

Interactive comment on “Technical note: in situ measurement of flux and isotopic composition of CO₂ released during oxidative weathering of sedimentary rocks” by Guillaume Soulet et al.

Guillaume Soulet et al.

guillaume.s.soulet@durham.ac.uk

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RE: Please see associated supplement file for a clear formatting of our responses.

RE: We thank Camille Cros for reviewing our manuscript and for her helpful feedback. Below we address these comments, along with corresponding changes made to the manuscript text.

The main objective of this study is to present the results from a new method estimating the amount and origins of CO₂ released during the weathering of sedimentary rocks. The released CO₂ might have two origins: the degradation of limestone by sulphuric

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acid and the (geo)respiration of organic carbon. The method is based on a respiration chamber drilled directly on the rock. The released CO₂ is measured by following the short-term (hours) accumulation of CO₂ in the respiration chamber after lowering the pCO₂ to near atmospheric pCO₂. Three sources of CO₂ could contribute to the accumulation of CO₂ in the chamber: the atmospheric CO₂ due to possible contaminations and/or leaks, carbonates and organic C. These three sources were successfully separated by analyzing the ¹²C, ¹³C and ¹⁴C isotopic composition of released CO₂. To this end, the CO₂ was trapped by two systems of zeolite that actively (hours) or passively (months) trap the released CO₂.

The study provides first estimations of CO₂ emissions by oxidative weathering of sedimentary rocks, which were unfortunately not compared to another method. I would say this is the main limit of this study. The isotopic analysis of CO₂ provided evidence of low contamination of sampled CO₂ by atmospheric CO₂, which validates the tightness of respiration chamber and method of CO₂ sampling. It also allowed providing first estimation of contribution of the two mechanisms of weathering contributing to CO₂ emissions (acid degradation of limestone versus organic C respiration), which could not be compared to another method. Although the main results could not be validated by using another independent method, these first estimations are useful and timely justifying a possible publication of this manuscript in BG. However, there are major drawbacks that deserve major revisions of the manuscript. First of all, the authors should acknowledge the fact that their method is not compared to other ones and is not replicated strongly limits conclusions about the accuracy, sensitivity and reproducibility of such method.

RE: A main concern of the reviewer is the lack of replication and comparison with other methods. To our knowledge, our study is the very first attempt to detect, measure, quantify, trap and partition the source of CO₂ emissions during weathering of sedimentary rocks in such settings where weathering and erosion rates are high. It is therefore not possible to compare our results to others. That is why, in the discussion

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section, we attempt to relate our results to other studies that have estimated the CO₂ flux at the scale of river catchments using geochemical proxies in river water. The fluxes are of the same order of magnitude, yet, they are obviously different. We provided some explanations for the discrepancies in the original manuscript. In terms of replication, this is challenging. Our measurements are not set up in a laboratory where parameters could be controlled. Instead we are working directly in the field where environmental parameters vary with time and space. For example, a single chamber may be expected to provide different fluxes through time as a response to seasonal environmental changes (temperature, humidity). If one were to compare two different chambers, they are likely to yield different results at the same time because of local differences in the weathering substrate (caused by differences in the chemistry of the weathered rock, fracturing, connectivity, porosity, slope of the rock face. . .). Therefore, to take this method further, we would recommend a field set up which allows for repeated measurements over seasons, and one with multiple chambers to examine the importance of weathering substrate. Accordingly, to acknowledge that one method is outlined in our manuscript (with active and passive CO₂ approaches), and so there is no comparison to an alternative method, we provide a summary of the above discussion in the revised version (revised manuscript section 3.3 P12 L15-27).

Why did you not compare the results obtained by several respiration chambers?

RE: Our Technical Note is a “proof-of-concept” study, of which the goal is to test and discuss the feasibility of directly measuring CO₂ emissions in sedimentary rocks during weathering and our ability to trap this CO₂ to measure its isotopic composition and determine its source. We demonstrate here it is possible, and the results from only one chamber are needed for this purpose. Comparing the results obtained from several chambers would be very interesting but it is the focus of a very different study which, for instance, would aim to discuss the variability over space and time of the CO₂ emissions and source proportions.

Why did not compare your estimation of released CO₂ based on short term mea-

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surement of CO₂ accumulation in chamber with the amount of CO₂ you trapped after several months of passive CO₂ trapping by zeolite. This comparison could be a first way to evaluate your method of estimation.

RE: See detailed answer below.

The method of partitioning of CO₂ sources is absolutely not well introduced and explained. For example, P5 L3-6 you should explain that these three sources of CO₂ (atmospheric, limestone, organic C) have different isotopic composition. And you should give some order of magnitude maybe. The system of equations (9) should be carefully explained, in particular all the variables must be defined (what does Fm mean?). RE: Modified accordingly. We reword this section to make it clearer to the reader and all variables are now properly defined (see P8 L15-29).

(what does Fm mean?)

RE: Fm is a defined radiocarbon metric relating to the ¹⁴C-to-¹²C ratio measured in the sample normalized to that of a standard. The metric was already defined in the original manuscript and appropriate references cited (P7 L21-24).

Table 3 must include the isotopic composition of air of the site.

RE: The information was already available in Table 2 (sample DRA17-ATM-2703) although we acknowledge that it was not clearly stated. We moved this piece of information to Table 3 to make it clearer to the reader.

Results and discussions must be presented in distinct sections to clearly separate facts from their interpretations (and fit to the standard of BG).

RE: We feel that a section “Results and discussion” is fitting for this manuscript – results are presented in Tables 2, 3 and 4 and in Figure 3. Other technical Note papers at Biogeosciences have the same format (e.g., Yoon et al., 2016; Call et al., 2017). Instead we added subsections (see sections 3.2.1, 3.2.2 and 3.2.3) and modified the title of section 3.3 to make it more informative (now “3.3. First order comparison of

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the magnitude of our CO₂ fluxes with other methods estimating CO₂ fluxes”). An introductory paragraph is added to this section to highlight some limitations of our study and justify our comparison with other indirect methods.

To my opinion, the estimation of released CO₂ by short-term measurement should be compared to the amount of CO₂ trapped by zeolite. If this is not comparable, I expect detailed explanations of reasons.

RE: We assume that the Reviewer refers to any difference between the active trapping CO₂ flux measurements, and the mass of CO₂ on the passive trap (accumulated over ~3 months). We are grateful to Reviewer 1 for an opportunity to expand on this interesting question. Before answering, let's relate the passive trapping to short-term flux measurements. Passive sampling is a practical application of the first Fick's law (Bertoni et al., 2004). In our case it is related to the diffusion (D) of CO₂ molecules in air caused by the gradient of CO₂ partial pressure between that of the chamber (pCO_{2,Ch}) and that of the zeolite trap (pCO_{2,zeolite}). This diffusion is defined for a period of time (Δt) and is limited to the internal side of the tube linking the chamber to the zeolite trap, i.e. the diffusion path characterized by the tube length (L) and section area (a). It results in the trapping of a certain mass of carbon (mC) in the zeolite trap. In this case, first Fick's law may be written as follows: $p_{CO_2,Ch} - p_{CO_2,zeolite} = \frac{m_C}{\Delta t} \frac{L}{aD} \frac{RT}{PM_C} \cdot 10^{-6}$ (R1-1) where R is the gas constant, T is temperature, P is pressure and MC is the molar mass of carbon. Factor $106 \times RT/PMC$ converts grams of carbon to cm³ of CO₂, and pCO₂ is here in ppm (cm³/m³). Note that the pCO_{2,zeolite} in the zeolite trap is equal to 0 ppm, since the zeolite is the CO₂ absorber. The equation thus reduces to: $p_{CO_2,Ch} = \frac{m_C}{\Delta t} \frac{L}{aD} \frac{RT}{PM_C} \cdot 10^{-6}$ (R1-2) Equation (R1-2) allows us to reconstruct the average partial pressure of CO₂ in the chamber pCO_{2,Ch} during the sampling duration (Δt). Eq. R1-2 also indicates that the passive trapping is only directly linked to the partial pressure in the chamber over Δt. In other words, passive sampling is not related in a simple way to the flux of CO₂ entering the chamber. The above text should partially

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answer the Reviewer's comment. However, we can try to go further. Let's assume that the evolution of the pCO₂ in the chamber can be described (as we do in our manuscript for short-term flux measurements; see Eq. 7-8) following an exponential law (Pirk et al., 2016), we can express the pCO_{2,Ch} in the chamber based on other parameters: $pCO_{(2,Ch)} = 1/V_{Ch} [q/\lambda (1 - \exp(-\lambda\Delta t)) + m_0] RT/(PM_C) \cdot 10^6$ (R1-3) where V_{Ch} is the volume of the chamber, q is the initial rate of carbon accumulation in the chamber, m₀ is the initial mass of carbon in the chamber (a value that corresponds to 400ppm of CO₂ in the volume of the chamber). λ , per unit of time, is the parameter that describes the diffusive processes responsible for the non-linear accumulation of carbon in the chamber (e.g. Fig. 3 in the manuscript). Note that Δt is very large (~ 3 months and thus $\sim 150,000$ minutes), thus $\exp(-\lambda\Delta t) \sim 0$, and Equation R1-3 simplifies to: $pCO_{(2,Ch)} = 1/V_{Ch} [q/\lambda + m_0] RT/(PM_C) \cdot 10^6$ (R1-4) Note that Eq. R1-4 can be written only if we assume that the initial rate of carbon accumulating in the chamber (q) does not change over time. This is a very large assumption that we expect to be violated because q is unlikely to stay constant over time for various reasons including natural variability in CO₂ production and also changes in the diffusive processes when pCO₂ builds up in the chamber. Equating Eq. R1-2 and Eq. R1-4 we obtain: $m_C/\Delta t L/aD RT/(PM_C) \cdot 10^6 = 1/V_{Ch} [q/\lambda + m_0] RT/(PM_C) \cdot 10^6$ (R1-5) Hence we can derive the rate at which carbon accumulates into the chamber based on the passive trapping parameters and λ , which is measured in the field over short time periods (during the active trapping – see Eq. 7-8 in the main text): $q = \lambda(m_C/\Delta t L/aD V_{Ch} - m_0)$ (R1-6) The flux can be inferred from the later equation using the internal surface area of the chamber (S_{Ch}; same as S in the main text). If q was in gC/min, then the flux of carbon Q in gC/m²/year is: $Q = \lambda(m_C/\Delta t L/aD V_{Ch} - m_0) \cdot 525600/S_{Ch}$ (R1-7) We can determine most of the parameters of equation (6) independently from the flux (Q or q), except for λ . For instance m_C, m₀, V_{Ch}, S_{Ch}, Δt , a and L can be measured and D (diffusion of CO₂ in air) can be inferred/estimated from the literature. However, λ is determined using the short term flux measurements, along with the flux (i.e., Q or q). Thus estimating the flux of CO₂ based on the rate

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of carbon trapped in the passive trap ($mC/\Delta t$) is not independent from the short term CO_2 flux measurements. Thus comparing the fluxes obtained from the mass of carbon mC recovered using the passive trap and using Eq. R1-7 and the direct measurement, is somewhat circular because they are not determined independently from each other. For longer monitoring of field work sites, the mass of carbon trapped is still informative but only qualitatively since mC or better else the rate carbon trapping per unit of time ($mC/\Delta t$) are proportional to the flux of carbon Q to the chamber and the “leakiness” parameter λ . This is illustrated easily by writing equation Eq. R1-7 differently: $m_C/\Delta t \hat{=} Q/\lambda$ (R1-8) Interpretations of changes in $mC/\Delta t$ are thus qualitative at this stage, and so beyond the scope of the present Technical Note. In the revised version we added some discussion clarifying that, based on our current knowledge and measurements, passive traps can be used to provide qualitative constraint on mass fluxes over time (see revised manuscript P10 L1-8). We propose that future work investigates whether the parameter λ can be characterised for a chamber independently from the active CO_2 flux measurements. If it can, the passive trap method can be used not only qualitatively (e.g. to look for changes in the mass of CO_2 collected on passive traps through time), but quantitatively (i.e. the monthly time-integrated CO_2 flux).

Title of section 3.3 is not clear and does not reflect the content. It seems that the objective of this section is to make a first comparison of estimation made by this study with published results from other sites.

RE: Indeed the objective of this section is to provide a first-order comparison between our results and other indirect river-catchment scale estimates of CO_2 fluxes from around the world. We changed the title of this section to: “3.3 First order comparison of the magnitude of our CO_2 fluxes with other methods estimating CO_2 fluxes”

If I understand well, your estimated amounts are far above the ones present in the literature. You should give some interpretations of these differences including the fact that your method has some bias that could lead to overestimations. First, the drilling can generate hyperactive surface by providing dust (small particles with high surface ar-

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eas). Second, fresh surface is rich in organic C and limestone (because not previously exposed to O₂). The CO₂ may diffuse from pores of surrounding rock to chamber signifying that the surface of rock contributing to these estimations is larger than the sole surface of chamber.

RE: We partly replied to this comment in the Reviewer's detailed point P11L16. Regarding the additional specific points raised here by the reviewer: Hyper-reactive surface by providing dust while drilling. The weathered marls in which we drilled are compact at depths greater than ~10cm (Mathys and Klotz, 2008; Osstwoud Wijdenes and Ergenzinger, 1998). But they are not extremely hard rock, and the chamber was drilled in about 1 or 2 minutes producing a coarse powder (that we actually needed to further grind to fine powder in the lab for our geochemical analyses). So we don't think that this powder was extremely reactive. Furthermore, before sealing the chambers the powder left inside the chamber was blown away using a compressed-air gun to minimize this phenomenon. We added a sentence in the revised manuscript stating we removed the powder before sealing (see revised manuscript P4 L19-20). The rock surrounding the surface of the chamber contributes to the CO₂ flux. We agree that the rock surrounding the surface of the chamber contributes to the CO₂ flux, just because the weathering process naturally occurs at some depth within the rock face (probably in the regolith where gas can penetrate through cracks). We realize that we might not have been clear enough about this point. What we call "rock" in the original manuscript should actually be referred to as the regolith which extends to up to ~20cm depth (Mathys and Klotz, 2008; Osstwoud Wijdenes and Ergenzinger, 1998; Maquaire et al., 2002). Thus when we drilled the chamber, we created a headspace, into an "ongoing-weathering" rock, in which CO₂ can accumulate. This makes us able to measure a CO₂ flux when we lower the pCO₂ to that of the atmosphere. This net flux is the one we want to measure. We added this information in the Study Area section (revised manuscript P4 L2-9) as well as in the Results and discussion section 3.1 (revised manuscript P9 L23-27).

Detailed comments: P3L11: why did you set up these two methods of trapping? The

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idea must be introduced before.

RE: We dropped the mention of the two methods of trapping from the introduction. Furthermore the rationale behind using active and passive trapping was already explained in the method section of our original and revised manuscript.

P4L4. The rock-drill was used to dig a hole or a cylinder. This is only a part of the chamber.

RE: The rock-drill was used to drill directly into the rock/regolith a cylindrical chamber – 40cm-deep with an inner diameter of 2.9 cm. This is indeed only the headspace of the chamber. The rest of the chamber including how it is closed and sealed is described in the following lines (P4 L6-13 of the original manuscript)

P4L24-27 The drilling makes powder that can stay on the surface. I guess that dust is highly reactive compared to rock that, has already been exposed to weather and oxidation since many years. This should be stated and discussed somewhere, maybe in the discussion section.

RE: A relatively coarse powder is produced during drilling (with some coarse flakes). However, the rotating flute of the drill bit carries away most of the powder out of the hole/chamber. This allowed us to sample the powder to measure its organic and inorganic carbon contents and isotopes. Importantly, before sealing the chamber, the rock powder left in the chamber was blown away from the inside using a compressed air gun. This should minimize the impact of dust on the measured bulk CO₂ flux. A sentence stating this point was added in the revised version of our manuscript (P4 L19-20).

P6 L11-14 This text has no meaning for me, could you try to better explain? Concerning this section on the estimation of CO₂ release, how did you manage the fact that released CO₂ can accumulate in water present in the rock under the form of carbonates?

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RE: Indeed, a part of the CO₂ could be dissolved in the interstitial water under the form H₂CO₃ to form carbonate anions, of which a part could be released to the Laval stream water (the stream that drains the catchment where we installed the chambers). However, we are actually interested in measuring the net flux of CO₂ to the atmosphere. Plumbing the whole system, i.e., quantifying the portion of CO₂ that is emitted to the atmosphere as well as that that is released to the Laval stream as the form of carbonates anions after redissolution or as a result of Eq. 3 is out of the scope of this study.

Equations 9. You must say that this system of three equations can calculate three unknowns: atmospheric CO₂, limestone originating CO₂, organic C originating CO₂. Define all variables. Results and discussions must be separated. That will clarify your results and explanations.

RE: These comments are related to comments already addressed above.

P8L18-20. Not necessary, the dissolution of CO₂ in water and formation of carbonates could lead to a non linear response.

RE: We do agree in principle. However rock water content seems to be very low as it does not look wet and we don't see any water dripping at all. So we doubt that the process described here by the reviewer can impact significantly the changes in pCO₂ we observe repeatedly during our sequences of CO₂ monitoring. Instead we keep thinking that a host of diffusive processes (Pirk et al., 2016; Kutzbach et al., 2007) are most likely to explain these non-linear changes.

P9L1-2 This decrease could result from an exhaustion of CO₂ of pores surrounding the chambers (at the beginning of measurement these pores contribute much to the accumulation of CO₂ in the chamber and they become empty with time).

RE: We do agree. This is what we explained at P9 L6-9 in the original manuscript.

P9L17 I disagree. The amount of atmospheric CO₂ is given by your system of equa-

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tions (9)

RE: The manuscript text was correct as written. Third equation of the system of equations (9) is: $f_{\text{Atm}} \cdot Fm_{\text{Atm}} + f_{\text{RockOC}} \cdot Fm_{\text{RockOC}} + f_{\text{Carb}} \cdot Fm_{\text{Carb}} = Fm_{\text{Chamber}}$ (R1-8) Since rock-derived organic carbon and the carbonates are devoid of radiocarbon (because they are very old – $\sim 160,000,000$ years old, whereas ^{14}C is not measurable anymore after $\sim 50,000$ years), hence their radiocarbon activity is 0. This implies that: $Fm_{\text{RockOC}} = Fm_{\text{Carb}} = 0$ (R1-9) Combining (R1-8) and (R1-9), it comes: $f_{\text{Atm}} = Fm_{\text{Chamber}} / Fm_{\text{Atm}}$ (R1-10) Thus the relative amount of atmospheric CO_2 (f_{Atm}) is calculated as written at P9 L17 in our original manuscript.

P9L20 Cite Table 4

RE: Sentence at P9L20 refers to stable carbon isotopes reported in Table 2. So we guess that the reviewer meant Table 2 instead of Table 4. Accordingly we now cite Table 2 in the revised manuscript (P10 L19).

P10 L10-11 You should better explain why do you make a correction for atmospheric CO_2 although this contribution was already considered in your system of equations? After reading Table 4, I understood but you should better explain in the text. RE: Modified accordingly, we added the specific information (P11 L31 to P12 L3 in the revised version)

P10 L21-22 Change titles, they are not helpful for the understanding. RE: We already addressed this comment (see above)

P11 L3 You should add text to explain that your method must be compared with other (direct or indirect) methods on the same site. RE: This is the aim of section 3.3 where we compare our method of direct CO_2 flux measurements to other estimations of CO_2 fluxes. In the revised version, we hope the title of section 3.3 is now clear enough.

P11 L5-9. The logical link between these sentences is not obvious. RE: Modified accordingly, see P13 L18 in the revised manuscript: "This statement is supported by

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the average anion [...]"

P11L16 the numbers “19 to 37 gC m⁻² yr⁻¹” must be compared to “206 gC m⁻² yr⁻¹” of your study? The difference is enormous and deserves some explanations.

RE: We agree the difference is large. We already provided some explanations at P11L18-20 of the original manuscript. We could have added that seasonality might be another explanation, as CO₂ flux during winter months flux could be very different than that during summer months as a results of changes in temperature and water content with impacts on the kinetics of rock weathering. We actually expect that the direct CO₂ flux measurements would change over the course of the year. The estimates using dissolved calcium in river average several months. So one cannot expect that our direct flux CO₂ measurements (for 1 discrete location on a given day) perfectly match the CO₂ flux estimate using Laval stream chemistry (0.8 km² averaging several months). Taken individually these CO₂ fluxes are not comparable. What we felt important was to show that in erosive environments both fluxes are high compared to other geochemical carbon transfers (e.g. silicate weathering CO₂ consumption). We do not expand much on these explanations as our manuscript is a Technical Note. So this kind of discussion goes beyond the aim we set to our original manuscript. As Reviewer #2 notes, we explain a method that can now be installed more widely to explore these questions.

Figure 1: I do not see what pictures B and C bring to the story.

RE: We felt important to show a larger view of the field, as well as that the chamber are not drilled in soil horizons. In the case other reviewers would suggest that these pictures are superfluous, we will be happy to take them off of the paper.

Have you checked that all the materials you use, especially the products used to seal and make tight (e.g. expansive foam etc), does not emit CO₂?

RE: We don't use expansive foam. Instead, we used outdoor silicon sealant (see

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P4L11 in the original manuscript). First we checked that the silicon sealant was not containing any curing agent like acetic acid, which may chemically alter the substrate around the hole. Second the flux measurements were performed when the sealant was fully dry (see P4L14). Flux measurements presented here were performed on March 2017, i.e., 3 months after we installed chamber H6 in December 2016. We are very confident that the sealant we use has no impact on our direct CO₂ flux measurements.

Please also note the supplement to this comment:

<https://www.biogeosciences-discuss.net/bg-2017-454/bg-2017-454-AC1-supplement.pdf>

Interactive comment on Biogeosciences Discuss., <https://doi.org/10.5194/bg-2017-454>, 2017.

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