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An eddy covariance theory of using O_2 to CO_2 exchange ratio to constrain measurements of net ecosystem exchange of any gas species☆

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ABSTRACT

After many decades of efforts, it remains a challenge to accurately measure mass and energy exchanges between biosphere and atmosphere. The widely used, dry air-based eddy covariance (EC) approach underestimates surface net available energy and nighttime ecosystem respiration and reports photosynthesis under conditions when none should occur. So far many explanations for these problems have been suggested but convincing evidence and reliable solutions have yet to be found. There is a need for critical thinking about the very foundation of current EC theory and for fundamentally different ways of making flux measurements. Here I propose a new EC theory that constrains measurements of net ecosystem exchange (NEE) of any atmospheric gas species with the ecosystem O_2 to CO_2 exchange ratio (g), also known as oxidative ratio. The fundamental equation of the new theory is derived. I show that if $O_2 + g$ CO_2 is treated as a virtual bi-molecular gas species, denoted as gCO_4, then the fundamental equation of the new theory is identical in form to the fundamental equation of EC when the ecosystem budget of a single atmospheric constituent (e.g. N_2 or Ar) or dry air is used to constrain NEE measurements of atmospheric gas species. A convenient method for measuring g is also described. Compared with the current, dry air-based approach, the proposed gCO_4-based approach uses less restrictive assumptions, avoids indirect calculations of multiple variables, and thus prevents losses of flux covariances. Existing O_2 measuring technologies can be improved in response time to meet the requirements of the new approach. The adoption of the gCO_4-based approach will greatly enhance the scientific and societal values of flux sites and networks by eliminating measurement biases and by providing value-added datasets to enable understanding the oxidation state of the biosphere.

1. Introduction

Measurements of net ecosystem exchange (NEE) of atmospheric trace gases, water vapor, and sensible heat with the eddy covariance (EC) approach have been widely made to study biosphere–atmosphere interactions, global change biology and ecology (Baldocchi et al., 2001). Yet such measurements are still highly uncertain. The current EC approach underestimates the net available energy at the surface, resulting in the so-called energy imbalance problem (e.g. Wilson et al., 2002; Leuning et al., 2012). It also underestimates the nighttime ecosystem respiration (e.g. Goulden et al., 1996; Gu et al., 2005). These two underestimations have been observed nearly universally at EC sites across the world, regardless of the complexity of landscape, vegetation types, climate conditions, instrumentation (open- vs. closed-path analyzers and different geometries of sonic anemometers), and the level of technical skills of the researcher. Convincing explanations have yet to be found even though many attempts have been made. Additionally, open-path EC systems often report net uptake of CO_2 during cold winters when photosynthesis should not occur, which is an artifact likely caused by instrument heating (Burba et al., 2008). The ubiquity and recalcitrance of the energy imbalance and nighttime respiration underestimation problems and the false reporting of photosynthesis call for careful reexamination of the very foundation of the current EC approach, which unfortunately has been done rarely (Kowalski, 2012). If possible, fundamentally different ways of measuring NEEs should be explored so that data obtained with independent approaches can be cross-checked.

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c	molar density (mol m^{-3})
g	ecosystem O_2 to CO_2 molar exchange ratio
gCO_4	$O_2 + g\ CO_2$ (symbol)
h	eddy flux measurement height (m)
J	the vector of the molecular diffusional flux (mol m^{-2} s^{-1})
N	net ecosystem exchange (mol m^{-2} s^{-1})
S	source/sink intensity of an atmospheric constituent (mol m^{-3} s^{-1})
t	time (s)
u	horizontal (2D) wind velocity field (m s^{-1})
v	3D wind velocity field (m s^{-1})
w	vertical velocity (m s^{-1})
X	mixing ratio, molar density ratio of a specified atmospheric gas species to dry air (mol mol^{-1})
z	vertical distance from soil surface (m)
χ	molar density ratio of a specified atmospheric gas species to gCO_4 (mol mol^{-1})

List of subscripts

dry	dry air (all atmospheric components minus water vapor)
s	the specified atmospheric gas species whose flux is to be measured
gCO_4	$O_2 + g\ CO_2$

At the core of the current EC approach is the use of mass balance of dry air (a complex mixture of all atmospheric gas species minus water vapor) to constrain eddy flux measurements. The exact implementation of this constraint has evolved over time with the early assumption of zero vertical flux of dry air being replaced with the more general assumption of zero NEE of dry air (Webb et al., 1980; Paw et al., 2000; Leuning, 2007; Lee and Massman, 2011; Gu et al., 2012).

Two basic issues affect the effectiveness of the current, dry air-based EC approach. Firstly, no matter which assumption of the dry air constraint (zero vertical flux or NEE) is adopted, a paradox arises (Gu et al., 2012): If one is interested in measuring the flux or NEE of CO_2 or CH_4 (methane), which is part of dry air, one has already implied the flux or NEE of dry air is not zero and thereby violated a key assumption in the first place! This paradox could only be avoided if the sources of dry air exactly balance the sinks in the ecosystem. As ecosystems exchange with the atmosphere many dry air components (CO_2, O_2, CH_4, nitric and nitrous oxides, volatile organic compounds, etc.), it is hard to imagine that the sources and sinks of dry air can ever cancel each other. Thus the current theoretical framework of EC is not self-consistent, which has species-specific consequences (Gu et al., 2012).

Secondly, the density of dry air cannot be measured directly and has to be calculated indirectly from the measurable atmospheric variables of pressure, temperature and water vapor density using ideal gas law. Measurement errors as well as flow distortions and spatial separations of different sensors all contribute to uncertainty in the calculated instantaneous density of dry air and associated variances and covariances (Gu et al., 2012). Because temperature is needed to compute dry air density, instrument heating becomes a problem for the dry air-based EC approach (Burba et al., 2008). Perhaps more importantly, conventional arithmetic averaging schemes, which are central to the EC approach, cannot preserve ideal gas law across spatial and temporal scales (Kowalski, 2012).

Gu et al. (2012) proposed that the NEEs of N_2 and Ar are essentially zero and therefore can be used to constrain the NEE measurements of atmospheric gas species with the EC approach. Compared with the current, dry air-based approach, the theoretical, N_2 or Ar-based approach has advantages. Ideal gas law is not needed to compute the turbulent eddy fluxes and almost all terms in the fundamental equation of EC can be determined with direct measurements. Also the theoretical, N_2 or Ar-based approach can be applied to any other gas species while the dry air-based approach can only be applied to species for which the assumption of zero NEE of dry air can be made without substantial biases (see Gu et al., 2012 for in-depth discussion). However, it may be difficult, in the near future, to develop a fast-response technology capable of measuring N_2 or Ar molar densities with sufficient accuracy. So the search for an alternative EC approach needs to continue.

The ecosystem – atmosphere exchange of CO_2 is tightly coupled to the exchange of O_2. The ecosystem O_2 to CO_2 molar exchange ratio, also known as oxidative ratio, is a fundamental emergent property and is determined by the oxidation state of the ecosystem (Randerson et al., 2006; Masiello et al., 2008). In this paper I show that the coupling between ecosystem O_2 and CO_2 exchanges can be exploited for a fundamentally different EC approach. More specifically, I propose an EC theory that uses the ecosystem oxidative ratio as a constraint for measuring NEEs of any atmospheric gas species. A new fundamental equation for applying the O_2/CO_2-based EC approach is derived. As the next sections will show, this new approach is less restrictive in measurement requirements and basic assumptions than the current, dry air-based approach and is expected to produce more reliable measurements of NEEs of atmospheric gas species.

As discussed later, it is not necessary for the proposed O_2/CO_2-based EC approach to assume a constant ecosystem O_2 to CO_2 molar exchange ratio over extensive time periods. The new approach only requires that this exchange ratio remains unchanged at the time scale within which there are measurable variations in the mixing ratios of O_2 and CO_2 (with respect to dry air) in the fully mixed air near the surface. Ecosystem processes can cause variations of such magnitude at sub-daily time scales.

An added benefit of applying the O_2/CO_2-based EC approach is that future flux sites and networks will provide measurements of atmospheric O_2 concentration and the ecosystem O_2 to CO_2 molar exchange ratio, in addition to those variables currently available. The data of O_2 concentration can be used as an independent constraint for regional carbon balance estimation with the inversion approach. The measurements of ecosystem O_2 to CO_2 molar exchange ratio allows continuous monitoring of the oxidation state of the terrestrial biosphere in response to climate change and human activities (Randerson et al., 2006). These measurements will also enable a better partitioning of global and hemispheric carbon sinks between the ocean and land (Keeling et al., 1996). Thus the O_2/CO_2-based EC approach will greatly enhance the scientific and societal values of flux sites and networks in the future.

The challenge for the proposed approach lies in O_2 measuring technologies suitable for EC applications. Because of the close coupling between O_2 and CO_2 exchanges, atmospheric O_2 is expected to fluctuate with the same magnitude as atmospheric CO_2 (~tens of ppm or more) at time scales less than diurnal. Thus any O_2 analyzers will need to achieve the same level of absolute accuracy as CO_2 analyzers in order to measure biologically originated O_2 signals in the atmosphere. However, the atmospheric background O_2 (~210,000 ppm) is much higher than the atmospheric background CO_2 (~400 ppm). Thus it is much more challenging to measure atmospheric O_2 than CO_2. Despite the challenge, currently multiple technologies are already available to measure atmospheric O_2. These include interferometry (Keeling, 1988), mass spectrometer (Bender et al., 1994), paramagnetism (Manning et al., 1999), and vacuum ultraviolet radiation (Stephens et al., 2003). They all have achieved a ppm-level precision and accuracy. Thus the current atmospheric O_2 measuring technologies may have already met the