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Technical note: A closed chamber method to measure greenhouse gas fluxes from dry sediments

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Abstract. Greenhouse gas emissions from dry aquatic sediments are probably globally relevant. However, they are difficult to measure because of the often rocky substrate and the dynamic nature of the habitat. Here we tested the performance of different materials to seal a closed chamber to stony ground both in laboratory and field experiments. Using on-site material consistently resulted in elevated fluxes. The artefact was caused both by outgassing of the material and production of gas. The magnitude of the artefact was site dependent – the measured CO_2 flux was increased between 10 and 208%. Errors due to incomplete sealing proved to be more severe than errors due to non-inert sealing material.

Pottery clay as sealing material provided a tight sealing of the chamber to the ground and no production of gases was detected. With this approach it is possible to get reliable gas fluxes from hard-substrate sites without using a permanent collar. Our test experiments confirmed that CO_2 fluxes from dry aquatic sediments are similar to CO_2 fluxes from "normal" soils.

Introduction

CO_2 emissions from dry freshwater systems represent a largely overlooked process in the global carbon cycle. Recent research indicates that drying and rewetting of freshwater sediments creates hot spots of carbon mineralization and thus CO_2 emissions, which are probably relevant on a global scale (Gomez-Gener et al., 2015; Reverey et al., 2016; Von Schiller et al., 2014). However, existing knowledge is scarce and mainly based on regional studies from e.g. the U.S.A. (Gallo et al., 2014) or Spain (Gómez-Gener et al., 2016).

One reason for the shortage of available data is probably the lack of a reliable method to measure sediment-atmosphere gas fluxes in these habitats. The closed chamber approach is the most wide spread method to measure gas fluxes from terrestrial habitats on a small scale (Matson and Harriss, 1995). The method has been extensively tested (Christiansen et al., 2011; Pumpanen et al., 2004) and is generally accepted to give good results. However, standard closed chamber protocols cannot be used in most dry aquatic systems because sealing the chamber to the ground is difficult. In soil science, the chamber is often pushed into the soil to seal it towards the atmosphere. If that is not easily possible or if repeated measurements at the same spot are planned, a permanent collar is installed. Dry sediments in streams or at the shore of lentic waterbodies at low water level are often rocky and pushing the chamber into the ground is not possible. Installation of a permanent collar is also

problematic, because of the dynamic nature of the habitat. Under flooded conditions, a collar will affect hydrodynamics and might change sedimentation patterns. In streams, turbulence created by a permanent installation might erode the sediment.

There are different options for sealing a chamber to the ground. The use of flexible rubber gaskets is not possible, because especially streambeds are often stony. A foil as has been tested for a "flying" floating chamber (Lorke et al., 2015) is also difficult in the presence of larger stones. The most promising option is the use of a ductile material. In the past, sediment material collected from the site has been used to seal the chamber (Gomez-Gener et al., 2015). However, such procedure might produce artefacts, because the sealing material is not inert and might produce especially CO_2. Thus, there is currently no reliable method available to measure greenhouse gas (GHG) fluxes from dry sediments.

In this study we conducted laboratory tests with different sealing materials to check for tightness and inertness. We then applied the most promising material in a field trial. As a result we give recommendations how to perform GHG flux measurements in dry aquatic sediments.

Materials and methods

1.1 sealing materials

We tested both commercial sealing materials (pottery clay and a silicon material) as well as different natural materials from a streambed (sand, mud) (Table 1). The natural material was collected by a shovel not reaching below a depth of approximately 5 cm and stored in polypropylene boxes until use. If not directly used for on-site measurements, it was stored under laboratory conditions and used within 3 days. To test the effect of a biologically very active material, a part of the sand was amended with glucose to stimulate CO_2 production.

1.3 test for inertness

To test, whether a material produced or consumed CO_2 or CH_4 we put 20-30 g (depending on density of material) of each material into a 1000 ml glass with a twist off lid. If possible the material was portioned into ten beads of about 1.5 cm diameter. The gas analyzer was connected with PTFE tubing to two Swagelock® connectors which were installed in the lid. The gas in the glass was then circulated through the gas analyzer and back into the glass and changes of gas mixing ratios were monitored for seven minutes. From the linear increase of the mixing ratio in the last five minutes of incubation, gas production rates were calculated. The detection limit of this test was 2.49 mmol kg^{-1} d^{-1}. We performed three replicates. Tests were performed between 24 and 28°C. After each measurement at ambient conditions we lowered the CO_2 concentration in the glass to about 140 ppmv by flushing with argon to look for eventual outgassing of the material and then measured potential CO_2 increase as described before for ambient conditions.

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1.2 test for tightness

To test the effectiveness of different materials in sealing the chamber, we used a laboratory setup. A custom made closed chamber made from opaque PVC tube, inner diameter 16 cm, height 8.06 cm with 2 Swagelock® connectors was placed on a paving slab made of exposed aggregate concrete (Figure S1). The rough surface created by the pebbles in the concrete resulted in gaps of variable shape and diameter between stone and chamber. The particular sealing material was placed around the chamber and pressed to seal the gaps. The chamber was connected to the gas analyser and the whole system flushed with Ar to lower the CO_2 mixing ratio to near zero. Then the Ar supply was stopped and the gas inside the chamber was circulated through the gas analyser and back. The mixing ratio of CO_2 was recorded for up to 17 h.

1.4 field test

In order to confirm the main findings from the laboratory experiments and to test application of the sealing materials under realistic conditions, field tests at three different locations were made. Tests were carried out on sandy and muddy sediments at the Elbe river and in the drawdown area of Rappbode Reservoir, a drinking water reservoir in the Harz mountains (Rinke et al., 2013). The same setup as used in the laboratory test was brought to the field (Figure S2). The chamber was placed on the ground and sealed using either clay or material from the site (Figure S3). A little water was added to the clay to make it more ductile. At Rappbode Reservoir we also applied a commercially available soil respiration chamber in combination with an IR-analyzer (SRC+EGM4, PP-Systems, Amesbury, U.S.). It was also sealed with clay for the measurements. Temperatures during field tests were between 25-27 °C at bridgesoil site, 16-19 °C at river sand site, and 27-31 °C at Rappbode reservoir respectively. Three replicate measurements were done at exactly the same site.

1.5 analysis

We measured the CO_2 concentration in 30 s intervals with a Fourier-Transform-Infrared (FTIR) Spectrometer (GASMET DX4000, Temet Instruments, Finland) after passing the gas stream through an in-line moisture trap (Drierite, USA) at a rate of 2.9 L min^{-1}. The standard deviation of the CO_2 analysis at ambient concentrations was 3 ppmv. Thus the detection limit for CO_2 change rates in our 5 minute laboratory incubations was 864 ppm d^{-1}.

For the field tests we calculated the flux of CO_2 [mmol m^{-2} d^{-1}] from the linear rate of change of CO_2 inside the chamber:

$$J = \frac{dp_i}{dt} * F * h_{eff} * 10^{-3} \quad (1)$$

with $\frac{dp_i}{dt}$ as the change of the mixing ratio with time [ppm d^{-1}], F [mol m^{-3}] is a unit conversion factor (formula 2), and h_{eff} as the effective height of the chamber headspace (formula 3). F in mol m^{-3} results from

$$F = \frac{10^5\ bar}{R * T} \quad (2)$$

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with R the ideal gas constant 8.314 J K^{-1} mol^{-1} and T the air temperature [K]. The effective height of the chamber h_{eff} = 0.12 m was calculated from the inner volume of chamber plus FTIR analyser:

$$h_{eff} = \frac{V_{chamber} + V_{GASMET}}{A} \quad (3)$$

with $V_{chamber}$ is the inner volume of the chamber, V_{GASMET} the inner volume of the analyser, and A = inner surface area of the chamber. The lowest detectable CO_2 flux in a 5-minute measurement was 4.05 mmol m^{-2} d^{-1}.

Together with the CO_2 data the FTIR analyser delivered CH_4 and N_2O mixing ratios. Thus, during the field tests we also looked for the effect of the sealing material on the fluxes of CH_4 and N_2O.

Results and discussion

Our measurements with the closed chamber on the concrete plate in the laboratory tests showed that the choice of the sealing material affected the outcome of the measurements. All sealing materials produced an initial increase of the CO_2 mixing ratio in the chamber if measurements started at low CO_2 (Figure 1). However, only in the chambers sealed with clay or the silicon material the mixing ratio became constant at a level well below ambient, which shows that these materials on the long run did not produce CO_2 and provided a tight sealing. All the on-site materials resulted in continuously rising CO_2 concentrations well above the ambient mixing ratio of about 400 ppmv. This clearly shows that the on-site materials produced CO_2 and that this potentially affected the CO_2 concentration in the chamber.

Incubation of sealing material in closed incubation vessels confirmed that indeed the on-site material produced CO_2 with variable rate while CO_2 production by clay or putty was at or below the detection limit (Table 2). But if clay and putty were not producing CO_2 – what was then causing the initial rise in CO_2 in the clay and putty sealed chamber? Our chamber tests on the concrete plates showed that there was an initial increase of CO_2 in clay or putty sealed chambers only at artificially lowered mixing ratio (Table 2). If measurements were performed at ambient CO_2, CO_2 in the clay and putty sealed chambers stood constant, while it was increasing in the chambers sealed with the on-site materials. Outgassing of the material was also observed when incubating the sealing material in closed vials at artificially lowered pCO_2. We conclude that the initial rise in CO_2 with clay and putty was caused by out-gassing of the material rather than by production of CO_2.

Field tests showed consistently higher CO_2 fluxes if the on-site material was used compared to clay (Figure 2). The deviation was different between sites from a small but still significant ($p = 0.04$) difference of 10 % to up to 208 % at the sandy river site. Thus, using on site material to seal chambers produces a site depending over-estimation of the CO_2 flux. Compared to the artefact by non-inert sealing material, the effect of incomplete sealing was even worse. Leakage of the chamber resulted in non-linear concentration changes during measurements and very low CO_2 fluxes (Figure 3).

We never observed a significant flux of CH_4 during our field tests, confirming earlier results which showed very low fluxes of CH_4 from dry sediments (Gomez-Gener et al., 2015). However, if the chamber was sealed with the on-site material a

small CH_4 flux of up to 4.1 mmol m^{-2} d^{-1} was detected at the reservoir site. This shows that when analysing CH_4 fluxes, care must be taken not to use methanogenic material to seal the chamber.

We also observed small fluxes of N_2O. At the bridgesoil site, the flux of 0.12 ± 0.02 mmol m^{-2} d^{-1} was the same with clay and on site material. In contrary, at the reservoir site using clay, the N_2O flux was below the detection limit while a flux of 0.09 ± 0.04 mmol m^{-2} d^{-1} was measured when the on-site material was used. Thus, similar to CH_4, using sealing material from an anoxic zone might create an artificial N_2O flux.

Sealing the chamber in the field with clay proved to be convenient. For ensuring good sealing performances using clay, wetting the sealing material directly prior to use proved to be useful to increase mouldability and to enhance adhesion to the ground and to the chamber. Forming sausages of clay that could be placed quickly around the chamber lead to a quick and easy sealing procedure taking 1-2 min depending on practise and nature of the surroundings (Figure S3). The clay can be reused after each measurement. However, care must be taken to remove adhering soil particles. Tests had shown that using dirty clay has the potential to produce artefacts (data not shown).

The fluxes between 75 and 241 mmol m^{-2} d^{-1} are very similar to results obtained in Spain (209 ± 10 mmol m^{-2} d^{-1}, (Gomez-Gener et al., 2015) and in Arizona (44 mmol m^{-2} d^{-1}, (Gallo et al., 2014)). Our measurements in two contrasting temperate habitats confirm that dry sediments emit similar amounts of CO_2 as soils (Raich and Schlesinger, 1992).

Conclusions

When measuring with closed chambers on rocky ground the most important concern is to get a proper sealing between chamber and atmosphere. Indicators for leakage are non-linear concentration changes in the chamber and extraordinary low fluxes. We strongly recommend the use of an inert sealing material. Pottery clay proved to be both convenient and effective. We do not completely exclude the use of on-site material, but checks are necessary if the particular material does produce artefacts. Carried out carefully, closed chamber measurements of greenhouse gas fluxes at stony sites and dry sediments are possible.

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Tables

Table 1: Substances tested as sealing materials.

substance	description
Clay	Potter's clay
River sand	Sand collected from the shores of the river Elbe (coordinates: 52° 7.92' N, 11° 39.42' O), sieved (2 mm) and homogenized before use.
Putty	"Silly Putty", dilatant compound by DOW CORNING® based on silicon polymers.
River sand + glucose	Sand collected from the shores of the river Elbe, spiked with a high concentration glucose solution (100 g L^{-1}), incubated for 2 days = positive control for biological activity.
River mud	Mud collected from the shores of the river Elbe (coordinates: 52° 7.62' N, 11° 39.04' O)
Bridgesoil	Fine particulate soil collected from fluvial deposits of the river Elbe (coordinates: 52° 7.62' N, 11° 39.04' O)

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Table 2: Performance of different sealing materials in lab experiments (mean±SD). number in brackets indicates number of replicates below the detection limit (DL); n=3 except for River mud (n = 4) and River sand + glucose (n = 6). Chamber = chamber on paving slab. CO_2 production = sealing material in glas vessel.

	Chamber test [mmol m^{-2} d^{-1}]	Chamber low CO_2 [mmol m^{-2} d^{-1}]	CO_2 production [mmol kg^{-1} d^{-1}]
Clay	< DL	29 ± 1	2.5 ± 0.7 (1)
Putty	< DL	27 ± 5	< DL
River mud	5.94	20 ± 11	15.3 ± 3.2
River sand	10.80	42 ± 29	2.9 ± 3.7
River sand + glucose	55.38	104 ± 50	31.7 ± 2.4
Bridgesoil	5.94	22 ± 8	8.4 ± 1.6

Figures

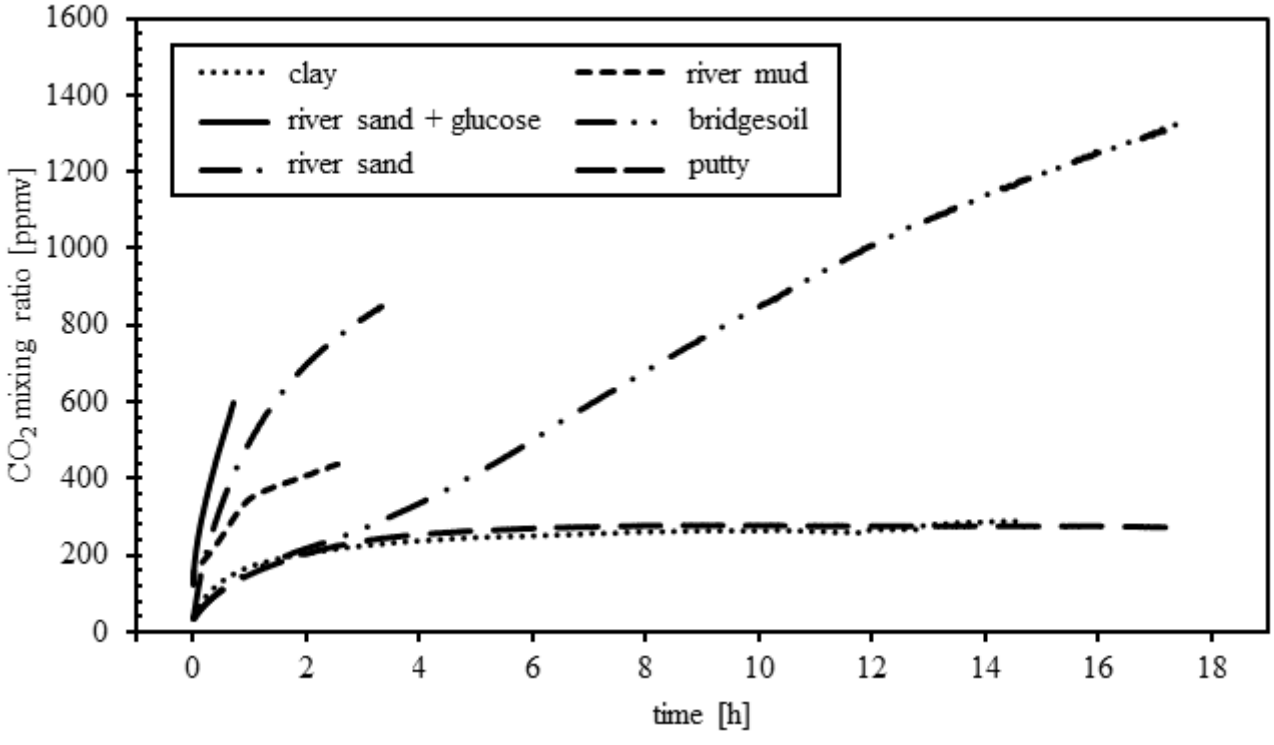

Figure 1: CO_2 concentration during long-term laboratory chamber experiments with different sealing materials.

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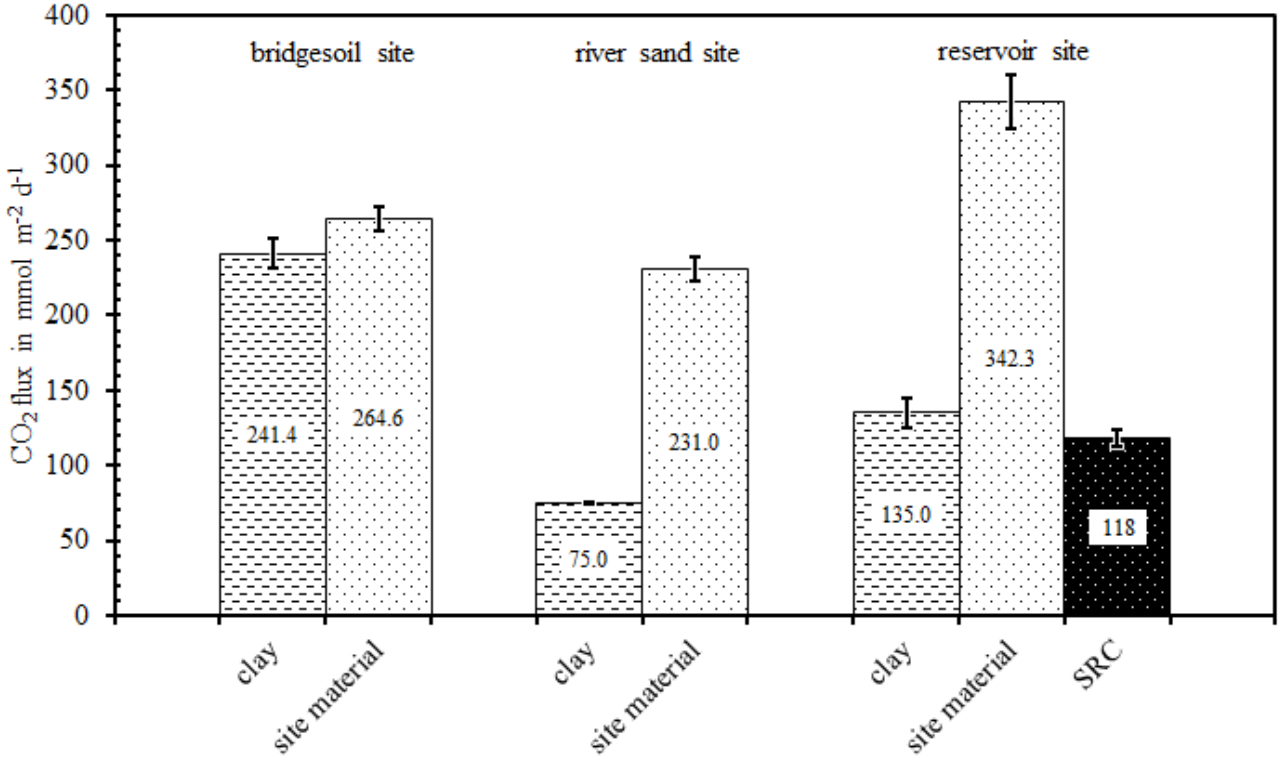

Figure 2: Mean CO_2 fluxes detected in the different sample groups during field experiments (mean ± SD, n = 3; reservoir site n = 4). SRC = soil respiration chamber + IR analyser, sealed with clay.

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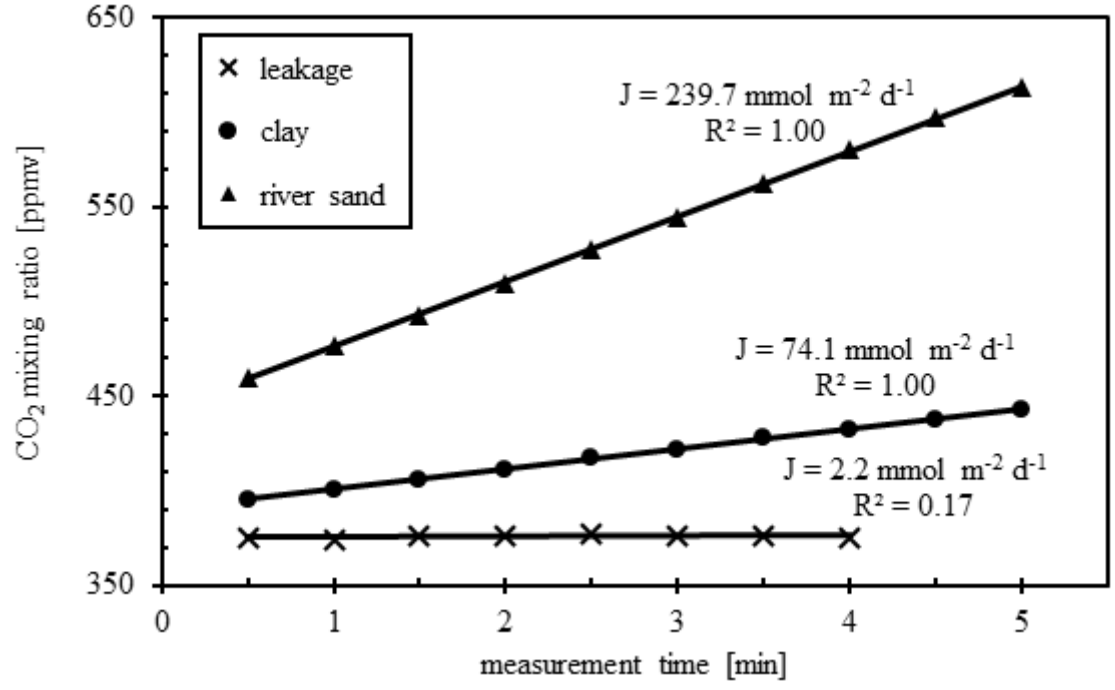

Figure 3: Example showing typical progression of CO_2 concentration during field measurements with clay and ambient material (example: river sand site).