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

10   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 terrestrial

15   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.,

20   2014). However, existing knowledge is scarce and mainly based on regional studies from e.g. the U.S.A. (Gallo et al., 2014), Spain (Gómez-Gener et al., 2016), the UK (Gilbert et al., 2016), or Italy (Bolpagni et al., 2017).

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 widespread method to measure gas fluxes from terrestrial habitats on a small scale (Livingston and Hutchinson, 1995). The method has been extensively tested (Christiansen et al.,

25   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. Even small leaks can significantly affect flux measurements (Hoffmann et al., 2017; Hutchinson and Livingston, 2001). 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. Pushing the chamber into the soil also minimizes

lateral diffusion through the soil under the chamber (Hutchinson et al., 2000). This approach has been successfully used to quantify GHG fluxes from muddy dry aquatic sediments (Jin et al., 2016; Koschorreck, 2000). However, 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 (Gilbert et al., 2016) is often not possible, because especially streambeds are often stony. Using a weighted foil (Steudler and Peterson, 1985) 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 stony 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 on 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 (Töpfereibedarf Dorothea Weber, Magdeburg, Germany) and a silicon material (Silly Putty, Dow Corning, Midland, Michigan, United States) 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.

1.2 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 for 25 g of material was 2.24, 0.07, and 0.02 mmol kg^{-1} d^{-1} for CO^2, CH_4, and N_2O respectively. We performed three replicate measurements. 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.

1.3 test for tightness

5   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

10   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. We performed 3 repetitive short term (12 min) measurements. After the third measurement we kept the chamber in place and continued recording the mixing ratio of CO_2 and CH_4 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

15   realistic conditions, field tests at three different locations were made. Tests were carried out on stony 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). We wetted our fingers before handling the clay to increase its plasticity. At Rappbode Reservoir we also applied a commercially available soil respiration chamber in

20   combination with an IR-analyzer (SRC+EGM4, PP-Systems, Amesbury, U.S.). Air 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

25   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:

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

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

$$F = \frac{10^5 \; bar}{R * T} \tag{2}$$

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:

$$h_{eff} = \frac{V_{chamber} + V_{GASMET}}{A} \tag{3}$$

5 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}, for CH$_4$ and N$_2$O the detection limit was 0.14 mmol m^{-2} d^{-1}

Together with the CO$_2$ data the FTIR analyser delivered CH$_4$ and N$_2$O mixing ratios. Thus, we also looked for the effect of the sealing material on the fluxes of CH$_4$ and N$_2$O.

10 Differences between treatments were checked by a t-test after checking for normality (Shapiro-Wilk) and homogeneity of variance (Bartlett) using the software R (R-Core-Team, 2016).

Results and discussion

The ability of different sealing materials to provide a tight sealing was tested with the closed chamber on a concrete plate in the laboratory. These tests showed that the choice of the sealing material affected the outcome of the measurements. All

15 sealing materials produced an initial increase of the CO$_2$ mixing ratio in the chamber if measurements started at low CO$_2$ (Figure 1a). 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 provided a tight sealing. Furthermore these results show that both materials did not produce CO$_2$ (Table 1). 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

20 this potentially affected the CO$_2$ concentration in the chamber. Similar to CO$_2$ also CH$_4$ initially increased in all experiments (Figure 1b). For clay the mixing ratio levelled off at about 1 ppm, well below the atmospheric concentration. This confirms that clay provided a tight sealing also for less water soluble gasses and shows that clay did not produce CH$_4$. With the other sealing materials CH$_4$ did not reach the atmospheric concentration during the experiment except with river mud which clearly produced CH$_4$.

25 The inertness of the material was further tested by incubating sealing material in closed incubation vessels. These experiments 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. We did not detect a significant production of CH_4 in our inertness experiments (data not shown). However, our FTIR analyser showed some outgassing of ammonia from the putty material (data not shown). Therefore, but also because it is cheaper and environment friendly, we performed our field tests only with clay.

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 % at the bridge soil site 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. The results obtained with clay at the reservoir site were similar to the measurements with a tested (Pumpanen et al., 2004) soil respiration chamber, showing the reliability of our measurement setup. 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.

Not inserting the chamber into the sediment might enable lateral diffusion beneath the chamber walls. This may affect flux measurements especially at sites with porous sediments. Potential artefacts can be minimized by keeping the measuring time as short as possible – a few minutes only (Hutchinson and Livingston, 2001). Lateral diffusion is not a problem in waterlogged or compact sediments.

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. It is well known that wetting of dry soils triggers CO_2 production (Birch, 1958). In our experiment, the clay was slightly wetted but the data do not show any CO_2 production (Figure 1). Thus, wetting the clay to increase its plasticity was not a problem. 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). To prevent concentration changes in the chamber during the sealing process, we recommend the use of a chamber with

removable lid. Such a chamber could be sealed to the ground while open to the atmosphere. 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.

References

Birch, H. F.: The effect of soil drying on humus decomposition and nitrogen availability, Plant Soil, 10, 9-31, 1958.
Bolpagni, R., Folegot, S., Laini, A., and Bartoli, M.: Role of ephemeral vegetation of emerging river bottoms in modulating CO_2 exchanges across a temperate large lowland river stretch, Aquat. Sci., 79, 149-158, 2017.
Christiansen, J. R., Korhonen, J. F. J., Juszczak, R., Giebels, M., and Pihlatie, M.: Assessing the effects of chamber placement, manual sampling and headspace mixing on CH4 fluxes in a laboratory experiment, Plant Soil, 343, 171-185, 2011.
Gallo, E. L., Lohse, K. A., Ferlin, C. M., Meixner, T., and Brooks, P. D.: Physical and biological controls on trace gas fluxes in semi-arid urban ephemeral waterways, Biogeochemistry, 121, 189-207, 2014.
Gilbert, P. J., Cooke, D. A., Deary, M., Taylor, S., and Jeffries, M. J.: Quantifying rapid spatial and temporal variations of CO_2 fluxes from small, lowland freshwater ponds, Hydrobiol., doi: 10.1007/s10750-016-2855-y, 2016. 1-11, 2016.
Gómez-Gener, L., Obrador, B., Marcé, R., Acuña, V., Catalán, N., Casas-Ruiz, J. P., Sabater, S., Muñoz, I., and Schiller, D.: When Water Vanishes: Magnitude and Regulation of Carbon Dioxide Emissions from Dry Temporary Streams, Ecosystems, doi: 10.1007/s10021-016-9963-4, 2016. 1-14, 2016.
Gomez-Gener, L., Obrador, B., von Schiller, D., Marce, R., Casas-Ruiz, J. P., Proia, L., Acuna, V., Catalan, N., Munoz, I., and Koschorreck, M.: Hot spots for carbon emissions from Mediterranean fluvial networks during summer drought, Biogeochemistry, 125, 409-426, 2015.
Hoffmann, M., Pehle, N., Huth, V., Jurisch, N., Sommer, M., and Augustin, J.: A simple method to assess the impact of sealing, headspace mixing and pressure vent on airtightness of manual closed chambers, J. Plant Nutr. Soil Sci., doi: 10.1002/jpln.201600299, 2017. n/a-n/a, 2017.
Hutchinson, G. L. and Livingston, G. P.: Vents and seals in non-steady-state chambers used for measuring gas exchange between soil and the atmosphere, Eur. J. Soil Sci., 52, 675-682, 2001.
Hutchinson, G. L., Livingston, G. P., Healy, R. W., and Striegl, R. G.: Chamber measurement of surface-atmosphere trace gas exchange: Numerical evaluation of dependence on soil, interfacial layer, and source/sink properties, Journal of Geophysical Research: Atmospheres, 105, 8865-8875, 2000.

Jin, H., Yoon, T. K., Lee, S. H., Kang, H., Im, J., and Park, J. H.: Enhanced greenhouse gas emission from exposed sediments along a hydroelectric reservoir during an extreme drought event, Environ Res Lett, 11, 124003, 2016.

Koschorreck, M.: Methane turnover in exposed sediments of an Amazon floodplain lake, Biogeochemistry, 50, 195-206, 2000.

5 Livingston, G. P. and Hutchinson, G. L.: Enclosure-based measurement of trace gas exchange: applications and sources of error. In: Biogenic Trace Gases: Measuring Emissions from Soil and Water, Matson, P. A. and Harriss, R. C. (Eds.), Methods in Ecology, Blackwell, Oxford, 1995.

Pumpanen, J., Kolari, P., Ilvesniemi, H., Minkkinen, K., Vesala, T., Niinisto, S., Lohila, A., Larmola, T., Morero, M., Pihlatie, M., Janssens, I., Yuste, J. C., Grunzweig, J. M., Reth, S., Subke, J. A., Savage, K., Kutsch, W., Ostreng, G., Ziegler,
10 W., Anthoni, P., Lindroth, A., and Hari, P.: Comparison of different chamber techniques for measuring soil CO_2 efflux, Agr Forest Meteorol, 123, 159-176, 2004.

R-Core-Team: R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria, 2016.

Raich, J. W. and Schlesinger, W. H.: The global carbon dioxide flux in soil respiration and its relationship to vegetatiom and
15 climate, Tellus, 44, 81-99, 1992.

Reverey, F., Grossart, H.-P., Premke, K., and Lischeid, G.: Carbon and nutrient cycling in kettle hole sediments depending on hydrological dynamics: a review, Hydrobiol., 775, 1-20, 2016.

Rinke, K., Kuehn, B., Bocaniov, S., Wendt-Potthoff, K., Büttner, O., Tittel, J., Schultze, M., Herzsprung, P., Rönicke, H., Rink, K., Rinke, K., Dietze, M., Matthes, M., Paul, L., and Friese, K.: Reservoirs as sentinels of catchments: the Rappbode
20 Reservoir Observatory (Harz Mountains, Germany), Environmental Earth Sciences, 69, 523-536, 2013.

Steudler, P. A. and Peterson, B. J.: Annual Cycle of Gaseous Sulfur Emissions from a New-England Spartina-Alterniflora Marsh, Atmos. Environ., 19, 1411-1416, 1985.

Von Schiller, D., Marcé, R., Obrador, B., Gómez, L., Casas, J. P., Acuña, V., and Koschorreck, M.: Carbon dioxide emissions from dry watercourses, Inland Waters, 4, 377-382, 2014.

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)

5 **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 test: chamber on paving slab, final flux in long term experiment (Figure 1). Chamber low CO$_2$: chamber on paving slab gassed with N$_2$ prior to measurement. CO$_2$ production: sealing material in glass 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

(a)

(b)
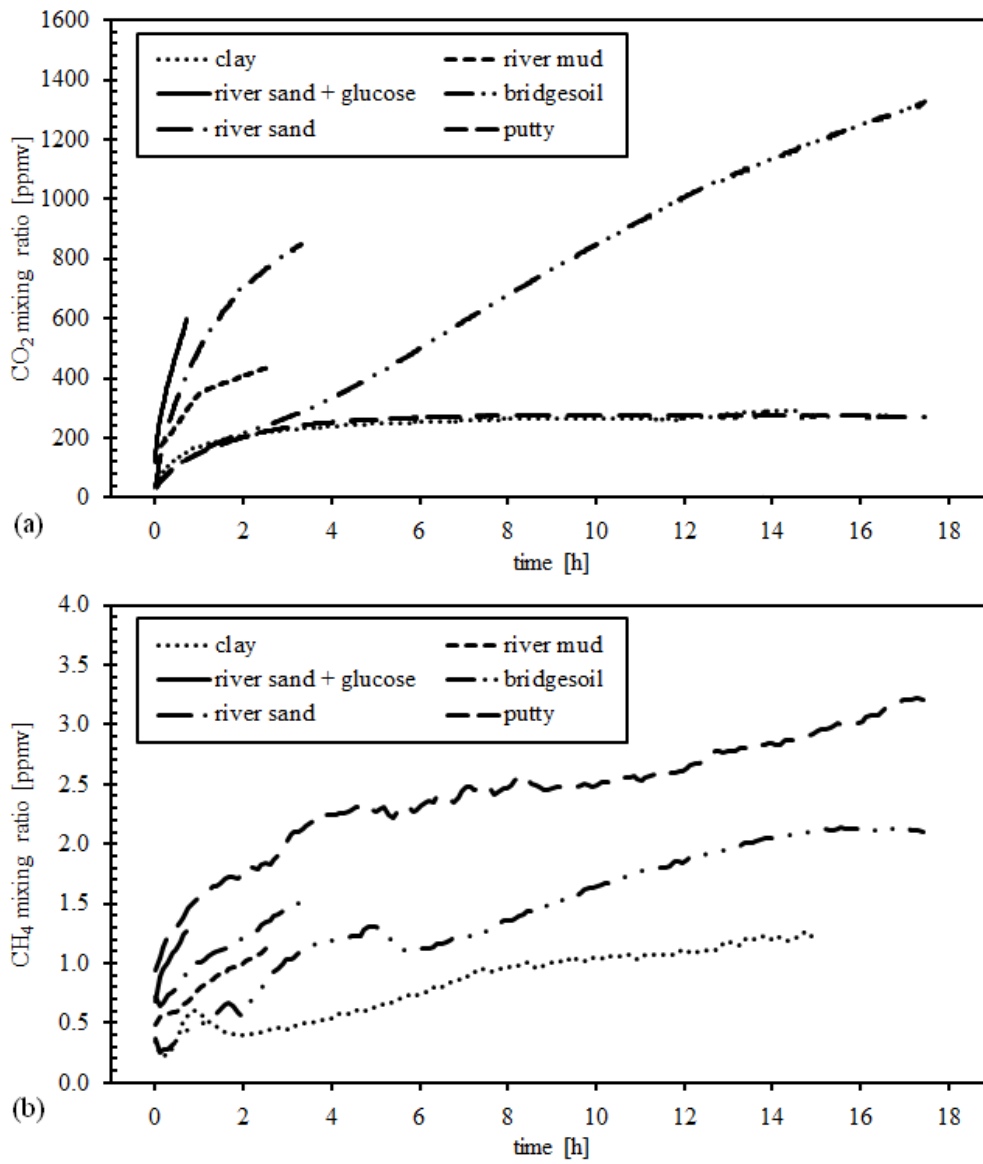
Figure 1: CO₂ (a) and CH₄ (b) mixing ratio during long-term laboratory chamber experiments with different sealing materials.
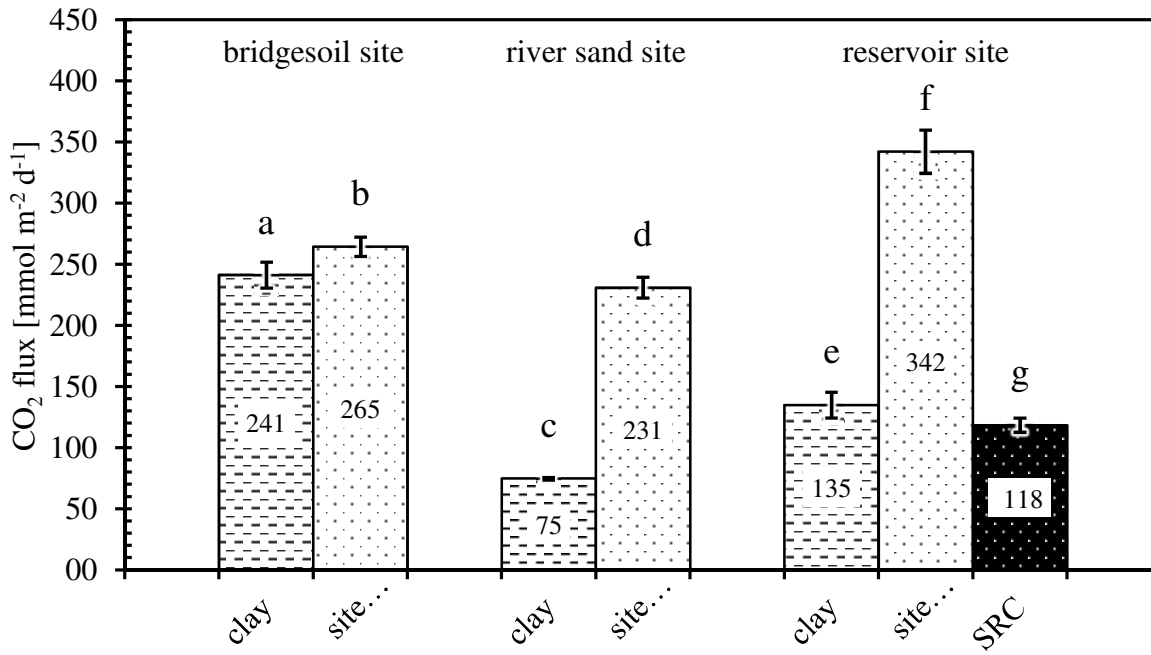
Figure 2: Mean CO_2 fluxes detected in the different sample groups during field experiments (mean ± SD, n = 3; reservoir site n = 4). SRC = soil respiration chamber + IR analyser. Different letters indicate significant difference between columns.
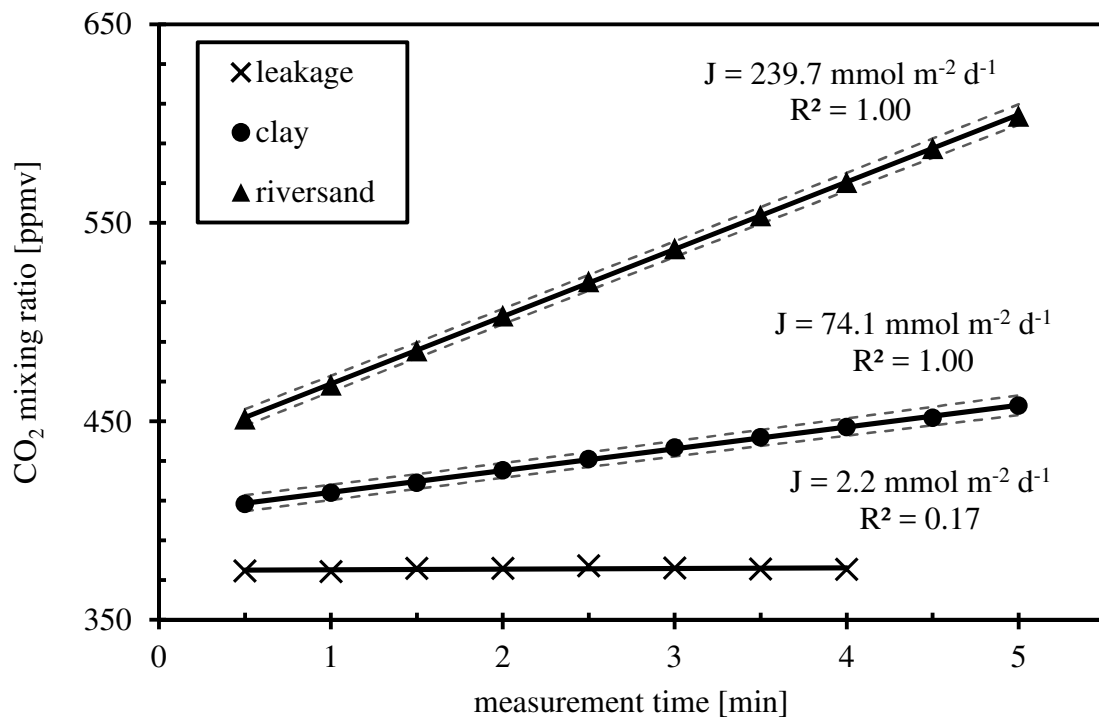
Figure 3: Example showing typical progression of CO_2 concentration during field measurements with clay and ambient material (example: river sand site). For "leakage" measurements the chamber was placed on the sediment without applying any sealing material (small holes were visible). Dotted lines indicate 99.9999 % error bands.