Author's response to Anonymous Referee #1

We would like to thank the anonymous referee #1 for his/her interest in our study, his/her extended review and his/her very helpful and detailed comments, which have largely contributed to improve our manuscript.
Below, we have responded on the comments point by point.

General Comments Anonymous Referee #1

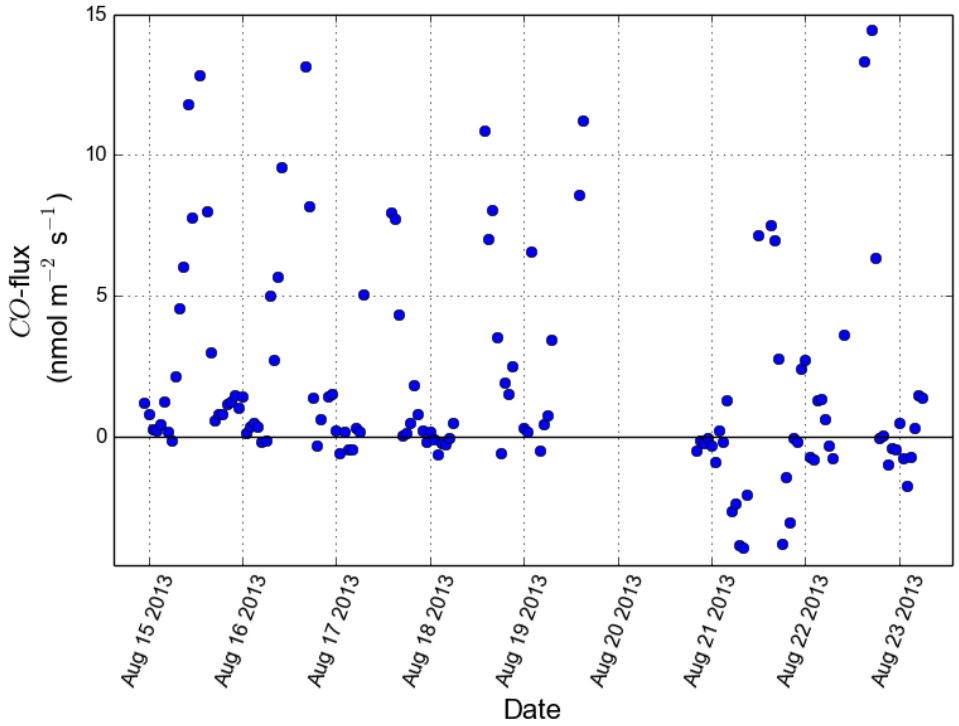
The paper is well written and summarises a lot of data from a range field and lab studies. It is novel in that is uses a range of CO_2 and CO measurement techniques to investigate photodegradation in the field (though only for three days) and the laboratory. The findings of the work are interesting and raise questions for future photodegradation experiments
However, the eddy covariance and gradient flux measurements do not appear to have much relevance assuming the objectives of the paper were to assess photodegradation and thermal degradation. If the objective of the work was to measure CO_2 and CO fluxes in an arid system then EC and GF data would be appropriate to be included.

We agree with the reviewer and have reduced the part about Flux Gradient (FG) and Eddy Covariance (EC) in the Methodology and the Results section. This part was originally included to:

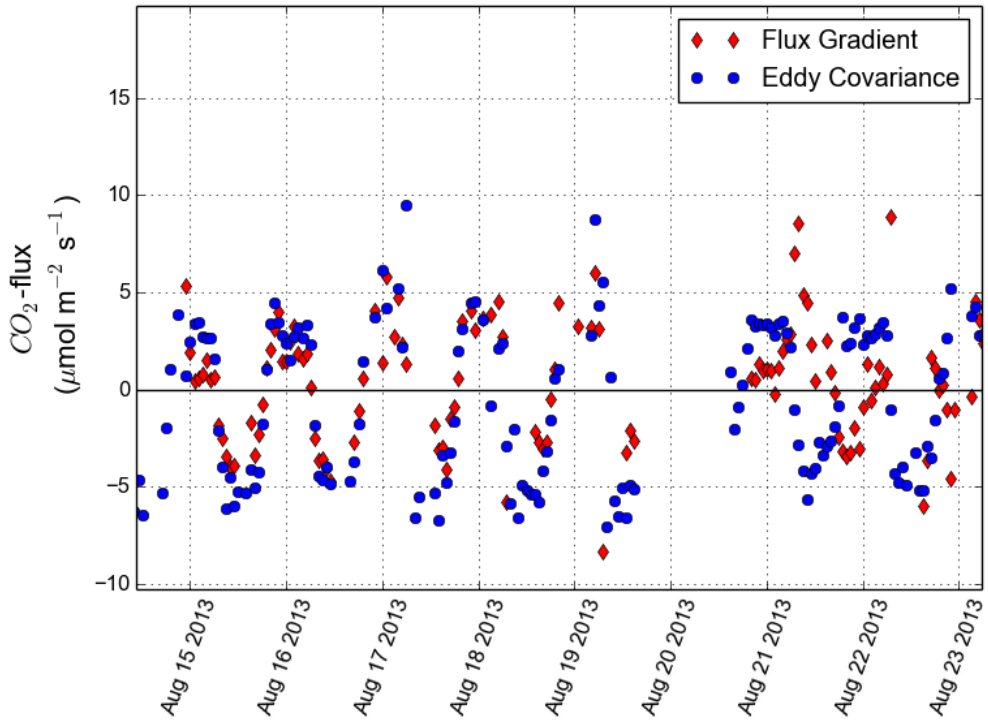
- show the comparability of the FG measurements to the EC measurements, which might be of interest when studying the FG CO flux measurements;
- show that the ecosystem was not (yet) in dormant state, wherefore direct comparison between chamber and FG (for the assessment of photodegradation) was not possible, as initially planned.

We have moved the text and Figure 1A (now Figure 7) to the Supplementary Materials. The new figures (new Figure 1 and Figure 7) are added to the revised manuscript and also added to this document.

We would like to keep the FG data for CO flux included. Figure 1B (now Figure 1) was included to show that CO fluxes were not only measured in the chamber but were also observed on larger scale, which supports our idea that thermal degradation plays a role in CO exchange in arid ecosystems. Also, the new Figure 1 shows the effect of rain in FG CO emissions (increased uptake after rain event), which was also observed by the flux chamber, supporting the idea that this is not a local chamber artefact.



New Figure 1 for in manuscript: CO fluxes over 8 days in August. A large rain event took place on 20th of August.



New Figure 7, for in Supplementary Materials: EC and FG CO_2 fluxes over 8 days in August. A large rain event took place on 20th of August.

It would appear that due to a leak in the opaque treatment, the field experiment for photodegradation was only three days long which may also reduce the relevance of this work to addressing the objectives of the paper.

Although three days are not enough to quantify photodegradation fluxes over the season, we consider it still sufficient for a general assessment of the role of photodegradation for the following reasons:

- The circumstances during these three days were optimal for photodegradation: no clouds, dry organic material on the surface and dry conditions for over 3 weeks. We feel that, if photodegradation plays a major role in arid conditions, as suggested in previous studies (with fluxes of 1 µmol m^{-2} s^{-1}), it should also have been observed during these three days.
- Furthermore, while the opaque chamber was only functional for three days, the transparent chamber was functional for the entire experiment. This data showed that the three days (5-8 August) were very similar to the rest of the period:
  - For CO_2 fluxes, the transparent chamber fluxes (for 5-8 August) showed a very strong dependency on air temperature and less on soil temperature and radiation (Figure 3A, C). The data from the whole period showed a very similar dependence on air temperature (as red line in Figure 3A).
  - For CO fluxes, the transparent chamber fluxes (for 5-8 August) showed a very strong dependency on chamber temperature (Figure 3D) and less on air temperature (Figure 3B). This observation was also made for the other transparent chamber flux data, as can be seen in Figure 4A and B.
  - Transparent chamber flux data from the full measurement period were studied in relation to radiation, especially during cloudy days. However, no indication for direct radiation induced fluxes was found.

Therefore, the only pieces of work included in this paper that appropriately address the title which the authors have chosen is the laboratory data.

Our main objective, reflected in the title, was to study photo and thermal degradation in an arid ecosystem. We feel that the role of thermal degradation (for CO fluxes) is adequately addressed.
For photodegradation, we present sufficient data for our conclusions: if direct photodegradation plays a major role, as suggested by some studies, it should have been visible in this sunny region with arid organic material on the surface, also during these three days. Also, the material which was chosen for the laboratory experiment, was directly taken from the field site, e.g. from an arid ecosystem, wherefore we feel that the title of the manuscript still represents the content of the research.

For each measurement technique, there is a separate method, however I felt that the Materials and Methods section did not adequately describe the experimental plan for each of the methods used and lacked detail in some aspects

We have elaborated the laboratory part of the Methodology-section. The added information can also be found in this document, at one of the specific comments responses.

Specific comments Anonymous Referee #1

The comments and corrections advised by the anonymous referee are implemented in the corrected manuscript. The posed questions are answered here.

P2436 L4 How many soil collars were inserted? In the photodegradation assessment part of the work, it was stated there was 6 fixed chamber positions, is it the same for the earlier part of the methodology?

The section on soil collars is clarified in the Methodology-section. The following information has been added:

- The soil collars were the same as described in the earlier part of the Methodology. During the whole experiment, 6 fixed chamber positions were in use. Two chambers (one opaque, one transparent) were shifted over these positions.

P2436 L8 The transparent chambers removed 50% of the radiation, is this still a valid representation of what would be occurring under natural conditions?

When ordering the chambers, we specified to have at least 50% transparency in the UV-wavelength band.

We have contacted KIT to inquire about precise transmittance of the material per wavelength band. They have measured the materials which were used for our chambers. Over the wavelength band 280-700 nm, transmittance of 90% or higher was reported. The used material is Acryl glass XT solar, 3 mm, UV-transmitting.

The following information is now added to the Methodology-section and the Discussion-section:

For in Methodology:

- The transparent chambers are made of UV-transparent Acryl glass XT solar (3mm, UV-transmitting). It was tested by KIT for transmission rates. Transmittance in wavelength band 280-700 nm was 90% or higher.
- Transmittance per wavelength band of the laboratory plexiglass was provided by the manufacturer and was 0.2% (250 nm), 6% (260 nm), 36% (270 nm), 74% (280 nm), 90% (290 nm) and approximately 94% at longer wavelengths.

For in Discussion:

- The occurrence of photodegradation depends on the wavelength frequency and not on the intensity. The reduced intensity of 90% only causes possible photodegradation fluxes to be smaller. However, a flux magnitude of 1 µmol m^{-2} s^{-1}, as measured by a previous study, would still have been observable if reduced by 10%.

The slightly reduced radiation does not affect the quality of the thermal-degradation measurements, since the chamber temperatures are measured inside the chamber. Besides, as stated in P2446 L21, the chamber temperatures do not represent the

natural temperature of the ecosystem but by its 'warming design' had the potential to show the existence of (an enhanced effect) of thermal degradation.

The temperatures inside the chamber were higher than the temperatures outside the chamber. Although this will result in higher fluxes inside the chamber compared to the ecosystem around it, the correlation between temperatures inside the chamber and the CO-flux should be representative for the ecosystem. The laboratory study shows a similar relationship between temperature and CO-flux. According to our results, the temperatures outside the chamber are high enough to induce significant thermal degradation fluxes. This is supported by the measured CO fluxes by the Flux Gradient technique.

Can the authors please comment on why they did not artificially enhance the UV (i.e. artificial lighting) within the chambers to bring it back up to natural conditions. Or change the chambers to a more UV transparent media to be able to more accurately assess the effect of UV under these conditions.

Artificially enhancing UV radiation to natural levels in a field experiment is very difficult and would require constant UV measurements inside and outside the chamber, and an automatically adjusting light source. This was for practical reasons not possible.

P2437 L17 The authors have stated there were 6 fixed chamber locations but then when they tested the transparent chambers at "both locations", what were the "both locations"? I thought assessing the field chambers before applying the photodegradation treatment showed very good experimental design but the change from 6 to 2 was a bit confusing. Also the data presented in Figure 2, looking at the colours assigned to I assume each different chamber, then there are only 5 chambers including the one that was bare.

The use of different chamber locations is clarified in the text and below the figure. The following information has been added:

- The 'both' locations which are mentioned, are the exact same locations which are measured by the transparent and opaque chamber between 5-8 of August.

P2437 L21 The authors assessed the flux chambers for CO2 and CO production, but only mention that they found CO production – for which they did not correct the data for. Please insert some statement with reference to the CO_2 production during the blank testing.

No chamber CO_2 production was found. A sentence has been added to the manuscript.

P2438 L7 Was the grass material cut to a specific size (e.g. 2 cm lengths) or ground? Was the soil material sieved to a consistent size?

Extra information on the soil and grass samples is added to the manuscript. The following information has been added:

- The grass was cut just above the surface, resulting in grass stems of between 20 and 80 cm. The grass was not ground, to keep it in natural conditions. The soil was not sieved, also to keep it as close as possible to natural field conditions.

P2438 L9 The photodegradation part of the laboratory experiment did not assess photodegradation in the soil. In these arid systems bare soil would be an important part of the ecosystem and bare soil has been assessed in the other parts of the experimentation, including the chamber measurements and the thermal degradation experiment in the laboratory. Can the authors please comment on why photodegradation of the soil was not assessed?

- Previous photodegradation studies have mostly focussed on organic materials in the form of grass. Soil material is already further decomposed and less easy-degradable material is present. Furthermore, most of the surface in the field site was covered with dead organic material, wherefore soil radiation exposure was small and hard to estimate. For these reasons, grass material was the main focus of our laboratory study.
- Also, to simulate the soil exposure in a laboratory study, non-disturbed soil samples should be taken and representatively being set up and radiated in the laboratory. This was not possible with our set up and samples.
- Future photodegradation studies should take possible photodegradation soil fluxes into account and design their experimental set up accordingly.

P2438 L15 During the photodegradation laboratory experiment, how long was the grass samples assessed for CO_2 and CO?

The following details have been added to Methodology part of the manuscript.

<u>The photodegradation experiment</u>:

- The metal cylinder with acrylic cap was connected to the FTIR by use of stainless steel tubing. The cap was closed with screws. The transmittance of the acrylic cap was measured at 10 nm steps. Transmittance was 0.2% (250 nm), 6% (260 nm), 36% (270 nm), 74% (280 nm), 90% (290 nm) and approximately 94% at longer wavelengths.
- The metal cylinder (inner diameter=6.5cm, h=26cm, area=33 cm^2, loosely filled with grass) receives 45 W m^{-2} nm^{-1} at 375 nm (peak emission UV-A lamp) and 30 W m^{-2} nm^{-1} at 310 nm (peak emission UV-B lamp). Natural levels of UV-A at 375 nm are approximately 1.2 W m^{-2} nm^{-1}, natural levels of UV-B at 310 nm are approximately 0.6 W m^{-2} nm^{-1}.
- The grass was a mix of the grasses described fieldsite part of the Methodology-section.
- Grass in the cylinders was positioned in a way that at least 80% of surface bottom was covered with grass material.
- Every treatment was performed for 30 minutes.

<u>The thermal degradation experiment</u>:

- The glass flask (inner diameter=6.7cm, h=16cm) was connected with stainless steel tubing to the FTIR. The grass was dried, not ground and loosely distributed in the glass flask (2 grams). The soil was dried, and 30 gram was taken, which covered approximately 1 cm (height) of the glass flask.

Temperature steps were done in 20 minute steps. After approximately 5 min, stabilization in the CO production could be observed.

P2439 L22 I assume that they data presented in figure 1 is from transparent chambers only, the dates mentioned for the transparent and opaque chambers overlap according to the dates on the figure and in the text. Could the authors please clarify on the figure title as well as in the methods section of the manuscript?

In the Figure 2 description, it is added that the figure only shows transparent chamber data. More explanation is added below:

- If the referee means (old) Figure 1, the data presented here is from Eddy Covariance and Flux Gradient data (upper panel), and from Flux Gradient-data (lower panel), so not from the chambers.
- If the referee means Figure 2, indeed only transparent chamber data is shown here. This was chosen to avoid a too chaotic figure. For CO_2, (panel 2A), the fluxes from the opaque chamber lay very close to the transparent chamber. For CO, a clear difference is visible as soon as the 'opaque' chamber is covered.

P2440 L2 Are these locations without organic surface material, the same ones referred to as bare soil (green diamonds on the figure), if so please be consistent with the names for these points.

Information belonging to Figure 2 and in the Discussion is clarified with the following information:

- Locations without organic surface material are the same one as referred to as bare soil.

P2440 L10 Was the field photodegradation experiment which took place over three days only undertaken as a comparison of 1 chamber for each treatment (i.e. one for opaque and one for 50% transparent)? While the authors have been very clear that this data is representative of only three days, can they comment on the relevance of this very limited window in time to the overall system dynamics?

The original plan of the field photodegradation experiment was a comparison of 1 chamber for each treatment on different locations and over a longer time. Unfortunately, a leak has formed early in the experiment.
While the direct comparison was done for three days, we have the opinion that the data is representative for photo and thermal degradation in arid conditions and therefore can give an indication for the overall ecosystem dynamics, for the following reasons:

- The circumstances during these three days were optimal for photodegradation: no clouds, organic material on the surface and dry conditions for over 3 weeks. We feel that, if photodegradation plays a major role in arid conditions, as suggested in a previous study (with fluxes of 1 µmol m^{-2} s^{-1}), it should also have been observed during these three days.
- The experiment was done in the beginning of August with maximum radiation intensities of 860 W m^{-2}. Only in the months June and July, the radiation

intensities are slightly higher (up to 900 W m^{-2}). However, it is unexpected that photodegradation only takes place when radiation is more than 860 W m^{-2}. During the experiment, the ecosystem was at the driest point expected in a year: the upper soil layers had been dried out, no rain had fallen for over three weeks and very high radiation intensities (cloudless days) were available. In these conditions, no photodegradation was measured.

- During the rest of the year, the ecosystem is wetter and receives lower radiation levels. We therefore expect that photodegradation does also not play a role during the rest of the year.

- We expect thermal degradation to be an active process during most of the year but, since dependent on temperatures, to be very small in winter. However, more important, when soil water content goes up, the CO emission will be more buffered by soil CO uptake. Therefore, the net emission during the day, as observed during the experiment, might turn into net uptake.

P2441 L2 Is there a P value for this statement, using the phase "significantly higher" indicates that a statistical analysis has been undertaken.

The sentence has been changed in the manuscript

P2441 L5 Why was such a short period of CO flux measurement presented in Figure 4? Assuming that this is the same data presented in figure 2 then a far greater period of measurement occurred.

The reason for this choice was stated on page 2440, L11, but has been elaborated in the revised manuscript with the following information:

- As mentioned in the Methodology section, the chambers were moved every few days. Every location showed slightly different flux values (as visible in Figure 2, every location with a different colour). Therefore, for analysis such as done in Figure 4, only data from one location was chosen.
- For the manuscript, this period was chosen for it stable climatic factors (no rain, stable wind and no clouds), but similar patterns were visible for other periods.

P2441 L7 Is there a possibility that there was no relationship between the incoming radiation and CO fluxes because the experimental procedure greatly reduced the incoming radiation?

- In the manuscript, we state that we expect that there is indeed no (observable) relationship between incoming radiation and CO fluxes. However, there is an indirect relationship by the indirect warming of the chamber, causing thermal degradation fluxes.
- The slightly reduced radiation does not affect the quality of the thermal-degradation measurements, since the chamber temperatures are measured inside the chamber. Besides, as stated in P2446 L21, the chamber temperatures do not represent the natural temperature of the ecosystem but by its 'warming design' had the potential to show the existence of (an enhanced effect) of thermal degradation.

- The temperatures inside the chamber were higher than the temperatures outside the chamber. Although this will result in higher fluxes inside the chamber compared to the ecosystem around it, the correlation between temperatures inside the chamber and the CO-flux should be representative for the ecosystem. The laboratory study shows a similar relationship between temperature and CO-flux. According to our results, the temperatures outside the chamber are high enough to induce significant thermal degradation fluxes. This is supported by the measured CO fluxes by the Flux Gradient technique.

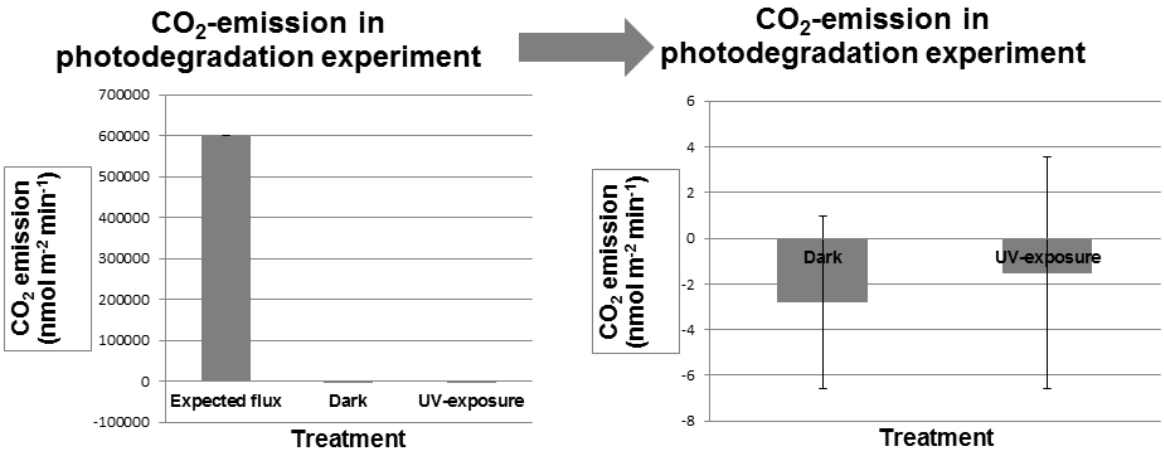
P2441 L17 Why is the data for the laboratory photodegradation experiment not shown? I would have liked to have seen the data for this. At the very least, "data not shown" should have been in this sentence.

In this author's response, we have added graphs of the laboratory photodegradation measurements (see below).

The photodegradation laboratory data did not show any enhanced fluxes under UV-exposure. Since a figure would not add anything to our message, and we wanted to reduce the length of the manuscript, we decided to not include the figure. We have added a 'not shown' to the Results section for clarification.

Below the figure, a comparison with expected values (based on previous studies) is made.

In the laboratory, no (significant) photodegradation fluxes were observed, independent of type of radiation (A or B) or the type of material (different grasses were tried, not shown). An increase in amount of grass increased the CO_2 emission both in dark and UV conditions, indicating a remaining respiration flux. When grass samples were not dried, fluxes were higher. However, respiration was not the focus of this paper, wherefore this data is not shown in the manuscript.



***Left figure**: Measured average CO_2 emission under 'Dark treatment' (no radiation) or 'UV exposure' (UV-A and UV-B radiation) in comparison to expected photodegradation fluxes. Rutledge (2010) measured 1 µmol m^{-2} s^{-1} of photodegradation fluxes. Assumed is: all surface in experimental setup is covered*

with grass, UV-radiation is responsible for 50% of photodegradation fluxes and the laboratory experiment has 20 times more UV-radiation than natural, than 1x0.5x20x60x1000=600.000 nmol m^{-2} min^{-1} photodegradation fluxes can be expected.
***Right figure**: Zoom in of left figure.*
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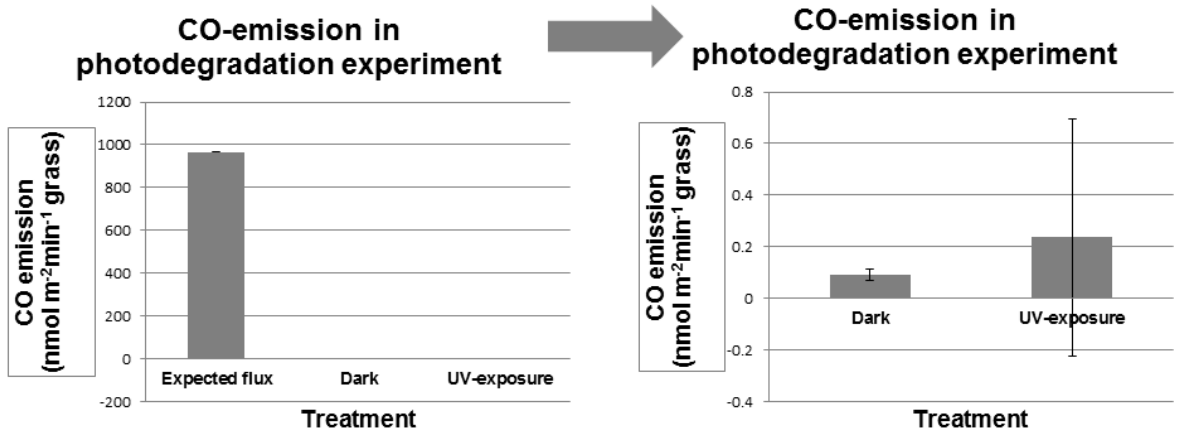

***Left figure**: Measured average CO emission under 'Dark treatment' (no radiation) or 'UV exposure' (UV-A and UV-B radiation) in comparison to expected photodegradation fluxes. Schade (1999) measured photodegradation CO fluxes of approximately 1.6 nmol m^{-2} s^{-1} ($100*10^9$ molecules cm^{-2} s^{-1}) under normal radiation. Assumed is: all surface in experimental setup is covered with grass, UV-radiation is responsible for 50% of photodegradation fluxes and the laboratory experiment has 20 times more UV-radiation than natural, than 1.6x0.5x20x60=960 nmol m^{-2} min^{-1} can be expected.*
***Right figure**: Zoom in of left figure.*

P2442 L4 I assume that these are the "bare soil" locations as displayed on Figure 2.

This has been clarified in the manuscript.

P2442 L10 While I accept that rainfall events do lead to flushes of CO_2 from soil, some of the rainfall events were between chamber shifts, so some of the post-rain flushes may have been emphasised by a shift in the chamber to one of the 6 locations which may have had a naturally slightly higher flux.

We believe that the majority of the sudden CO_2 flux increase is due to the rain event, for the following reasons:

- During the days after the rain event (especially the nights), the fluxes were strongly going down while measuring on one fixed location. This was not observed before. Also, the same sudden increase was visible in the leaking chamber (not shown).
- A sudden higher uptake of CO was observed, indicating an enhanced biological activity.
- The enhanced biological CO uptake as well as the increased CO_2 respiration was also visible in the FG data (see new Figure 1 and 7).

Technical comments Anonymous Referee #1

We thank the referee for the extended comments which were very useful. They are implemented into the reviewed manuscript and not further discussed here.