

## Vaisala CARBOCAP® Carbon Dioxide Probe GMP343:

# Equilibrium sampling in soil, snow and aquatic ecosystem measurements

**This application note describes the equilibrium sampling method to be used with the Vaisala CARBOCAP® Carbon Dioxide Probe GMP343 for measurements of CO<sub>2</sub> concentrations and fluxes in soil, snow or aquatic ecosystems. Some practical hints are provided for the different environments to ensure successful and trouble free measurements. This application note has been prepared in cooperation with Lammi Biological station and Department of Forest Ecology at University of Helsinki.**

## Introduction to methods for measuring CO<sub>2</sub> concentrations and CO<sub>2</sub> flux in soil, snow and aquatic environments

In terrestrial ecology, soil CO<sub>2</sub> efflux, usually measured with chamber techniques, plays an important role in the CO<sub>2</sub> exchange between the land surface and the atmosphere. Recently, the CO<sub>2</sub> concentration gradient method has become popular in studying the CO<sub>2</sub> transport within the soil and between the soil and the atmosphere [1, 2, 3]. The CO<sub>2</sub> produced in the soil is transported between the soil layers and from the soil to the atmosphere mainly by diffusion. The CO<sub>2</sub> efflux can be determined from the concentration gradients in the soil layers and between the soil and the atmosphere. This gradient method is especially suitable for studying the vertical distribution of CO<sub>2</sub> production in the soil and for studying the processes affecting the CO<sub>2</sub> efflux.

Continuous chamber measurements of soil CO<sub>2</sub> efflux are difficult to carry out in winter, because of the snow cover

spanning several months in the arctic and boreal regions. Calculating diffusion of CO<sub>2</sub> through the snow pack from CO<sub>2</sub> concentration gradient provides an alternative for chamber measurements of CO<sub>2</sub> flux in winter [4, 5]. The same principles apply in the snow and soil measurements, i.e. the diffusion properties determine the diffusion rate of CO<sub>2</sub> through the snow/soil.

In aquatic ecology, measurements of dissolved CO<sub>2</sub> (e.g.  $p\text{CO}_2$ ) have important applications in estimation of CO<sub>2</sub> transfer across water-atmosphere interface and in calculations of metabolic rates of aquatic communities. It is possible to calculate the amount of dissolved CO<sub>2</sub> in water from alkalinity, pH and dissolved inorganic carbon, see e.g. [6], but direct measurements of  $p\text{CO}_2$  are recommended to minimize possible analytical errors. The most common way to directly measure  $p\text{CO}_2$  is the headspace equilibration technique, where water sample is equilibrated with a headspace gas from which the CO<sub>2</sub> concentration is analyzed with infra red gas analyzer or with gas chromatography [7]. When water temperature is measured in connection with  $p\text{CO}_2$ , dissolved CO<sub>2</sub> can be calculated by applying Henry's law, see e.g. [6].

Aquatic systems can show quite large temporal variations in CO<sub>2</sub> concentrations. Periods of high primary production, i.e. high consumption of CO<sub>2</sub>, are short and laborious to track with the headspace technique. Conventional measurements of metabolic processes have been done by enclosing the aquatic community into a small bottle and incubating it for several hours before determining the change in gas concentration or amount of incorporated carbon [8]. Conditions in the enclosed bottle differ from those prevailing in nature, thus these methods are prone to give potentially erroneous results [8, 9]. Monitoring of metabolic gases *in situ* in free water gives a more reliable approach to estimate ecologically important processes such as primary production and community respiration.

Here a new system for continuous monitoring of CO<sub>2</sub> with a high temporal resolution is introduced. This new equilibrium sampling method is based on circulating air in a closed loop consisting of a CO<sub>2</sub> analyzer (the Vaisala CARBOCAP® Carbon Dioxide Probe GMP343 or the Module GMM221), a pump, gas impermeable tubing and a semipermeable tube, which allows gas exchange between the system and the material to be measured. The semipermeable tube is installed in water or in other

medium to be measured. The air inside the tubing is circulated by a pump and the gas concentrations inside the loop will reach equilibrium with the gas concentration outside the system. The response time in this diffusion driven system depends on characteristics of the gas permeable membrane and the ratio of equilibrating surface area to total volume of the loop.

## Instrument setup for equilibrium sampling

A typical measurement setup for equilibrium sampling includes several GMP343 probes (or GMM221 modules) to cover the whole vertical CO<sub>2</sub> gradient of interest in soil or water ecosystem. A measurement unit consists of a GMP343, a linear pump (SMG-4, 12VCD, Rietschle Thomas AB with 1.1 L min<sup>-1</sup> flow rate) and a stainless steel (RST jointless AISI 316L, 8 x 1.0 mm) and butyl rubber (Saint Germain IR 00022, 6 x 12 mm, VWR International) tubing for gas impermeable part of the loop (see Figure 1).

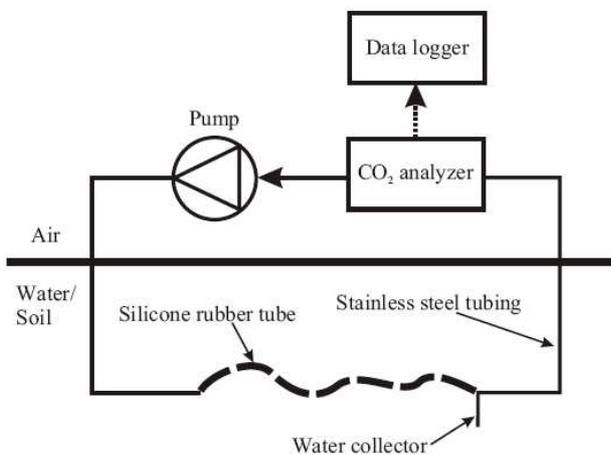


Figure 1. Schematic picture of the measurement setup.

The semipermeable part of the system consists of 6 x 1.5 mm silicone rubber tube (Rotilabo® Art:9572.1, Roth GmbH) with a stainless steel coil spring enclosed inside the tube (RST 0.5 x 5 x 1 000 mm) to prevent the silicone rubber tube from flattening due to outside pressure (see Figure 2). Gases, including water vapor, diffuse through the silicone rubber, thus it is recommended to add a dead-end stainless steel tube to collect water at the lower end of the upgoing stainless steel tube connected with T-joints (Svageelok, Helsinki Valve & Fitting Oy, Finland). Temperature probes (Philips KTY81-110, Philips

Semiconductors) are installed at each measuring depth. Here the analog output option is used with 0 - 5 V output signal and A/D converter (Nokeval Oyj, Finland) converts the analog signal to digital readings and logs it with a computer. The GMP343 probes and pumps were placed in a weather resistant installation box (see Figure 2).



Figure 2. Gas collector installation in the soil (on the left) and the installation box for the GMP343 probes (on the right).

## Determining the response time of gas collector for equilibrium sampling

Testing is needed to determine the response time of the silicone rubber tube in air or water. Tests in water can be performed by filling the silicon rubber loop with a span gas having a higher CO<sub>2</sub> concentration, e.g. 5 160 ppm. The surrounding water is bubbled to equilibrium with ambient air of CO<sub>2</sub> concentration around 400 ppm. Tests in the air can be conducted in a stainless steel tank with a constant CO<sub>2</sub> concentration. The loop, which is filled with a span gas having a higher CO<sub>2</sub> concentration (e.g. 4 500 ppm), is surrounded by roughly 400 ppm ambient CO<sub>2</sub> concentration. The CO<sub>2</sub> reading inside the tube is monitored as a function of time.

The effects of silicone rubber tube length and tube wall thickness on CO<sub>2</sub> diffusion are shown in Figure 2. By increasing the tube length and decreasing the tube wall thickness the response time can be slightly shortened. The rate of CO<sub>2</sub> concentration change follows the first-order exponential decay function; the corresponding half-times are presented in Table 1.

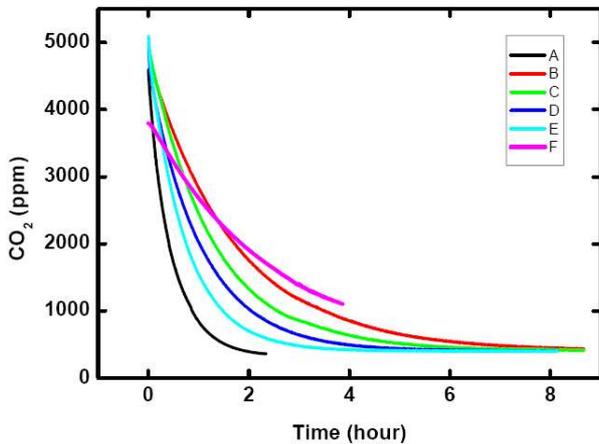


Figure 2: Response time curves with silicone rubber tubing and sintered PTFE chamber. See Table 1 for annotations.

Table 1. Half-times for tested gas collector materials. Letters A-F refer to legends in Figure 2.

Gas collector material		$t_{1/2}$ (hours)	
		Water	Air
Silicone rubber	1 meter 6/1.5 mm	1.18 (B)	1.67 (F)
	1 meter 5/1.0 mm	0.87 (C)	
	2 meter 6/1.5 mm	0.72 (D)	
	2 meter 5/1.0 mm	0.51 (E)	
Sintered PTFE		0.32 (A)	

A faster response time compared to the silicone rubber was obtained with a sintered PTFE chamber (length 123 mm,  $\varnothing$  32.5 mm, see Figure 3). Thus, the sintered PTFE is a promising material for gas collecting.

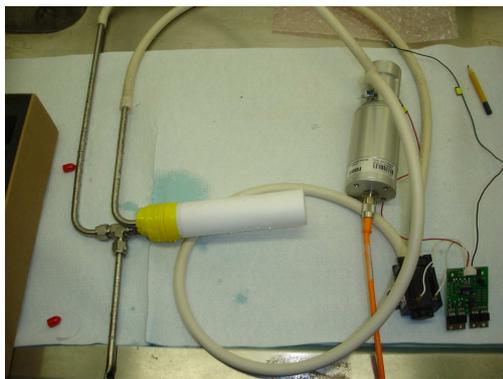


Figure 3. Test installation with a sintered PTFE chamber.

## Equilibrium sampling in soil and snow measurements

The equilibrium sampling method can be used to measure the CO<sub>2</sub> concentration in the soil profile. One installation

in a vertical face of soil pits at four depths (2, 7, 12, 22 cm) is described here. In addition to CO<sub>2</sub> concentration, soil temperature and water content data is needed to calculate the diffusivity in the soil.

The diffusivity of the soil and its correct determination play a crucial role in the CO<sub>2</sub> efflux values obtained with the gradient method. The diffusivity of CO<sub>2</sub> in the soil depends on total soil porosity, soil tortuosity, soil water content and transport distance. All these variables should be determined specifically for each soil layer to achieve accurate flux calculations. An alternative method for estimating soil diffusivity is to use a tracer gas such as radon. Tracer method, however, gives only the average diffusivity of the soil, thus continuous monitoring of soil water content together with the CO<sub>2</sub> concentration is recommended.

The CO<sub>2</sub> concentrations measured with the equilibrium sampling method in soil and snow show a clear seasonal pattern (Figure 4). The CO<sub>2</sub> concentrations increase with increasing soil depth. In addition, CO<sub>2</sub> concentration increase in every layer in early spring as snow thaws and soil water content increases. The interruptions in the measurements during thawing are caused by soil water entering the system.

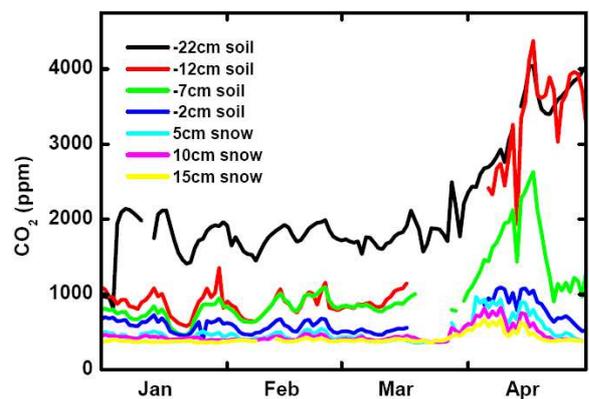


Figure 4. Daily average of CO<sub>2</sub> concentration in soil and snow during a period of January 2005-April 2006 using the equilibrium sampling method.

As a comparison to the equilibrium sampling method, GMP343 probes have been continuously used in soil CO<sub>2</sub> profile measurements for three years. The probes buried at 0, 5 and 17 cm depths give comparable results to the equilibrium sampling method between January and March

(Figures 4 and 5). Since April the equilibrium sampling method shows higher values, probably due to higher soil water content.

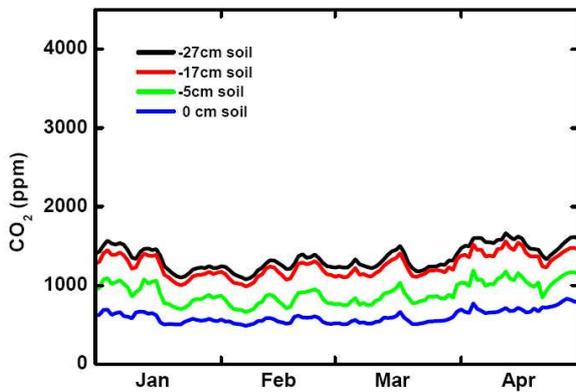


Figure 5. Daily average of CO<sub>2</sub> concentration in soil and snow during a period of January 2005-April 2006 measured with probes buried in the soil.

## Equilibrium sampling in aquatic ecosystems

In addition to soil and snow studies, equilibrium sampling can be used to study CO<sub>2</sub> profiles in aquatic ecosystems. GMP343 probes can be installed on a floating platform in an insulated water resistant box (see Figure 6). Gas collector tubings are installed in water at various depths (here 0.1, 0.5, 1.5, 2.0 and 3.0 m).

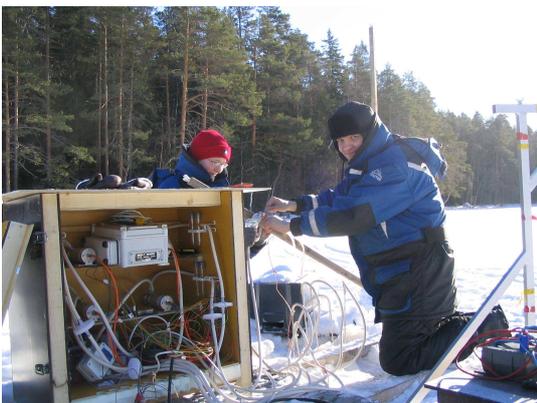


Figure 6. Installations on a floating platform.

CO<sub>2</sub> measurements can be performed through the whole open water period (Figure 7). Simultaneous measurements of water column photon flux density (PFD,  $\mu\text{mol m}^{-2}\text{s}^{-1}$ ) at 0.5 m depth are carried out to provide information on photosynthesis. Silicone rubber tubing of the gas collectors

in the lake are replaced once a month to control biofouling and its effects on the CO<sub>2</sub> concentration data. At the same time the water collectors are emptied.

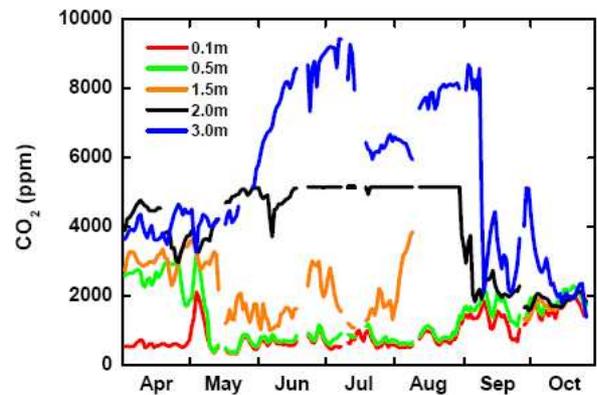


Figure 7. Daily average of pCO<sub>2</sub> at different water depths. GMP343 probes (measurement range 0...5 000 ppm) were used in all but the highest depth, where GMM221 module (measurement range 0...20 000 ppm) was used.

The developed measuring system has proved to be reliable. Despite some pump break-ups, continuous measurements of vertical CO<sub>2</sub> profiles in water over an open water period can be obtained using the method. The CO<sub>2</sub> concentrations show mostly a vertical gradient (Figure 7), where surface water is close to equilibrium with atmosphere and at 3 m depth high CO<sub>2</sub> concentration of almost 10 000 ppm exist. At 2 m depth the CO<sub>2</sub> concentration exceeded the measurement range of the GMP343 (0...5 000 ppm) during summer months. In October a complete mixing of water column from the surface to the bottom is seen, whereas springtime mixing looks incomplete (Figure 7).

The collected high time resolution data can be used to model the dependence of CO<sub>2</sub> consumption and production on environmental parameters and calculate the rates of community metabolism, i.e. primary production and community respiration [10]. The consumed or produced CO<sub>2</sub> in the euphotic layer over 30 minutes periods can be computed and a Platt-Jassby -type light-dependence curve can be fitted (so-called P-I curve) [11] to the exchange rate (Figure 8). This is a new method compared to the conventional measurements in laboratory or on ship's deck, which often result in fairly limited data sets.

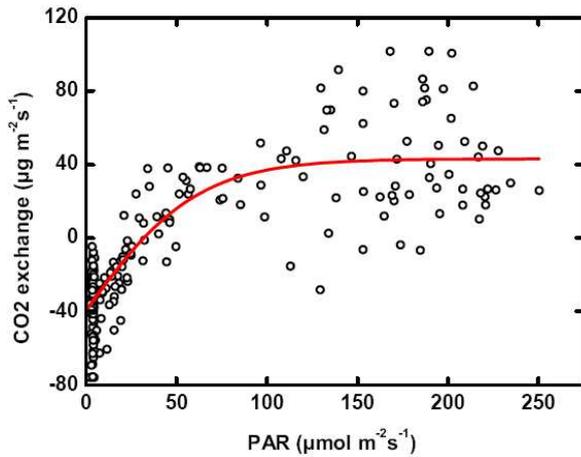


Figure 8. Example of photosynthesis vs. light (PAR,  $\mu\text{mol m}^{-2}\text{s}^{-1}$ ) response curve, fitted using the Platt & Jassby equation ( $r^2 = 0.73$ ) [11].

## Some practical hints for equilibrium sampling experiments

### Condensation of water vapor

Condensing water should be taken into consideration when designing an equilibrium sampling system. Air circulation in the gas collector should be secured by avoiding water blockage in the tubing. Suggested solutions are: 1) larger diameter in the tubes, 2) larger gas collector equipped with a water collector, which can be emptied from the soil surface or 3) chemical water absorbent in the system. It is good to keep in mind that if the system is in continuous use, the water absorbent needs frequent changing. In addition, a water condensing unit colder than the soil can be built, where water vapor can remain trapped instead of collecting into the gas collector.

In the GMP343 the heating option should be enabled to avoid water condensation on the optics.

### Pump reliability

The tested linear pumps (SMG-4, 12VCD, Rietschle Thomas AB) are designed for laboratory use.

The pump lifetime might be significantly reduced by operation in cold temperatures ( $< 5\text{ }^\circ\text{C}$ ), probably due to the plastic membranes of the pump breaking more easily at lower temperatures.

Pump lifetime depends also on the DC voltage applied in the system. When operating under the nominal voltage (12V), the rotation of the pumps is lowered and thus the lifetime of the pump extended.

### Power consumption

The described system operates using 12 V DC, so in principle it could be run with a battery. However, the power consumption is relatively high and thus in long-term use this option is more theoretical. The pumps operate with 6 W wattage and consume 320 mA current. The power consumption of GMP343 with heating option enabled is about 300 mA. Thus one measurement unit (consisting of one GMP343 and one SMG-4 pump) consumes at least 620 mA current, which in theory can be operated for less than 100 hours using an ordinary 12 V and 60 Ah car battery. In practice the operating time will be shorter, since the battery cannot be totally discharged. Thus the system should be operated with a mains current or with a solar panel supplying at least 620 mA current for each measurement unit.

### Aquatic measurement application

Experience from one year measuring period in lake environment showed the following:

1) Solid surfaces provide a growing site for aquatic sessile organisms, thus biofouling is often a major problem in long-term measurements within natural waters. Growth of periphytic algae can be prevented by covering the gas collector with light impermeable material, but this does not stop bacterial growth on the surfaces. However, toxic antifouling chemicals are not recommended. To avoid the harmful effect of biofouling on gas exchange the gas collector must be cleaned or replaced periodically.

2) Measurements with the described setup are restricted to surface waters of aquatic systems. Handling of long tubings is inconvenient, tricky and somewhat risky. In deepwater measurements the whole instrumentation should be enclosed in a water proof casing, which can be lowered to the measuring depth.

3) During times of low productivity the measuring system did not show adequate sensitivity due to slow response times. The problem can be overcome by improving the

response time by e.g. the sintered PTFE material. A remarkably good response time has been achieved by a gas collector, by dividing the circulating air into a hundred small silicone rubber tubes [12, 13]. However, making such a gas collector system water tight can be troublesome and its maintenance can be difficult. Thus, keeping the gas collector system simple and improving the response time by optimizing the material is recommended.

## Performance of the GMP343 in equilibrium sampling systems

The accuracy and precision of the GMP343 transmitters is adequate for soil profile CO<sub>2</sub> measurements, especially when the readings are averaged to 1 min. The GMP343 is resistant to moisture and corrosion. Probes have been installed in the forest soil at 0 cm, 5 cm, 17 cm and 27 cm depths since June 2004, where the soil is quite low in pH (pH values 3.5-4 in the surface and 4-5 in deeper layers). The soil had volumetric water content between 20-30% during most of the year and between 30-40% in the autumn and during snow thaw. Despite of these relatively harsh conditions, the probes have been working without problems all year round. The buried transmitters were equipped with a sintered PTFE filter cap and a modified calibration adapter. The heating option of the GMP343s was enabled to avoid water condensation on probe optics.

The heating option in the GMP343 should be used with caution if they are buried in the soil. The slight heating may affect the soil temperature around the probes. For example, snow melted earlier around the probes probably due to the heating. This "early spring" may change the conditions in the soil around the probes. However, the heating effect is not very significant deeper in the soil, where the heat is dissipated. This naturally depends on the heat conductivity of the soil. It is good to monitor the soil temperature near the probes (about 1 cm distance) and at further distance at the same depth to recognize the possible heating effect.

The measurement range of 0...5000 ppm may be too narrow for soil CO<sub>2</sub> profile measurements during the growing season. Here the CO<sub>2</sub> concentration was measured only at about 20-30 cm depth, but concentrations deeper in the soil can easily reach 20 000 ppm, thus probe measurement range should be selected according to the highest possible concentration.

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