Technical note: A closed chamber method to measure greenhouse gas fluxes from dry aquatic sediments Response to the reviews

We appreciate the fair reviews and address all points raised by the reviewers in our detailed response below. Our replies to the reviews are in red letters as well as any changes in the manuscript.

Reply to RC1

The technical note addresses the problem of sealing a chamber to a stony ground for performing flux measurements. Getting chambers gas-tight under such environmental conditions is indeed a problem. The note describes the testing of different sealing materials on the flux of CO2 and found that potting clay was a reliable sealing material. The study addressed inertness and tightness of the sealing materials in the lab and applied the sealing techniques under field conditions. I found this paper a nice short story on a technical problem of wide interest to people working with chamber techniques to measure gas fluxes. The study is well done and well described. I assume it will be of interest to many readers.

General comments: 1.Chamber measurement on soil ground also have the problem of tightness and gas diffusion through the soil between inside and outside the chamber. These general problems are only much stronger when the ground consists of gravel or stones instead of soil. The authors may wish referring to older literature on diffusion through soil below the chamber walls, e.g. G. P. Livingston and G. L. Hutchinson. Enclosure-based measurement of trace gas exchange: applications and sources of error. edited by P. A. Matson and R. C. Harriss, Oxford:Blackwell, 1995, p. 14-51; or, G. L. Hutchinson, G. P. Livingston, R. W. Healy, and R. G. Striegl. Chamber measurement of surface-atmosphere trace gas exchange: Numerical evaluation of dependence on soil, interfacial layer, and source/sink properties. J.Geophys.Res. 105:8865-8875, 2000. We added some references dealing with methodological aspects of chamber measurements on soils – especially to the second paragraph. The Livingston and Hutchinson 1995 was already cited – but originally we did cite the whole book (Matson and Harriss), not just the chapter. We now cite the chapter. We also added a paragraph about lateral diffusion to the discussion.

2.The lab tests of the sealing material were all done with CO2. CO2 is a water soluble gas, which may behave differently than other atmospheric gases that are not well soluble, like H2, CH4, CO. Our idea was to proof tightness, it is sufficient to proof that with one gas. We can assume that if the chamber is tight for one gas, the same should be true for other gases. H_2 diffuses faster than the other gases, but we do not think that diffusion is fast enough to affect our measurements. The solubility of CO_2 affects the link between CO_2 production (by microbial processes) and the CO_2 flux. The relation between CO_2 production and emission, however, is not part of our study.

To follow the reviewers idea and to include a less soluble gas, we added the CH_4 data to Figure 1 and discuss them in the text: “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.”

Some gases may also undergo chemical reactions, e.g. CO, NO, sulfur compounds. This is true, but our study focuses on greenhouse gases.

The field test addressed CH4 and N2O in addition to CO2. However, the tests for inertness were not done with gases other than CO2. I think this problem should be addressed in the discussion. We actually measured CH_4 in our laboratory experiments. We added the methane data to Figure 1 and discuss them in the text as explained above. In our inertness experiments we did not detect a significant production of CH_4. We added this information to the text: “We did not detect a significant production of CH_4 in our inertness experiments (data not shown)”.

3. The data shown in the bar graph (Fig.2) should be tested for statistically significant difference.

Difference was checked by a t-test after checking for normality and homogeneity of variance. We add this information to the manuscript and also indicate it in the figure.

Technical correction:

4. L.7: the dynamic nature of the habitat is not subject of the study. Yes – that is right. But it is a reason why permanent collars cannot be used.

5. L.14: give the companies which supplied the materials. We added the companies.

Reply to RC2

The study by Lesmeister & Koschorreck addresses the problem of measuring green house gas (GHG) gas (primarily CO2) fluxes from dry aquatic sediments with coarse particles. They address this methodological issue by combining in a concise way both laboratory and field tests. My major concerns are: - The lack of consistent testing of all three GHG analyzed here (CO2, CH4, N2O). - The lack of testing of the wetting of clay. - The lack of references to studies in terrestrial soils that have addressed some of these methodological problems in the past. Also, address how the results presented here could be applied to terrestrial soils. This would make the better also more interesting for a wider audience. See also some specific comments:

P1, Title: I suggest adding "aquatic" before "dry sediments". This is a good suggestion – we changed the title.

P1, L14: I suggest using "terrestrial" instead of "normal". OK – we changed the text.

P1, L21: There are some recent studies on GHG fluxes from dry sediments from other regions too (e.g. Bolpagni, Rossano, et al. "Role of ephemeral vegetation of emerging river bottoms in modulating CO2 exchanges across a temperate large lowland river stretch." Aquatic Sciences: 1-10; Jin, Hyojin, et al. "Enhanced greenhouse gas emission from exposed sediments along a hydroelectric reservoir during an extreme drought event." Environmental Research Letters 11.12 (2016): 124003; Gilbert, Peter J., et al. "Quantifying rapid spatial and temporal variations of CO2 fluxes from small, lowland freshwater ponds." Hydrobiologia (2016): 1-11.). We added those references

P1, L22-30: Make clear that it is possible to measure GHG fluxes from aquatic sediments, but that this measures have so far been limited to fine sediments because of methodological constraints. Thanks for this suggestion. We added: "This approach has been successfully used to quantify GHG fluxes from muddy dry aquatic sediments (Hyojin 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.".

P1, L23: "widespread". corrected

P2, L8: There is some methods, but only for fine sediments. Correct – we added this aspect as explained above and by adding "stony" at this point.

P2, L10: I think you should add "on" before "how". Corrected.

P2, L20: It is unclear if you really test CH4 flux (and N2O). We tested both CO_2 and CH_4. Some information on CH_4 was added to the results section: "We did not detect a significant production of CH_4 in our inertness experiments (data not shown).".

P2, L25: This detection limit is for CO2 and CH4? For CO_2. We added the detection limits for the other gases to the method section.

P2, L25: "Three replicate measurements"? Yes – corrected.

P3, L13; I miss more information on the characteristics of the chambers used. We used exactly the same chamber as in the laboratory experiments. The design of the chamber is explained on page 3, l.2-3.

P3, L14: The effect of adding water was not tested in the lab, was it? This my have influenced the results and needs at least some discussion. Unfortunately we did not perform wetting experiments with the clay. However, the clay we used was not really dry and we only added very little water to increase plasticity. In fact, we only wetted our fingers before placing the clay around the chamber. The results in Figure 1a show that the clay was not producing CO_2. Thus, we think that wetting of the clay did not affect our measurements. We changed in the method section: "We wetted our fingers before handling the clay to increase its plasticity". We also added to the discussion: "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. Thus, wetting the clay to increase its plasticity was not a problem.".

P3, L17: Specify if the temperatures reported here and in other parts of the text are air or sediment temperatures. We measured air temperature near to the soil. This is now specified in the text.

P4, L5: It seems strange that CH4 and N2O are presented so late. The title is about GHG but then the manuscript deals mostly with CO2. What were the limits of detection for CH4 and N2O? We added the detection limits for the CH_4 and N_2O flux: The lowest detectable CO_2 flux in a 5-minute measurement was 4.05 mmol m^{-2} d^{-1}, for CH_4 and N_2O the detection limit was 0.14 mmol m^{-2} d^{-1}

P4, L8-L22: For clarity and consistency, the text here could refer more explicitly to the concepts of inertness and tightness.

We re-formulated the paragraph to make those concepts more clear.

Table 1: Any brand name for the clay? We do not have a brand name. It was ordinary pottery clay. We add the company were we bought it.

Figure 1: Is "CO2 mixing ratio" the correct name for the y-axis? Yes. We corrected the figure legend accordingly. Why was the incubation for some materials shorter (<4h)? As soon as the CO_2 mixing ratio in the chamber exceeded the atmospheric mixing ratio, it was clear that the sealing material was producing CO2. There was no need to continue the experiment beyond this point. That is why we stopped the experiments as soon as the atmospheric mixing ratio was exceeded. In the cases were CO_2 did not reach the atmospheric mixing ratio we extended the experiment to see, whether there was a slow leaking in of atmospheric CO2.

Figure 2: Put the units of flux in parentheses. corrected. Statistical tests comparing the fluxes could be added to this figure. Difference was checked by a t-test after checking for normality and homogeneity of variance. We added this information to the method section. We also added the information about statistical difference to the figure.

The SRC results should be highlighted more in the text. We added a comment on the SRC results in the text: "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."

Reply to RC3

The study of Lesmeister and Koschorreck addresses the important issue of an airtight, non-influencing sealing strategy of chambers when measuring GHG emissions from dried aquatic sediments with coarse particles. Therefore different materials are tested within an approach, which combines a laboratory experimental setup with a short field study to find the most appropriate sealing material. In general the study is well designed and written, and thus suitable for publication in AMT. However, I have some major concerns:

- within the abstract/ introduction especially the problem of coarse (rocky) material is mentioned (L7), however, the field study seems to only test the different sealing materials on sand and mud but not on coarse material (e.g. gravel). Actually, our field measurements were not done on sand or mud but on quite stony ground with a lot of gravel. The ‘”on-site” material used for sealing was taken in the vicinity of our measuring site. We were especially looking for stone free material for sealing. Our original method description was misleading. We changed it to: “Tests were carried out on stony sediments…”. Here is a photograph showing the gravel at the river site:

- did you tested whether only slightly inserting the chamber into the sand or mud would have yield in similar results during the field study (important for generalization of made statements!)? It was not possible to insert our chamber into the substrate. At the reservoir site it was possible to insert a commercially available soil respiration chamber (with sharp edges) a little bit into the substrate. We comment on those measurements in the results and discussion.
- testing silicone for sealing is mentioned in section 1.1 (L14), but not tested during the field study (or mentioned) Yes – that is right. Both clay and putty performed acceptable in the laboratory test. We decided to proceed only with clay, because it was cheaper and environment friendly. Furthermore the putty material was releasing ammonia. We added this information to the results.
- was the wetted clay tested during the laboratory test as well (L14: "a little water was added to the clay")? Unfortunately we did not perfom an “inertness experiment” with wetted clay. As explained in our reply to reviewer 2 we do not think that wetting the clay triggered microbial activity. We now address this aspect in the discussion.
- I am curious about the drastic differences between on-site material and clay used for sealing at the river sand site and at the reservoir site during the field study. From where was the on-site material taken to seal the chamber? Might it be that the measurements were generally disturbed cause the material was taken from around the chamber? No – the material was taken several meters away from the chamber.
- is it right, that the field study only consisted of three to four repetitious measurements per sealing material and site? Yes. The effects were quite clear. So we decided that more replicates were not necessary.
- might the time needed for sealing (1-2 min) yield in an already increased chamber starting concentration which biases lateron flux calculation? Yes – there was slight increase during sealing – but only a few ppm of CO_2. ppm versus time curves were apparently linear. We do not think that this affected our measurements. For future measurements, however, we recommend the use of a chamber with removable lid. Then the sealing can be done while the chamber is still open to the atmosphere. We added this suggestion to the discussion: “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."

Depite of this, there are also some minor concerns:

- Did you test for saturation effects (due to small chamber size and rather high CO2-emissions)? We are not sure whether we understand this comment. We did not perform long term measurements in the field. We wanted to measure *in-situ* fluxes. Thus, we tried to do the measurements as fast as possible.
- what kind of statistic test was performed (P4, L24) and was the test performed for the n of only 3-4. - in general more details about used statistics are needed! Statistical tests comparing the fluxes should be added to this figure. The low n should be mentioned here. Difference was checked by a t-test checking for normality and homogeneity of variance. We add to the methods: "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)."
- P1 L4 erases "probably" The reviewer is probably right, but we think that there are currently not enough data to be 100% sure about this statement. There is actually a global initiative trying to verify the global relevance (http://www.ufz.de/dryflux/). We would like to keep the "probably"
- P7 Tab. 2 caption: capitalize "number" corrected.
- Fig. 1: check the y-axis? The Y-axis label is correct. We changed the figure legend accordingly. Why was the incubation time different for the different materials As soon as the CO_2 mixing ratio in the chamber exceeded the atmospheric mixing ratio, it was clear that the sealing material was producing CO_2. There was no need to continue the experiment beyond this point. That is why we stopped the experiments as soon as the atmospheric mixing ratio was exceeded. In the cases were CO_2 did not reach the atmospheric mixing ratio we extended the experiment to see, whether there was a slow leaking in of atmospheric CO_2.

Could you add a error band around the line displaying the deviation during the three repetitive measurements (same for Fig. 3)? Figure 1 shows the results of single measurements. Thus, it is not possible to ad error bands. Obviously, our method description was not clear here. We modified it to: "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."

We added error bands to Figure 3.

- Fig. 3: how was the leakage measurement performed during the field study? We just placed the chamber on the sediment without any sealing. There were small holes visible. We extended the figure legend accordingly.
- please add "aquatic" to the titel ("dry aquatic sediments") OK – we changed the title.
- How does Lorke et al. fit as a reference to the MS, if measurements were not performed on dried sediments but water (floating chamber)? We cited that paper not because it contains measurements on dry sites but because it contains an innovative chamber sealing strategy: a foil sealing to a non-flat and moving water surface. We think that at least considering the use of a flexible foil fits well to our introduction. During the revision process we discovered references were a foil was used on soils. Thus, we replaced the Lorke et al reference by Steudler and Peterson (1985).
- Numbering is wrong (1.3 comes before 1.2) Right – corrected.
- please add a space between 28 and ◦C at P2 L26 corrected.
- please directly address that the laboratory test is only able to detect the combined effect of leakage and CO2 production (which is still suitable for the purpose of the study)! That is only partly right. In the cases were we had CO_2 production we indeed could not get information about tightness. However, in cases where we have a long term value below the atmospheric mixing ratio we are pretty sure, that the material is both inert and tight. Theoretically, a continuous leakage of CO_2 into the chamber could be exactly compensated by CO_2 consumption in the chamber. But we have no reason to assume that our chamber or sealing material consume CO_2 to keep the CO_2 concentration sustainable below ambient.

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. 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 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), 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., 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) ~~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 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~~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 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~~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. 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 realistic conditions, field tests at three different locations were made. Tests were carried out on stony~~andy 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). We wetted our fingers before handling the clay to increase its plasticity~~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.). Air t~~T~~emperatures 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:

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

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

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

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:

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

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}, for CH_4 and N_2O 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_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.

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 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 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.

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.

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.

Lorke, A., Bodmer, P., Noss, C., Alshboul, Z., Koschorreck, M., Somlai-Haase, C., Bastviken, D., Flury, S., McGinnis, D. F., Maeck, A., Mueller, D., and Premke, K.: Technical note: drifting versus anchored flux chambers for measuring greenhouse gas emissions from running waters, Biogeosciences, 12, 7013-7024, 2015.

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, 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 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 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)

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

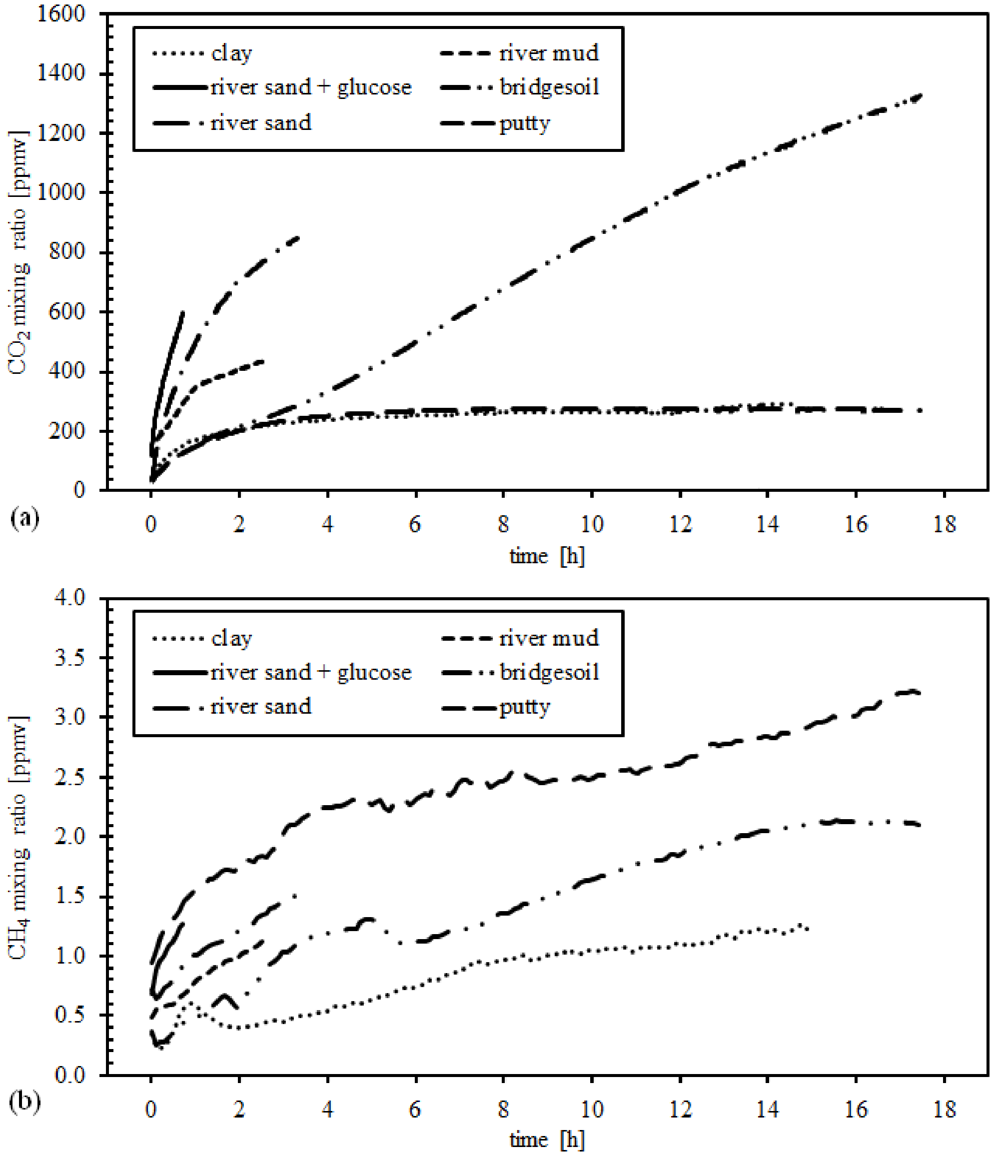

Figure 1: CO_2 (a) and CH_4 (b) mixing ratio during long-term laboratory chamber experiments with different sealing materials.

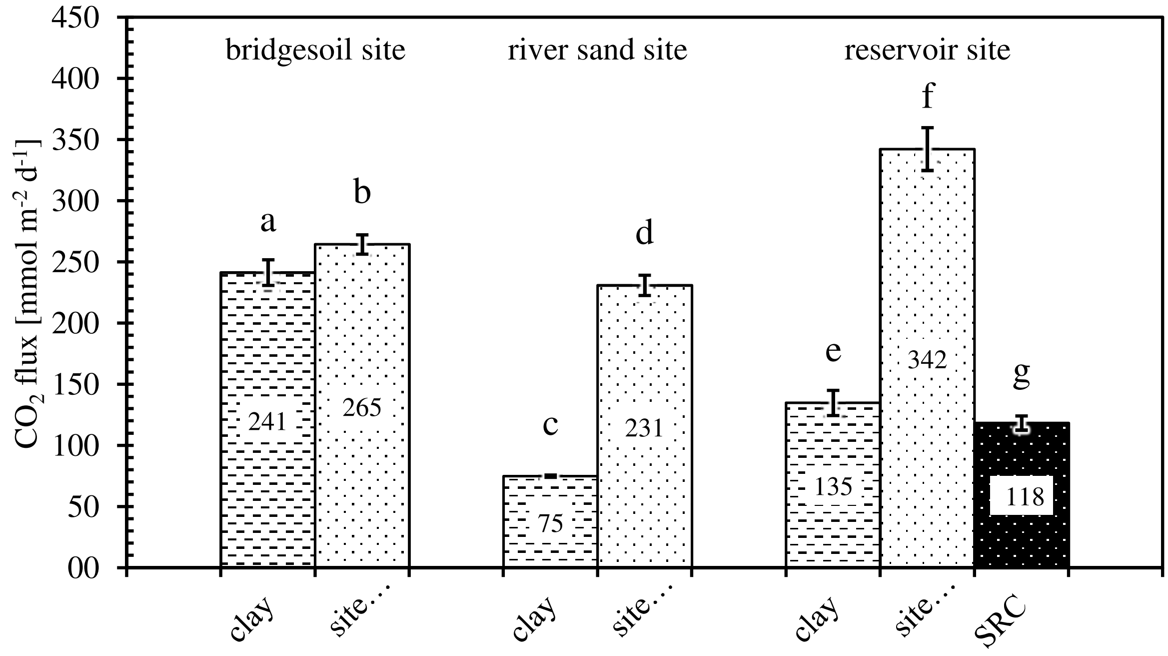

Figure 2: Mean CO$_2$ fluxes detected in the different sample groups during field experiments (mean ± SD, n = 3; reservoir site n = 4). SRC = soil respiration chamber + IR analyser. Different letters indicate significant difference between columns.

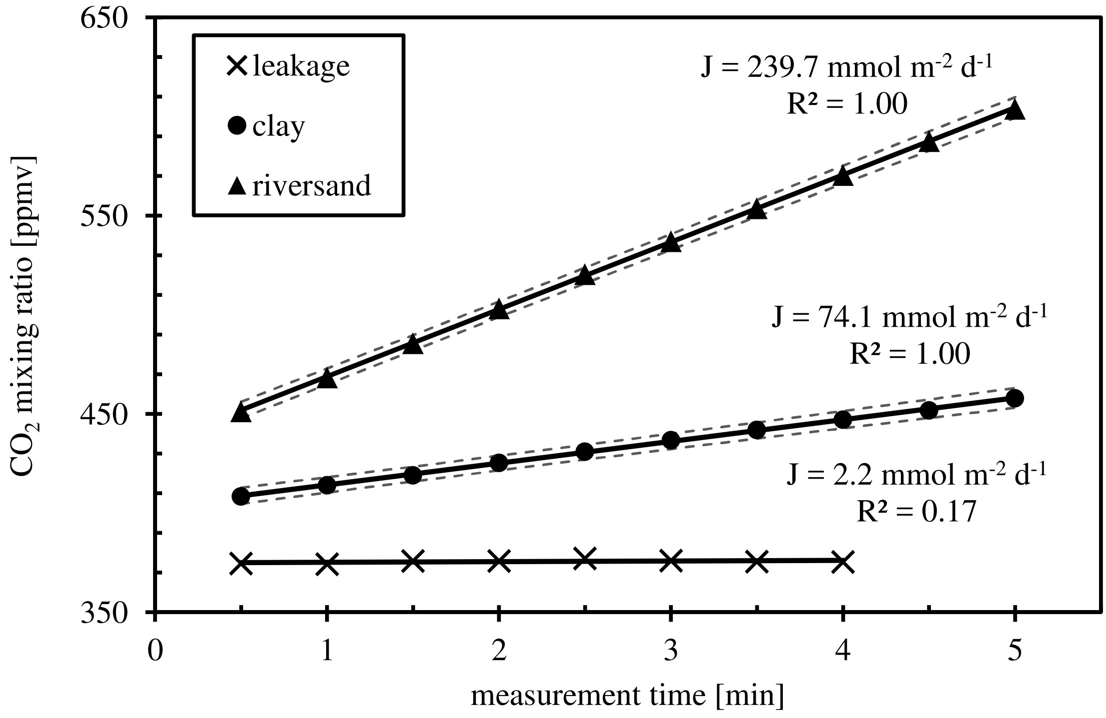

Figure 3: Example showing typical progression of CO$_2$ concentration during field measurements with clay and ambient material (example: river sand site). For "leakage" measurements the chamber was placed on the sediment without applying any sealing material (small holes were visible). Dotted lines indicate 99.9999% error bands.