Comment on “Using the gradient method to determine soil gas flux: A review” by M. Maier and H. Schack-Kirchner

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While Maier and Schack-Kirchner (2014) have produced a thorough bibliographical review concerning the gradient method, they have erroneously expressed the main equation upon which the method is based (their Eq. (1)). Gas transport due to molecular diffusion is defined by Fick’s law, which for the gas phase should be written:

\[ F(z) = -D_z \cdot \rho_a \frac{d \chi}{dz} \]  \hspace{1cm} (1)

In this equation, \( F \) is the upward gas flux (\( \mu \text{mol m}^{-2} \text{s}^{-1} \)), \( D_z \) the effective diffusion coefficient of the gas species in the soil or snow (\( \text{m}^2 \text{s}^{-1} \)), \( \rho_a \) the mean air density (\( \mu \text{mol m}^{-3} \)), and \( z \) (m) the vertical position. The gradient upon which molecular diffusion depends is that of the molar fraction (\( \chi \), ppm or equivalently \( \mu \text{mol m}^{-3} \)) and not molar density (\( \mu \text{mol m}^{-3} \); Kowalski and Argueso, 2011). Variations in \( \text{CO}_2 \) density need not imply variations in \( \text{CO}_2 \) molar fraction, because they can be brought about by simple changes in temperature as described by the ideal gas law. For this reason, and particularly in semiarid climates with large day–night soil temperature variations, significant and systematic errors are produced when density gradients are used to infer \( \text{CO}_2 \) diffusion.

In the following section, real field data are used to quantify the errors generated when soil \( \text{CO}_2 \) fluxes are calculated speciously based on density gradients, as by Maier and Schack-Kirchner (2014).

Errors in applying Fick’s law using density gradients

Gradients in soil temperature (\( T \)) and \( \chi \) were measured at “El llano de los Juanes” a shrubland plateau at 1600 m in the southeast of Spain (for site details see Serrano-Ortiz et al., 2009). Two \( \text{CO}_2 \) molar fraction sensors (GMM222, Vaisala, Inc., Finland) were installed, the shallow sensor at 2 cm and the deep sensor at 10 cm (\( \Delta z=0.08 \text{ m} \)), each accompanied by a thermistor (PT100). A data-logger (CR1000, Campbell Scientific, Logan, UT) measured every 30 s and stored 30 min averages. For these depths, the differences (shallow-deep) in \( \text{CO}_2 \) molar fraction (\( \Delta \chi \)) ranged from –2500 ppm to 0 (Fig. 1, panel A) and those in soil temperature (\( \Delta T \)) varied from –15 to 30 °C (panel B). Whereas \( \Delta \chi \) was consistently negative, \( \Delta T \) was positive during daytime and negative at night, with magnitudes that varied seasonally. Because of the asymmetry of the non-soil terms in the surface energy balance (net radiation and turbulent energy fluxes), daytime magnitudes are larger than those at night.

Fig. 1. Differences in \( \text{CO}_2 \) molar fraction (\( \Delta \chi \)) and temperature (\( \Delta T \)) between the shallow (2 cm) and deep (10 cm) sensors from April 27th of 2013 to August 21st of 2014.

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When using the erroneous Maier and Schack-Kirchner (2014) version of Fick’s law, based on density gradients, CO2 effluxes are systematically overestimated during daytime (warm surface) and underestimated at night (cool surface; Fig. 2).

We have characterized the magnitude of such errors, which according to the gas law are directly proportional to $x_C$, over a global range of environmental conditions. For $x_C$, this can extend at least to 5000 ppm (Amundson and Davidson, 1990). The absolute errors that occur in estimating the flux based on density gradients can exceed 0.5 μmol CO2 m2 s$^{-1}$, and have relevant magnitudes over a representative range of conditions (Fig. 3).

In conclusion Fick’s law must be applied based on gradients in the molar fraction to avoid errors of the magnitude demonstrated here. Such errors are particularly important to avoid because they would systematically bias the temperature dependency of soil respiration (e.g., Arrenius or Q10 model parameters; Lloyd and Taylor, 1994), which is often required for extrapolating this influence on the atmospheric CO2 budget to future climate scenarios (Melillo et al., 2002).

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References


