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Determination of in situ gas diffusivity for the reliable estimation of soil fluxes through the gradient method

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Soil CO_2 fluxes represent a major source of CO_2 emissions, where small changes in their estimation provoke large changes in the quantification of the global carbon cycle. Recently, the gradient method that employs soil CO_2 probes at multiple depths has been offered as a way to inexpensively and continuously measure soil CO_2 flux. However, the use of the gradient method can yield inappropriate flux estimates due to the uncertainties mainly associated with the inappropriate determination of the soil diffusion coefficient. Therefore, in-situ methods to determine diffusion coefficient are necessary to obtain accurate CO_2 fluxes.
Here the data obtained during one year with two automatic soil CO_2 chambers along with CO_2 molar fraction data from 4 probes at 10 cm depth, were used to determine a model of soil diffusion coefficient (Ds), which was applied later to obtain the soil CO_2 fluxes by the gradient method. Another Ds model was obtained by injection and sampling of SF6 during several campaigns with different soil water content levels. Both Ds models obtained in situ were compared with another 13 Ds models published. We addressed three questions: 1) Can we use a previously published model, or do we need to determine Ds in situ? 2) How accurate are the CO_2 fluxes estimates obtained by the gradient method for different Ds models, compared with chamber-measured CO_2 fluxes? 3) Can we take a limited number of chamber measurements to obtain a good Ds model, or we need longer calibration periods?
Comparing the cumulative soil respiration for the different diffusion models, we found that the model with empirical calibration to the soil chambers had the best agreement with the chamber fluxes (<0.5% error). The SF6 model underestimated by chamber fluxes by 23% and the published models ranged from an underestimate of 78% to an overestimate of 14%. Most importantly, we found that a few days of measurements with a soil respiration chamber (with widely varying soil water content) are enough to build a model and obtain precise estimations of soil CO_2 fluxes through the gradient method.