂ molar fraction, it does not conform to our definition for CO₂ diffusion and so we will not refer to it as such.

2.1.2 Water vapour diffusion

Now we will observe that due to sources/sinks of water vapour, diffusion of water vapour can imply that other gases (including CO₂) diffuse in the opposite direction.

Let us consider two chambers as above but now with equal temperatures and total pressures, and identical proportions of dry air constituents as above; however, in this case all partial pressures are different because one of the two chambers also contains water vapour. When the membrane is removed, diffusion of matter occurs as water vapour moves towards the dry chamber according to gradients in its molar fraction; concurrently, “dry air” (including CO_2) migrates towards the moist chamber. In this case we have true diffusion of matter, including CO_2 , due to gradients established solely by sources or sinks of water vapour. Because such CO_2 diffusion is unrelated to source/sink terms for CO_2 , we may wish to exclude it from our definition of the turbulent CO_2 flux.

2.2 Scalar conservation

By careful selection of the relevant CO_2 scalar, it is possible to define the turbulent CO_2 flux as uniquely associated with the CO_2 sources and sinks whose characterisation is the ultimate goal of flux-tower research. The two examples above demonstrate how CO_2 transport and even diffusion can come about in the absence of relevant CO_2 source/sink terms, due to processes of heat and water vapour exchange. In order to avoid such influences and characterise transport associated uniquely with CO_2 surface exchange, the relevant eddy covariance must therefore be defined in terms of a scalar variable whose gradients are associated uniquely with CO_2 source/sink terms, i.e., one that is conserved through processes of heat conduction and water vapour diffusion.

During heat exchange, only two of our three variables meet the conservation criterion, while the other may be eliminated from consideration for the definition of turbulent CO_2 transport. In the first case (Sect. 2.1.1), both the molar fraction and the mixing ratio (c) are everywhere constant initially and remain so because they are conserved during expansion/compression processes associated with heat transfer within the fluid. This is not true for the CO_2 density (ρ_c); in our example both its initial gradient and subsequent redistribution by random motions (leading to a net flux CO_2 that does not qualify as CO_2 diffusion) are entirely due to thermal gradients. During mixing towards uniformity, expansion/compression due to heat conduction leads to ρ_c fluctuations unrelated to CO_2 sources/sinks. Thus it is inappropriate to define the turbulent CO_2 flux as proportional to a covariance with fluctuations in ρ_c . Examination of the second case will further demonstrate the inconvenience of this variable for the CO_2 scalar, and will also help us to choose between the remaining two.

Water vapour diffusion also represents a common atmospheric process for which two of our CO_2 intensity scalars are not conserved, and their behaviour in the second case (Sect. 2.1.2) helps to distinguish the most appropriate scalar for defining the turbulent CO_2 flux relevant to characterising surface exchange. Water vapour molecules added by evaporation displace CO_2 and other dry air molecules from the available volume. (This is most clearly seen for the extreme case just over a boiling surface, where water vapour pressure approaches total pressure and leaves little space for other gases.) Surface evaporation thus behaves as a sink term for the scalar ρ_c (depleting it locally), which is yet further evidence against ρ_c as the preferred eddy covariance scalar. The CO_2 molar fraction also is perturbed by water vapour diffusion. Indeed, the molar fraction of every gas in the mixture is sensitive to a material source/sink for any other gas constituent; water vapour is singled out here only because of its dominant role in surface exchange on Earth. Because evaporation

induces gradients in the CO₂ molar fraction and leads to CO₂ diffusion that is not relevant to CO₂ surface exchange, we find that true CO₂ diffusion as defined above is not truly what we seek to quantify in flux-tower research. For our definition of the turbulent flux, we are therefore left with the one scalar intensity variable, the mixing ratio, that is everywhere constant in our two examples, and remains so because it is conserved both through expansion/compression processes and also in the presence of water vapour diffusion.

3 The Turbulent CO₂ Flux

After some consideration and constantly recalling the objective of characterising surface exchange of CO₂, finally we can define the turbulent CO₂ flux (F_c) as being proportionate to random redistribution according to gradients and fluctuations in the mixing ratio (c). In a one-dimensional eddy covariance context, this flux may be expressed as

$$F_c = \rho_a \overline{w'c'} \quad (1)$$

where ρ_a is the dry air density, w is the vertical velocity component, and following micrometeorological tradition the overbar denotes a Reynolds average while primes represent deviations from the Reynolds average. This definition, although not new (e.g., Baldocchi et al. 1988), is perhaps now definitive and absolutely in repudiation of earlier work. To be clear, the turbulent CO₂ flux is taken as proportional to the covariance between a velocity component and the scalar defined according to mixing ratio, *not* CO₂ density ρ_c (except in rare isothermal, constant humidity situations). However, this does not imply a preference for the type of gas analyser to be used in the application of eddy covariance.

Eddy covariance can be applied to assess F_c using infrared gas analysers (IRGAs) of closed- or open-path design (Leuning and Judd 1996). Closed-path IRGAs bring gas samples to slowly varying, known temperature and pressure in a chamber before rapidly measuring densities of CO₂ (ρ_c) and water vapour (ρ_v), which are then converted to mixing ratios. High-frequency information is lost in the sampling process (in tubing), requiring covariance corrections that introduce uncertainty based on similarity assumptions (e.g., Massman 2000). Open-path IRGAs detect *in-situ* absorption by molecules in a fixed sensing volume to report ρ_c and ρ_v . When temperature fluctuations are also measured, then F_c as defined above can be calculated for the open-path case via “density corrections” that effectively remove influences of heat and vapour diffusion in the form of two WPL terms. (To rectify misinterpretations during and since the original WPL publication, the appropriate means of deriving these WPL terms is summarised in Appendix A.) The main disadvantage of open-path IRGAs is fallibility during rain. It is thus possible to define the turbulent CO₂ flux (F_c) in terms of mixing ratio (co-) variations using either type of IRGA, which is the first step towards the appropriate characterisation of sources and sinks of CO₂ at the surface.

4 Boundary-layer budget equations

Vertical mixing by turbulence is but one of many possible fates for CO₂ perturbations imposed by surface exchange, so that expressing the relationship between

the turbulent CO₂ flux at tower top and surface CO₂ source/sink terms generally requires the construction of a boundary-layer budget equation. Perturbations can accumulate locally (storage) and/or be transported elsewhere by turbulent (e.g., F_c) or non-turbulent motions. Molecular diffusion, because of its inefficiency (relative to turbulence) everywhere except very close to the surface, is traditionally grouped with the source/sink term and excluded from the definition of transport; this limits non-turbulent transport to larger scales. Before writing a budget equation, we will see how the same scalar conservation considerations expressed above elucidate the advantage of expressing budget equations in terms of the mixing ratio, whereas undesirable complications arise when expressing mass conservation for a control volume (the budget in terms of ρ_c).

In the context of eddy covariance and CO₂ surface exchange, it is inconvenient, but not incorrect, to develop a boundary-layer budget equation in terms of CO₂ density inside a control volume. One primary reason for this is that the surface exchange of water vapour and heat change the total CO₂ mass in the control volume and complicate the expression of the CO₂ budget, as shown mathematically by Leuning (2004, 2007). Evaporation adds air molecules at the surface, and in the absence of a change in layer state (pressure, temperature), the ideal gas law for the air layer requires the exit of other molecules at the top. Among the molecules exiting is a flux of CO₂ entirely unrelated to CO₂ surface exchange and therefore explicitly excluded from the above definition of F_c . More importantly for many situations, heat exchange determines expansion/compression that produces mean vertical velocities entirely relevant to the CO₂ mass balance for the volume, as is demonstrated by a simple hypsometric analysis.

When applied to an air layer below a tower measurement level, the hypsometric equation defines non-negligible, mean vertical transport due to layer expansion/compression. For a layer between pressure levels p_2 and p_1 , this classical equation in meteorology defines direct proportionality between layer thickness ($z_2 - z_1$) and mean temperature (\bar{T}) as

$$z_2 - z_1 = \frac{R}{g} \bar{T} \ln \left(\frac{p_1}{p_2} \right), \quad (2)$$

where g is the acceleration of gravity and R the gas constant. For a layer initially confined below a 30-m tall tower, an absolute temperature change of approximately 1 K involves a 0.1 m change in layer thickness, and therefore height due to the fixed lower boundary. If such a 1 K change occurs during a half-hour averaging period, the 0.1 m change in layer thickness implies a mean velocity of $60 \mu\text{m s}^{-1}$ at the layer top, which is significant in terms of the CO₂ mass budget.

Such a mean vertical motion and associated transport have deleterious consequences for the assessment of mass conservation in the boundary layer. The transport described is sizeable: at standard temperature and pressure (with 350 ppm of CO₂), the associated dry air flux includes mean CO₂ transport of $0.9 \mu\text{mol m}^{-2} \text{s}^{-1}$, hardly negligible compared to biological surface exchange. The hypsometric analysis thus demonstrates the inappropriateness of assuming incompressibility to simplify the CO₂ mass budget for a control volume, as is sometimes done (e.g., Finnigan et al. 2003). Such transport cannot be termed advection because it does not depend on a

vertical CO₂ gradient (Holton 1992); the transformation of advection into the convenient “flux form” depends on the same incompressibility assumption, and is therefore invalid in a mass conservation context. In addition, velocities on these scales are too small to be reliably measured by sonic anemometry (Lee 1998), and are unpredictable for situations over real topography. Such uncertainty in the mean vertical velocity represents a significant drawback for the expression of boundary-layer budget equations in terms of total CO₂ and net transport.

Hypsometric analysis also demonstrates the invalidity of the “governing constraint” proposed by WPL and recently criticised by Liu (2005). The mean velocity and CO₂ transport described by expansion/compression are entirely independent of turbulent exchange; for a nocturnal surface layer cooling in the absence of turbulence, hypsometric compression implies a downward vertical velocity at the layer top despite the lack of a turbulent density flux. Thus, the associated mean vertical velocity is not at all the same as that diagnosed from the WPL “zero dry air flux” assumption. Specifically, such hypsometric changes in layer thickness imply non-zero dry air fluxes at the layer top (flux measurement level), invalidating both the WPL “governing constraint” and the vertical velocity derived thereby, but not the WPL corrections whose validity does not hinge on this erroneous assumption (Massman and Tuovinen 2006; also see Appendix).

Because of its intimate relationship with the surface exchange of CO₂—independent of both expansion/compression processes and the behaviour of water vapour—the mixing ratio is the most appropriate variable for expressing a boundary-layer budget equation for CO₂. Fluctuations in the mixing ratio imposed by surface exchange can either accumulate locally or be moved about. Supposing horizontal homogeneity and a flat surface, the budget equation for the mixing ratio can be written following Baldocchi et al. (1988) as

$$\frac{\partial \bar{c}}{\partial t} + \bar{w} \frac{\partial \bar{c}}{\partial z} + \frac{\partial}{\partial z} \overline{w'c'} = S_c. \quad (3)$$

Changes in storage, vertical advection, and the (kinematic) vertical turbulent flux divergence on the left-hand side balance the source/sink term on the right. Since the CO₂ mixing ratio is conserved through all atmospheric processes other than mixing, the source/sink term is identically zero for a control volume containing no biota. Thus, only non-zero change in storage or advection can lead to a divergence of the vertical turbulent flux and thus disturb the equality between surface exchange and the turbulent flux (eddy covariance). The effects of water vapour exchange and expansion/compression processes are dramatically reduced: they affect only advection via the (e.g. hypsometric) vertical velocity, and then only in combination with a gradient in the CO₂ mixing ratio established by CO₂ surface exchange. Because this gradient rarely exceeds 10^{−6} m^{−1} (≈ 0.7 ppm m^{−1}) in turbulent conditions even very near an active vegetative surface (e.g., Rannik et al. 2004, Xu et al. 1999), such velocities usually affect the budget expressed in Eq. (3) only marginally so that the assumption of a constant flux with height is approximately valid. Only in conditions of incomplete mixing (stable boundary layer), or over inhomogeneous or complex terrain, should it be necessary to examine inequalities between the turbulent CO₂ flux—defined by the covariance between vertical velocity and the CO₂ mixing ratio—and surface exchange, once having corrected for the storage term.

5 Conclusions

When the goal is the characterisation of sources/sinks of CO₂ at the surface, the mixing ratio is the appropriate scalar intensity variable for defining the turbulent flux in terms of an eddy covariance. Definitions according to other scalars such as CO₂ density (ρ_c) or molar fraction are susceptible to contamination according to transport processes associated with sources/sinks of heat and/or water vapour. The mixing ratio also has clear advantages for use in boundary-layer budget equations. By contrast, equations for mass conservation in a control volume are vulnerable to large uncertainties associated with vertical velocities and hence mean transport, and may not be simplified by assuming incompressibility, as demonstrated by a hypsometric analysis. When the appropriate (WPL) corrections are applied, the turbulent flux can be measured by either open- or closed-path gas analysers.

Acknowledgements ASK is funded by a *Ramon y Cajal* fellowship of the Spanish Ministry of Education and Science; PSO benefits from a predoctoral grant from the *Junta de Andalucía*. Both enjoy funding from the regional government (*Junta de Andalucía*) project BACAEMÁ (RNM 332). Comments from two anonymous referees improved the quality of this article.

Appendix A: The WPL “Density Corrections”

Webb et al. (1980; WPL) identified the appropriate means of converting a covariance in terms of open-path CO₂ density (ρ_c) into a turbulent CO₂ flux (as defined in Sect. 3), but were inexact in both interpretation and terminology. Recently, Liu (2005) and Massman and Tuovinen (2006) have helped somewhat to advance the state of understanding, but misinterpretations associated perhaps with loose WPL terminology have left unclear the appropriate comprehension of “density effects”. This appendix is divided into two sections: the first presents the appropriate derivation of the WPL density terms, and the second briefly identifies the inadequacies in their interpretation by the original and subsequent authors.

A.1 Defining the WPL terms

The ideal gas law defines expansion/compression processes in terms of the total number density (n , mols of gas molecules per unit volume) as

$$n = \frac{P}{RT}, \quad (4)$$

where P is the pressure, R the universal gas constant, and T the temperature. For simplicity, we neglect the contribution of pressure fluctuations in modifying density, as is traditional in micrometeorology. When applying Reynolds averaging to the relevant variables (and employing a traditional simplification neglecting products of perturbation terms), we can derive an equation of state for turbulent fluctuations:

$$n' = -\frac{P}{RT^2}T'. \quad (5)$$

Because the contribution of pressure fluctuations has been neglected, Eq. (5) indicates that temperature fluctuations uniquely define parcel expansion/compression, entirely independent of constituent composition.

If all molecules are then labelled as belonging to either “dry air” (a) or “water vapour” (v) categories, these two components may be viewed as competing to occupy a temperature-determined volume:

$$n'_a + n'_v = -\frac{P}{RT^2}T'. \quad (6)$$

Equation (6) demonstrates the dependence of the number density of dry air (including CO₂) molecules on the water vapour number density. It is important to recognise that the “density effects” acting in Eq. (6) are independent of molecular mass, and thus not directly relevant to parcel density. When this equation is rewritten to isolate the dry air number density, two types of “density effects” become apparent:

$$n'_a = -\frac{P}{RT^2}T' - n'_v. \quad (7)$$

The first term on the right-hand side represents the effects of expansion/compression processes on the dry air number density. The second, however, is an independent effect associated with competition for available space by other ideal gas molecules, in this case water vapour, independent of their molecular mass. Were water vapour to have the same molecular mass as dry air, this second type of “density effect” would still operate without at all affecting parcel density. In fact, molecular mass is only important for any constituent (*i*), when we rewrite Eq. (7) by expressing the number density (n_i) as the density normalised by (effective) molecular mass (ρ_i/m_i) and resolve the equation in terms of dry air density:

$$\rho'_a = -\left(\frac{m_a P}{RT^2}\right)T' - \left(\frac{m_a}{m_v}\right)\rho'_v. \quad (8)$$

Equation (8) elucidates the non-conservative nature of gas density for dry air and indeed for all of its constituents (including ρ_c), and identifies two WPL effects that can produce fluctuations in ρ_c that are unrelated to CO₂ surface exchange. The first density effect is associated with changes in parcel volume (expansion/compression), while the second represents the effects of competition for available space by water vapour. The implications of Eq. (8) specifically for the CO₂ density ρ_c will become evident once such density effects are separated from density fluctuations associated with CO₂ surface exchange.

The next step in the WPL derivation, made explicit by [Massman and Tuovinen \(2006\)](#), is to recognise that fluctuations in CO₂ density (ρ'_c) can be expressed as a juxtaposition of independent influences. One type of fluctuation is associated with source/sink terms for CO₂ at the surface ($\rho'_{c,s}$) and directly related to fluctuations in the mixing ratio *c*. The other is associated with density effects ($\rho'_{c,D}$) as described in Eq. (8), and has no effect on the mixing ratio. The combination is formulated as the sum of two components, as follows:

$$\rho'_c = \rho'_{c,s} + \rho'_{c,D}. \quad (9)$$

Fluctuations in the dry air density (ρ'_a) may be treated likewise to allow combination of Eqs. (8) and (9), but first can be further simplified by an assumption not entirely unrelated to the WPL “governing constraint”. One of the primary motivations for the definition of “dry air” is to exclude the only terrestrial gas (water vapour) whose surface exchange and varying partial pressure are of sufficient magnitude to significantly

affect air composition and density. In the context of “density effects”, the surface exchange of other gases can be neglected, and it is approximately correct to assume no surface exchange of dry air ($\rho'_{a,S} = 0$). This assumption, implicitly introduced by Massman and Tuovinen (2006), is akin to applying the WPL “zero dry air flux” as a boundary condition (valid only at the surface), and effectively limits fluctuations in the dry air density to those associated with density effects, as

$$\rho'_a = \rho'_{a,D}. \quad (10)$$

Returning to the case of CO₂, the final consideration for the analysis of the defined density effects is that they have no impact on the mixing ratio c . Conservation of this variable through heat and water vapour exchange implies equality of relative density effects on dry air and its constituent CO₂:

$$\frac{\rho'_{c,D}}{\rho'_{a,D}} = \frac{\overline{\rho_c}}{\overline{\rho_a}}. \quad (11)$$

Substitution of Eqs. (10) and (8) into Eq. (11) allows the definition of the “density effects” acting on CO₂ density:

$$\rho'_{c,D} = -\frac{\overline{\rho_c}}{\overline{\rho_a}} \left(\frac{m_a P}{R T^2} \right) T' - \frac{\overline{\rho_c}}{\overline{\rho_a}} \left(\frac{m_a}{m_v} \right) \rho'_v. \quad (12)$$

When combined with Eq. (9), multiplied by the vertical velocity fluctuation and averaged, and finally with appropriate scaling according to mean dry air density, the derivation culminates in Eq. (24) of the original WPL publication, which correctly removes the “density effects” and allows the characterisation of the turbulent flux (F_c) representing surface exchange from eddy covariance data acquired using open-path gas analysers.

A.2 Errors in previous interpretations

Despite arriving at the appropriate equations to remove WPL terms representing “density effects”, the original WPL publication contained two fundamental misinterpretations, one arising directly from the other. The principle one is the assumption of a “zero dry air flux” at the measurement height, rather than exclusively at the surface. The hypsometric analysis in Sect. 4 of the present work demonstrates clearly that such an assumption is not appropriate, nor is it necessary, as shown by both Massman and Tuovinen (2006) and the above derivation. This first inaccuracy led directly to the second misinterpretation—the prediction of a vertical velocity at the measurement height. It is worth recognising that Eq. (12) can be viewed as the sum of two non-dimensional terms, one fluctuating with temperature and the other with water vapour density (ρ_v), whose sum multiplies the mean CO₂ density. When Eq. (12) is multiplied by the vertical velocity fluctuation, each WPL term attains units representing the product of a velocity scale and mean CO₂ density. Such velocity scales describe non-diffusive CO₂ transport (see Sect. 3) associated with density effects, but they should not be interpreted as representing a net movement of air.

In addition to these misinterpretations, WPL also introduced unfortunate terminology that may have further obscured understanding. The very title of the article—beginning with “Correction of flux measurements for density effects”—is misleading. In the first place, rather than “correction of flux measurements” the removal of WPL

terms permits flux determination from covariance measurements involving a non-conservative scalar. Secondly, the term “density effects” may tempt the reader to think in terms of parcel density, which is not entirely appropriate. As recognised in traditional meteorology and conveniently packaged in the definition of the virtual temperature, the role of water vapour in parcel density comes about due to its low molecular mass. However, as clearly expressed in Eq. (7), it is *number* (or molar) density, independent of molecular mass, that explains the water vapour WPL term. This confusion regarding the role of water vapour may explain the continued misinterpretation of “density effects” by other investigators.

While recent reassessments of the WPL derivations have led to some improvement in their understanding, Eq. (7) has been misinterpreted as being due exclusively to the effects of expansion/compression. For example, Liu (2005) attempted to define corrections for ρ_c covariances as an alternative to the WPL approach, but his Eqs. (10) and (11) are incorrectly based on the limitation of “density effects” to expansion/compression processes, and represent an unsound foundation upon which further derivations were based. Similarly, Massman and Tuovinen (2006) erred in describing the density effects on ρ_a as being uniquely associated with parcel expansion/compression. Unlike Liu however, they included the effects of water vapour fluctuations throughout their derivation, which is therefore ultimately correct.

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