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Pressure responses of portable CO_2 concentration sensors

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Here, we investigated the pressure response of five different models of portable CO_2 infrared sensors: GMP343 (Vaisala Oyj, Finland), ADC LCA-2 (The ADC Bioscientific Ltd., UK), and three different EGMs (PP Systems, UK). In the pressure range of 750–1000 hPa, we found that the analysers function systematically in an individual manner and the original pressure corrections that the manufacturers have provided are inaccurate from a few to tens of ppm. Therefore, we determined new empirical pressure correction functions for each sensor. The resulting corrections perform better than the original ones in the pressure, CO_2 concentration (370–490 ppm), temperature (5–21 °C) and water-vapour (4–11 g m^{-3}) range of this study. However, since the individual analysers had different pressure responses, we recommend that each individual instrument be tested in cases where changes in pressure may affect the results.

Introduction

Atmospheric carbon dioxide (CO_2) is widely monitored due to its role in the atmospheric energy balance. A variety of interactions with the biosphere affects the concentration of CO_2. Long-term field measurements are important to the current and future investigation of photosynthesis, respiration and carbon balance.

The eddy covariance (EC) technique is a direct way to determine whole-ecosystem exchange of CO_2. Alternative methods such as gradient measurements and a boundary-layer budget technique, based on mass balance principles, have also been used. To understand the partitioning of CO_2 fluxes between trees and understorey vegetation, smaller-scale measurement techniques are needed, e.g. different chamber-based systems with portable instruments. Estimates for annual budgets of CO_2 exchange by all of these techniques require continuous measurements under all kinds of atmospheric conditions.

Various atmospheric conditions, especially fluctuations in temperature and pressure, challenge the use of on the measurement devices and inversion methods. For example, pressure correction plays an important role when atmospheric pressure changes during long-term monitoring. The effect of atmospheric pressure change is a source of uncertainty also in measurements of vertical profile.

Manufacturers usually provide their own pressure correction equations that can be applied online or used afterwards in data inversion. However, individual instruments of the same model may also display individual behaviour and one equation with similar parameters might not be applicable to all individuals of the model. For example, Pimenoff (2005) concluded that the vertical CO_2 profiles measured in the atmosphere up to 1200 m with the Vaisala CARBOCAP® Carbon Dioxide Probe GMP343 (Vaisala Oyj, Vantaa, Finland) appeared to be incorrect due to unsatisfactory pressure correction. The same problem was observed during hot-air balloon flights (Laakso *et al*. 2008) in the spring of 2005. Since we were unable to find any published reports concerning experiments on pressure corrections despite an extensive literature search, we decided to investigate this problem in more detail.

Here, we studied the static pressure response of five different types of portable CO_2 infrared (IR) sensors (the environmental gas monitors EGM-2, EGM-3, EGM-4, ADC LCA-2 and the Vaisala CARBOCAP® Carbon Dioxide Probe GMP343, *see* Table 1 for details) in a pressure range from 1000 down to 750 hPa. Based on measurements, we determined new pressure correction functions for each sensor. To test the new corrections, we applied them to the boundary-layer CO_2 profile measurements from the hot-air balloon and compared the results with those in which the manufacturers' pressure correction equations were applied.

Material and methods

Experiments

We performed the pressure response experiments in a stainless-steel tank having a volume of approx. 1 m^3 (Fig. 1). The tank was covered with a 10-mm-thick acrylic plastic lid and the intersection between the tank and the lid was sealed with a normal window gasket. First, the sensors were held in the tank under ambient pressure for 2–3 min before the pressure began to decrease. We decreased the pressure by removing air from the tank with a pump. A typical rate of pressure change during the experiments was 12 hPa min^{-1} but different rates of pressure decrease were used (from 4 to 12 hPa min^{-1}). The lowest pressure was 750 hPa, corresponding to approximately an altitude of 2 km. To avoid the inhomogeneity of temperature and CO_2 concentration, the tank was equipped with a fan. Temperature, relative humidity (RH) and pressure were measured and logged with a Delta Ohm DO 9847 (Delta Ohm, Padova, Italy) using Pt100, Mk-33 and TP705 BARO sensors.

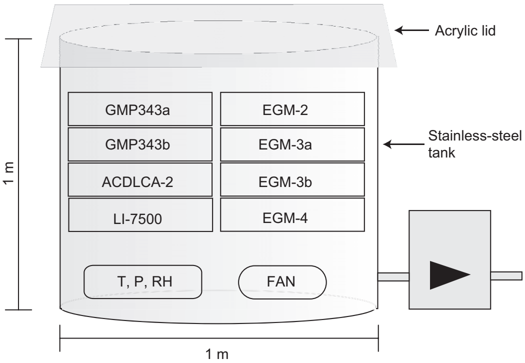

Fig. 1. Experimental setup.

The test was repeated 26 times at different ambient humidities, temperatures and CO_2 concentrations during 13–24 May 2005. In addition, we increased the CO_2 concentration to approx. 500 ppm three times by gently breathing into the tank before closing the lid. We used a Li-7500 (Li-Cor Inc., Lincoln, NE, USA) as an indicator of possible leakage of the tank. The readings of the LI-7500 were automatically corrected for pressure by the instrument. If the reading of the LI-7500 changed as a function of pressure, the test was omitted from our analysis. Altogether four repetitions were rejected.

To illustrate the effect of pressure, we applied the results on measurements of the EGM-4 and the two GMP343 analysers in a hot-air balloon. The analysers were placed approx. 1 m below the gondola base to avoid contamination from the burner of the balloon. During the flights, the maximum altitude was approx. 1600 m. Laakso *et al*. (2007) described the hot air balloon flights and sampling procedures in detail.

Analysers tested and their measurement principles

In this study, we used the CO_2 analysers listed in Table 1. All analysers were based on the attenuation of IR radiation by CO_2. The various EGM models and the ADC LCA-2 measure only one wavelength. First, the intensity of the IR radiation passing through the measurement chamber of the analyser is measured. The zero-level of CO_2 is provided by periodically removing all CO_2 from the measurement chamber. When the signals with and without CO_2 are compared, the attenuation due to CO_2 and thus the CO_2 concentration can be calculated.

In the GMP343 and LI-7500, two different wavelengths are measured. The GMP343 uses an electrically tuneable filter in front of an IR detector, while the LI-7500 has optical filters. One of the wavelengths is on the CO_2 absorption band and the other slightly to the side. Comparison of the attenuations at these two wavelengths provides the CO_2 concentration. The analysers also differ in sampling: the EGM models and the ADC LCA-2 pump air samples from the measured air into a closed measurement chamber (closed path), whereas the measurement chambers of the GMP343 and LI-7500 are open to the measured air (open path).

Background gases such as water vapour and oxygen affect IR radiation absorption by CO_2. The effect of water vapour is dependent on the absolute concentration of vapour molecules. Our tests were performed at such RH and temperatures levels that the absolute water-vapour molecule concentrations were relatively low. Thus water vapour had a minor effect on the measurements and can be ignored. The correction factors provided by the analyser manufacturers justified this assumption. We also checked this assumption by comparing the results obtained at different RH levels; only slight variation due to differences in RH was found.

Table 1. Different CO_2 analysers used in this study.

Sensor	Number of devices	Manufacturer
EGM-2	1	PP-systems, UK
EGM-3	2	PP-systems, UK
EGM-4	1	PP-systems, UK
GMP343*	2	Vaisala Oyj, Finland
ADC LCA-2	1	ADC Bioscientific Ltd., UK

* Vaisala CARBOCAP® Carbon Dioxide Probe GMP343.

Pressure corrections provided by the manufacturer

The measurement results of the CO_2 analysers are proportional to the absolute number of CO_2 molecules. The raw measurements must be corrected for the change in gas density with pressure and temperature and also for the pressure-broadening effects (Burch *et al*. 1962) on the IR absorption properties.

The outputs of the EGM-2 and EGM-3 are uncorrected raw data. The EGM-4 performs the pressure and temperature corrections automatically. We estimated the raw measurements of the EGM-4, using the correction functions backwards. This was done by dividing the reading by the correction factors for temperature and pressure.

The pressure correction factor, p_{cor}, for the EGM analysers is:

$$p_{\mathrm{cor}}(t) = a_0 + b_0 P(t) + c_0 P(t)^2 \tag{1}$$

where $P(t)$ is the current cell pressure in hPa. The pressure correction constants a, b and c include both the gas-broadening effects on the infrared absorption properties and the straightforward pressure dependence. The manufacturer (PP Systems) stated that $a_0 = 5.5815$, $b_0 = -7.481 \times 10^{-3}$ and $c_0 = 2.8960 \times 10^{-6}$. The GMP343 is based on a built-in temperature sensor, but the user should feed information on the other environmental characteristics such as pressure, water vapour and O_2 concentration. The RH values can be linked from another sensor (e.g. HMP75, Vaisala Oyj). The correction can also be done afterwards with confidential correction functions.

The output of the ADC LCA-2 are uncorrected raw data. The manufacturer suggests that the correction be made by dividing the reading for $CO_2(t)$, (ppm) by the difference between the pressure $P(t)$ (hPa) and water-vapour pressure that is calculated from the RH (RH(t),%) and saturation water-vapour pressure, e_{s}:

$$\mathrm{CO}_{2\,\mathrm{cor}}(t) = \frac{\mathrm{CO}_2(t)}{\frac{P(t)}{100} - e_{\mathrm{s}}(t)\frac{\mathrm{RH}(t)}{100}} \tag{2}$$

The manufacturer stated that saturation pressure e_s is 6.13753 × exp[T_a(18.564 − T_a/254.4)/(T_a + 255.57)]/1000 when the ambient temperature, T_a (°C), is above 0 °C.

Results

Manufacturer's corrections

The EGM-4 corrects the reading automatically with change in pressure. The outputs from the other models are uncorrected and, therefore, we corrected the data with the function provided by the manufacturer (Eq. 1). If the correction factors were satisfactory, the CO_2 concentration in Fig. 2A would be independent of pressure. However, we noted that the CO_2 concentration is approx. 40 ppm higher at low pressures than at ambient pressure.

A pressure-change experiment of the two identical GMP343 analysers is illustrated in Fig. 2C. During the measurements, only the temperature correction was on. The other corrections were off and we corrected the results later with the confidential MS Excel sheet provided by the manufacturer. There were individual differences in the readings because one sensor gave quite reasonable values after the manufacturer's corrections in the first set of experiments, while the other showed concentrations approx. 20 ppm lower at low air pressures than at ambient air pressure. Afterwards, there were signs that the correction constants may change over time, because when we repeated the measurements later the sensor that earlier successfully corrected the effect of pressure showed decreased readings at low pressures as did the other sensor previously. Nevertheless, the error caused by the pressure change was smaller in the GMP343 than in the various versions of the EGM.

A pressure-change experiment of the ADC LCA-2 analyser is illustrated in Fig. 2E. The output by the sensor is uncorrected and we corrected the data with the function provided by the manufacturer (Eq. 2). The readings decreased at low pressure.

The rate of pressure change (from 4 to 12 hPa min^{-1}) did not affect the results of any of the analysers.

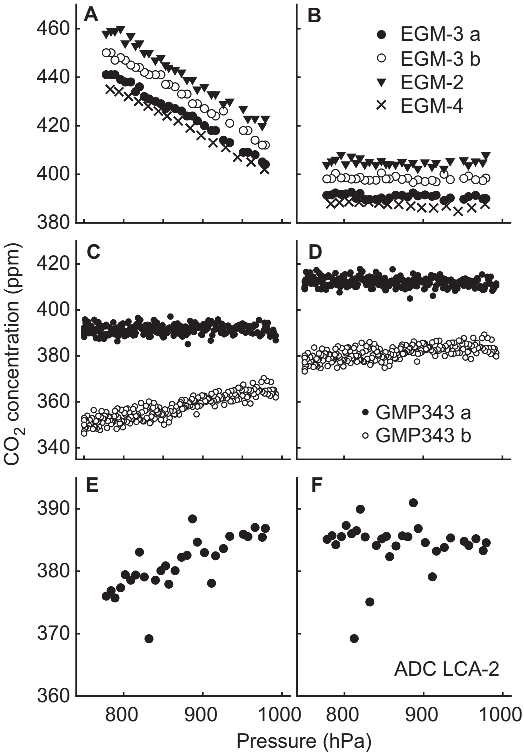

Fig. 2. Measured CO_2 concentration as a function of pressure. **A** and **B**: EGM-2, two EGM-3 and EGM-4. **C** and **D**: two identical GMP343. **E** and **F**: ADC LCA-2. In left-hand-side panels, the concentration is corrected with the pressure corrections of the manufacturers. In right-hand-side panels, the correction has been done with Eq. 3 and the independently defined device-specific parameters (Table 2).

New corrections

Since the correction functions provided by the manufacturers did not perform properly, we derived experimental correction curves that were able to reproduce the pressure response reasonably well. We noted that the effect of pressure is almost linear and therefore we corrected the reading with a second-order polynomial function:

$$C_c(t) = C_r(t)\left[a + b\left(\frac{P_0 - P(t)}{P_0}\right) + c\left(\frac{P_0 - P(t)}{P_0}\right)^2\right] \quad (3)$$

$C_c(t)$ is the corrected CO_2 concentration (ppm) at time t, $C_r(t)$ is the raw measurement of CO_2 concentration (ppm), $P(t)$ is the pressure inside the tank (hPa) and P_0 (hPa) is the pressure inside the tank at the beginning of each pressure-change test, i.e. ambient pressure. Since the CO_2 concentration was constant in the sealed tank during one experiment, we set parameter *a* to 1.0 and obtained the other constants *b* and *c* by regression (the least squares method), assuming that C_c is constant at any pressure. We set C_c to be the CO_2 concentration at the ambient pressure, i.e. the concentration at the beginning of the experiment. Here, we did not focus on the offset between the various analysers and between the absolute concentration in the air, since these can be easily corrected by calibrating the instrument, but instead focused only on the effect of pressure change.

Due to the form of our pressure correction, parameters *b* and *c* are tightly connected (r^2 = –0.77 to –1.00) (*see* Table 2). In addition, some of the instrument-specific parameters may also be partially associated with environmental factors but the scattering of the values cannot be explained by the temperature, RH or CO_2 concentration range of this study. However, parameter *b* of EGM-3 and EGM-2 models are negatively (r^2 = –0.62 to –0.36) and parameter *c* positively (r^2 = 0.39–0.62) correlated with the ambient pressure. Ambient CO_2 concentration did not affect the parameter values.

We had to determine two different sets of correction coefficients (A1 and A2) for the other GMP343 analyser, because the responses to the pressure were different in the two different sets of experiments (Table 2). In the two experiments, parameters *b* and *c* differed substantially but the parameters in the latter set of experiment (column A2) are relatively close to the parameter values of another GMP343 (column B). The two similar EGM-3 analysers gave identical responses and therefore we combined the results.

In Fig. 2B, the concentrations measured with the EGM models, that are introduced in Fig. 2A, are corrected with the new correction function (*see* Eq. 3). The used parameters are estimated independently using averages of all the other experiments (Table 2). The new correction (Fig. 2B) performed better than the original (Fig. 2A). Similarly, the new corrections for the two GMP343s (Fig. 2D) and the ADC LCA-2 (Fig. 2F) performed better in the same experiment than those of the manufacturers (Fig. 2C for GMP343, and Fig. 2E for ADC LCA-2). In general, the results remain the same if the parameters are defined using any of the experiments and validated using all the rest of the data. However, there is some unexplained scattering in the parameters (Table 2) that causes discrepancy in case of some repetitions.

To test the new functions over a wide pressure range, we applied them to the boundary-layer measurements of CO_2 profile at approx. 8:00 on 14 (Fig. 3, right-hand-side panels) and on 24 (Fig. 3, left-hand-side panels) April 2005. On 14 April, we used two individual GMP343 and one EGM-4 devices but only one GMP343 and one EGM-4 on 24 April. The concentration was corrected with the original functions provided by the manufacturers (Fig. 3, upper panels) and with the new functions introduced in this study (Fig. 3, lower panels). The original correction functions resulted in large differences in the profiles. The CO_2 concentrations measured by the EGM-4 and corrected automatically for pressure increased regularly between 300 m and 1600 m altitude while the GMP343 showed a relatively constant concentration at the respective altitudes. In another GMP343, the concentration appeared to decrease in the

Table 2. Number of experiments, means and standard deviations (σ_b and σ_b of the fitted device-specific parameters *b* and *c* (Eq. 3). The different values for GMP343 (A and B) are the results of two individual analysers. Columns A1 and A2 refer to two different sets of experiments of analyser A.

	EGM 4	EGM 3	EGM 2	GMP343 A1	GMP343 A2	GMP343 B	ADC LCA-2
Number of experiments	17	38	16	3	18	3	16
Mean *b*	1.30	1.20	1.17	1.04	1.18	1.37	1.11
σ_b	0.08	0.09	0.07	0.13	0.12	0.11	0.13
Mean *c*	1.97	2.27	2.30	2.19	2.11	1.72	1.79
σ_c	0.26	0.37	0.33	0.57	0.55	0.39	0.50

upper atmosphere (Fig. 3B). After correcting the concentrations with Eq. 3 and the device-specific parameters, we obtained rather stable concentration profiles throughout the altitude range.

Other equations for pressure correction were also used by other groups; e.g. Tang *et al.* (2003) continuously monitored soil CO_2 profiles with the GMT222 (Vaisala Oyj) and corrected the CO_2 reading, using

$$C_c(t) = C_r(t) - A C_r(t)\left[\frac{P(t)-P_0}{P_0}\right] \qquad (4)$$

where $A = 1.38$. However, the shape of the function is otherwise identical to that in Eq. 3, except that it does not have the second-order term. In general, researchers usually apply pressure corrections, using the software furnished with the CO_2 analysers.

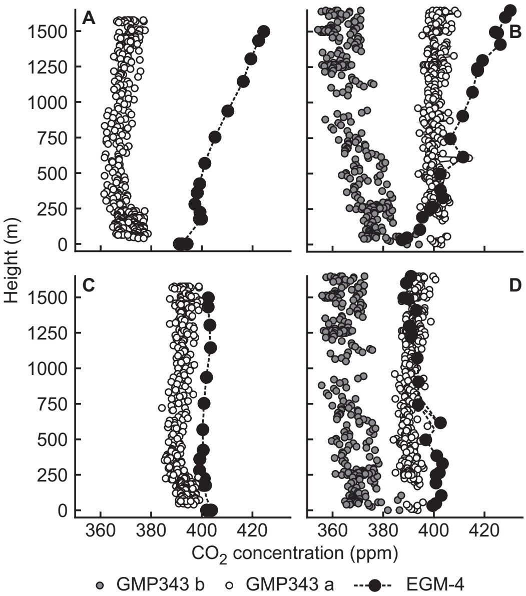

Fig. 3. Two measured CO_2 profiles obtained from hot-air balloon on (**A** and **C**) 24 and (**B** and **D**) 17 April 2005. In upper panels, measured values are pressure-corrected with original equations provided by the manufacturers. In lower panels, we corrected the values with Eq. 3 and the device-specific parameter values (Table 2).

Discussion and conclusions

To determine the effect of static pressure on the CO_2 concentration readings, we decreased the pressure by removing the air out from a tank that contained a homogenous air mass. We found that different CO_2 analysers were sensitive to changes in the pressure and performed systematically but individually. The changing pressure caused severe errors when the original manufacturers' corrections were used. Therefore, in research involving e.g. the vertical profiles of concentration, comparisons between different instruments over a period in which the ambient air pressure can significantly change, or chamber measurements at different altitudes, each single analyser needs to be tested individually for the changing conditions.

The pressure response of devices also creates problems if different days are compared. In Finland, atmospheric pressure varies typically between 960 and 1040 hPa, and the wrong pressure correction may lead to significant deviations from the true concentration. However, when these devices are used in chamber measurements, the incorrect pressure correction does not cause erroneous results because the pressure does not change substantially during one closure, which is usually only for a few minutes.

There seemed to be no systematic reason for the changes in values that occurred during analysis of the correction parameters, although temperature, CO_2 concentration and water vapour may also influence the effect of pressure in addition to their straightforward effects. In general, the analysers tested in this study were not designed to be used in a changing pressure environment and thus the repeatability of the measurement under changing conditions, without frequent calibrations, cannot be expected to be as favourable as the repeatability of devices designed to operate under changing conditions.

We carried out our measurements at RH between 33%–76%, and temperatures between 5–21 °C. Therefore our conclusions are not applicable to all tropospheric conditions but only to these ranges. In addition, we only tested pressures that were below the ambient pressure. Nevertheless, the new corrections performed better than the original ones in the pressure, CO_2 concentration, temperature and water vapour ranges of this study.

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