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

Enrique P. Sánchez-Cañete[a,b,*], Andrew S. Kowalski[b,c]

[a] Estación Experimental de Zonas Áridas (EEZA, CSIC), 04120 Almería, Spain
[b] Instituto Interuniversitario del Sistema Tierra en Andalucía, Centro Andaluz de Medio Ambiente (IISTA-CEAMA), 18006 Granada, Spain
[c] Dpto. de Física Aplicada, Universidad de Granada, 18071 Granada, Spain

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:

$$F(z) = -D_s \cdot \rho_a \frac{d\chi_c}{dz}. \quad (1)$$

In this equation, F is the upward gas flux (μmol m^{-2} s^{-1}), D_s the effective diffusion coefficient of the gas species in the soil or snow (m^2 s^{-1}), ρ_a the mean air density (μmol m^{-3}), and z (m) the vertical position. The gradient upon which molecular diffusion depends is that of the molar fraction (χ_c, ppm or equivalently μmol mol^{-1}) and not molar density (μmol m^{-3}; Kowalski and Argueso, 2011). Variations in CO_2 density need not imply variations in 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 CO_2 diffusion.

In the following section, real field data are used to quantify the errors generated when soil 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 χ_c 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 CO_2 molar fraction sensors (GMM222, Vaisala, Inc., Finland) were installed, the shallow sensor at 2 cm and the deep sensor at 10 cm (Δz = 0.08 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 CO_2 molar fraction ($\Delta\chi_c$) ranged from −2500 ppm to 0 (Fig. 1, panel A) and those in soil temperature (ΔT) varied from −15 to 30 °C (panel B). Whereas $\Delta\chi_c$ was consistently negative, ΔT 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.

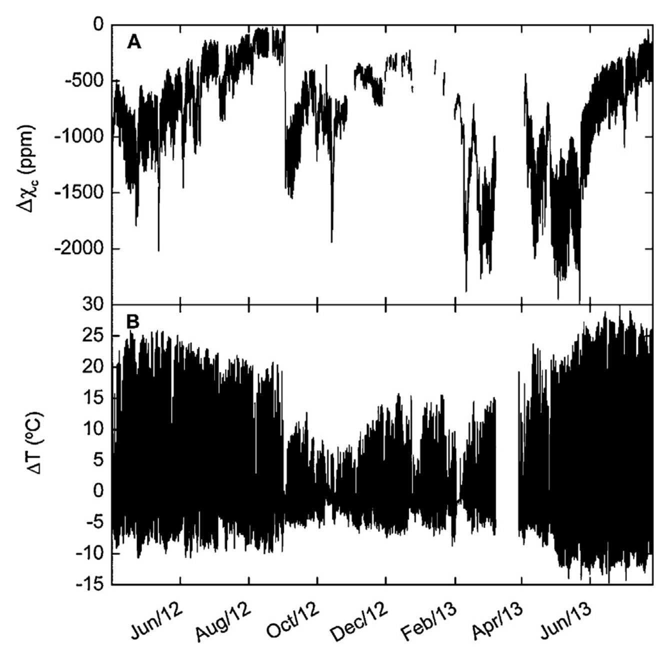

Fig. 1. Differences in CO_2 molar fraction ($\Delta\chi_c$) and temperature (ΔT) between the shallow (2 cm) and deep (10 cm) sensors from April 27th of 2013 to August 21st of 2014.

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* Corresponding author at: Instituto Interuniversitario del Sistema Tierra en Andalucía, Centro Andaluz de Medio Ambiente (IISTA-CEAMA), Avenida del Mediterráneo, S/N, 18006 Granada, Spain.
E-mail address: enripsc@ugr.es (E.P. Sánchez-Cañete).

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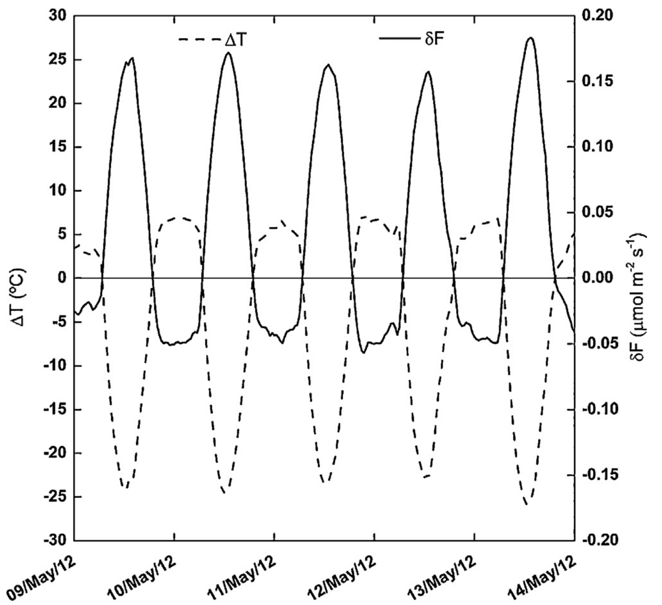

Fig. 2. Errors in the soil CO_2 efflux (δF) committed when incorrectly basing diffusion on CO_2 density gradients, and the associated soil temperature differences (ΔT), during six days in May 2012.

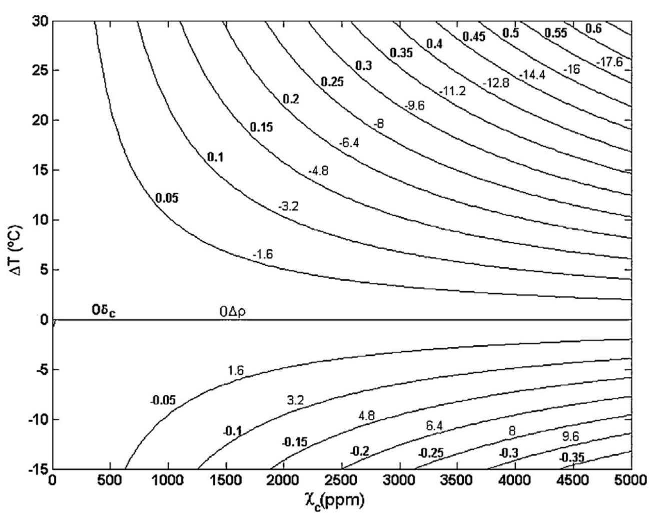

Fig. 3. Errors in soil CO_2 effluxes (δF, in μmol CO_2 m^2 s^{-1}, bold font) as related to density differences ($\Delta\rho$ in mmol CO_2 m^{-3}, normal font) caused by temperature gradients (ΔT, °C) in the absence of gradients in the molar fraction (χ_c). For these calculations, Δz was taken as 0.08 m and for simplicity a constant value was used for the CO_2 diffusion coefficient ($D_s = 2.5 \times 10^{-6}$ m^2 s^{-1}; Moldrup et al., 2000).

When using the erroneous Maier and Schack-Kirchner (2014) version of Fick's law, based on density gradients, CO_2 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 χ_c, over a global range of environmental conditions. For χ_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 CO_2 m^2 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., Arrhenius or Q_{10} model parameters; Lloyd and Taylor, 1994), which is often required for extrapolating this influence on the atmospheric CO_2 budget to future climate scenarios (Melillo et al., 2002).

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