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An innovative method for continuous measurement of soil CO_2 flux

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ABSTRACT

Herein, we present a method for continuous measurement of soil CO_2 flux that is completely new and distinct from existing instruments. The foremost difference is that instead of using an infrared gas analyser (IRGA), the new device measures soil CO_2 flux by means of a simple pressure sensor, measuring pressure transients inside a closed polymeric tube inserted into the soil. This allows continuous measurements even in soil placed in environments that could potentially damage IRGA. In addition, due to the innovative operating principle, measurements of soil CO_2 flux can be effortlessly performed also in strongly harsh weather conditions. Theoretical equations were derived for calculating soil CO_2 flux solely using measured transient values. The reliability of the equations was rigorously tested with a variety of experiments. Continuous measurements over four months, acquired in a high-emission area on the Island of Vulcano, compared favourably with the data obtained using an established method.

1. Introduction

The emission of CO_2 in natural environments is a phenomenon that has always aroused great interest in the scientific community. Over the years, many studies have investigated these emissions from a variety of angles: evaluation of global CO_2 emissions, ecological and agriculture investigations (Raich and Schlesinger, 1992; Batjes, 1996; Atkin et al., 2000; Shi et al., 2006; Fischer, 2008; Wang et al., 2011); gas hazards (Beaubien et al., 2003; Hernández Perez et al., 2003; Carapezza et al., 2011); volcano surveillance and geochemical explorations (Chiodini et al., 1996; Gerlach et al., 2001; Hernández et al., 2001; Faber et al., 2003; Granieri et al., 2006; Bergfeld and Evans, 2011; Federico et al., 2011; Camarda et al., 2012). In addition to CO_2 emitted directly from volcanoes, CO_2 of natural origin is released into the atmosphere mainly through soil, and as a result, most studies have focused on soil CO_2 flux measurements. These measurements have been performed with diverse methods according to the aim of the research. Some methods perform extensive measurements of CO_2 emissions over a large area, while others measure soil CO_2 flux at a determinate point. Extensive measurements are often used in research primarily to evaluate an ecosystem's carbon exchange and/or total budget emission. Single point measurements are used, inter alia, in agricultural studies; in geochemical exploration with the aim to highlight an anomalous zone of emission and to link soil degassing with tectonics; and in volcanic surveillance to monitor soil CO_2 flux over time. The method most used for extensive measurement is eddy covariance analysis (Law et al., 1999; Pilegaard et al., 2001; Lewicki and Hilley, 2009). Single point measurements of soil CO_2 flux can be performed directly by measuring concentration gradients in the soil (Baubron et al., 1990; Russell et al., 1998) or indirectly using tailor-made methods. The two indirect methods mainly used are the accumulation chamber method (ACM) (Norman et al., 1992; Bekku et al., 1995; Chiodini et al., 1998) and the dynamic concentration method (DCM) (Camarda et al., 2006). The two methods use very different operating principles and have advantages and disadvantages related to the research for which they are utilised (Carapezza and Granieri, 2004; Camarda et al., 2009). However, both employ an infrared gas analyser (IRGA). In both methods, a sample of soil gas is introduced into the instrument, potentially exposing it to damage by corrosive gas species or liquid water; consequently, neither method is widely applicable, especially for continuous measurements, in environments with sulphurous or acidic species, or in conditions that may lead to condensation phenomena inside the instrument. In addition, these two methods cannot be used to take continuous measurements in environments with harsh weather conditions such as high wind speed, recurrent intense rain, or thick snow, without great difficulty.

On these grounds, we have developed a new measurement method for soil CO_2 flux that is able to efficiently perform continuous measurements in the above-mentioned extreme environmental conditions and can also serve as a valid alternative to existing measurement methods in any other environment. The method couples a specially designed instrument, named CADEMASO, to a theoretical model, based on the gas transport laws through porous media (Sahimi, 1995). Experimental tests aimed to calibrate CADEMASO and to test the reliability of the method are reported, and long-term

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continuous field measurements are compared with a canonical method.

2. The instrument: CADEMASO

2.1. Operating principles

The operating principle of CADEMASO is based on the measurement of pressure transients inside a closed polymeric tube that are generated by the various rates at which gases permeate through it in an equilibration process. The features of this transient depend on the gas species involved as well as their partial pressures. The gaseous phase usually present in soil is composed mainly of a binary system of CO_2 and air. In such a binary system (Fig. 1A), during an exchange process between gas inside and outside the tube, there is a valid linear relationship between the rate of increase of P_t inside the tube at the beginning of the processes and CO_2 partial pressures (De Gregorio et al., 2009):

$$\left(\frac{\partial P_t(t)}{\partial t}\right)_{t=0} = \frac{A}{Vh}(Kp_{CO2} - Kp_{air})(P_{aCO2} - P_{inCO2}) \quad (1)$$

where $[(\partial P_t/\partial t)_{t=0}]$ is the first derivative of equation describing variation of total pressure inside the device at $t=0$; A is the area of the membrane surface, V is the internal volume of the tube, and h is membrane thickness; Kp_{CO2} and Kp_{air} are the permeability coefficients of CO_2 and air, respectively; P_{aCO2} is the equilibrium partial pressure of CO_2; and P_{inCO2} is the initial partial pressure of CO_2 inside the tube. The instrument configuration (Fig. 1B) consists of a polytetrafluoroethylene (PTFE) capillary tube connected at its ends to two-way electrovalves. On the other end, one electrovalve is attached to a membrane pump. The system is equipped with a pressure transducer interposed between one end of the tube and the electrovalve. The use of PTFE as a polymeric membrane ensures the generation of detectable pressure transients owing to the difference between Kp_{CO2} and Kp_{air} (De Gregorio et al., 2005). The PTFE tube is inserted into the medium of interest, with the rest of the components on the outside. The sampling sequence is divided into two steps: in the first step, the two electrovalves are kept open with the pump active for 2 min. This operation has the aim to introduce air into the tube and provides the disequilibrium condition necessary to trigger the pressure transient. In the second step, the electrovalves are closed, and the total pressure inside the device is measured every 30 s for 10 min. The sampling sequence is completely automated using a tailor-made electronic device, allowing continuous measurements.

2.2. Calibration coefficient

According to Eq. (1) for associating values of $[(\partial P_t/\partial t)_{t=0}]$ to P_{aCO2} values, we must determine the terms P_{inCO2} and $[A/Vh(Kp_{CO2} - Kp_{air})]$. As shown in De Gregorio et al. (2009) the last term can be determined experimentally by calculating $[(\partial P_t/\partial t)_{t=0}]$ for different $(P_{aCO2} - P_{inCO2})$ values and computing the angular coefficient of the straight line fitting these values. Further, if in the calibration experiments the value of P_{inCO2} is kept negligible with respect P_{aCO2}, a value of angular coefficient that can be used as a calibration coefficient (C) for computing P_{aCO2} directly from $[(\partial P_t/\partial t)_{t=0}]$ can be obtained. However, the obtained C value is valid only for the specific features and conditions used in the laboratory. In fact, as reported in formula (1), C depends on A/Vh and hence on PTFE tube geometry, volumes of fittings, and Kp values of the gases. To use the device in the field, an understanding of the dependence of C on the above-mentioned parameters was necessary.

2.3. Variability of calibration coefficient in response of different device configurations

Knowledge of this variably geometric response is necessary because the configuration of the device used in the field will be unavoidably dissimilar from the configuration adopted in the laboratory

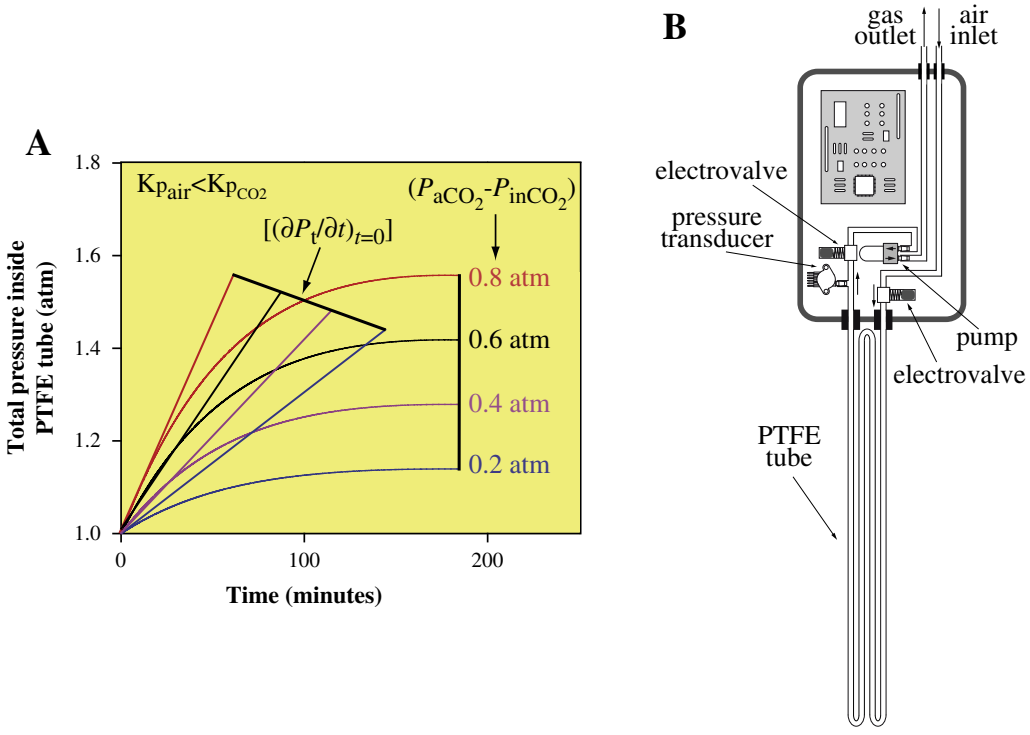

Fig. 1. Summary panels illustrating theoretical and practical characteristics of the CADEMASO device: (A) theoretical lines showing that in a matrix of CO_2 and air, the value of $[(\partial P_t/\partial t)_{t=0}]$ is proportional to the difference between the partial pressure of CO_2 inside (P_{inCO2}) and outside (P_{aCO2}) the PTFE tube. (B) Operative scheme and main components of CADEMASO.