Author’s response to Anonymous Referee #2

We would like to thank the anonymous referee #2 for his/her interest in our study and his/her helpful comments, which have largely contributed to improve our manuscript. Below, we have responded on the comments point by point.

General comments anonymous referee #2

This discussion paper examines the CO_2 and CO emissions from photo- and thermal degradation in an Italian grassland. Results from the laboratory experiment suggest that previous studies may have overlooked the importance of thermal degradation in contributing CO_2 and CO emissions. It is also one of the first few that attempted to measure radiation-induced CO_2 and CO fluxes in field. They concluded that previous studies may have overestimated the role of photodegradation. Data that support this conclusion, however, were relatively weak: photodegradation-induced flux was only measured in field for three days; only one pair of transparent and opaque chambers was used; the UV transmission of the gas chamber was poor (~50%). I suggest the authors to systematically discuss the limitations of their experiment.

A limitation-discussion is added to the Discussion-part of the manuscript (in Paragraph 4.1, last part of ‘Photo and thermal degradation’ and in Paragraph 4.2, last part of ‘Photo and thermal degradation’). In here, the following details are discussed:

- The (UV-) transmission of the flux chambers (§4.1);
- The relevance of the ecosystem for photodegradation measurements and the possible influence of respiration fluxes (§4.1);
- The warming effect of chamber design and implications for thermal degradation measurements (§4.2);
- The comparison of FG and FC thermal CO emissions (§4.2).

These subjects are also discussed in this Author’s response, as answers to the referee’s questions.

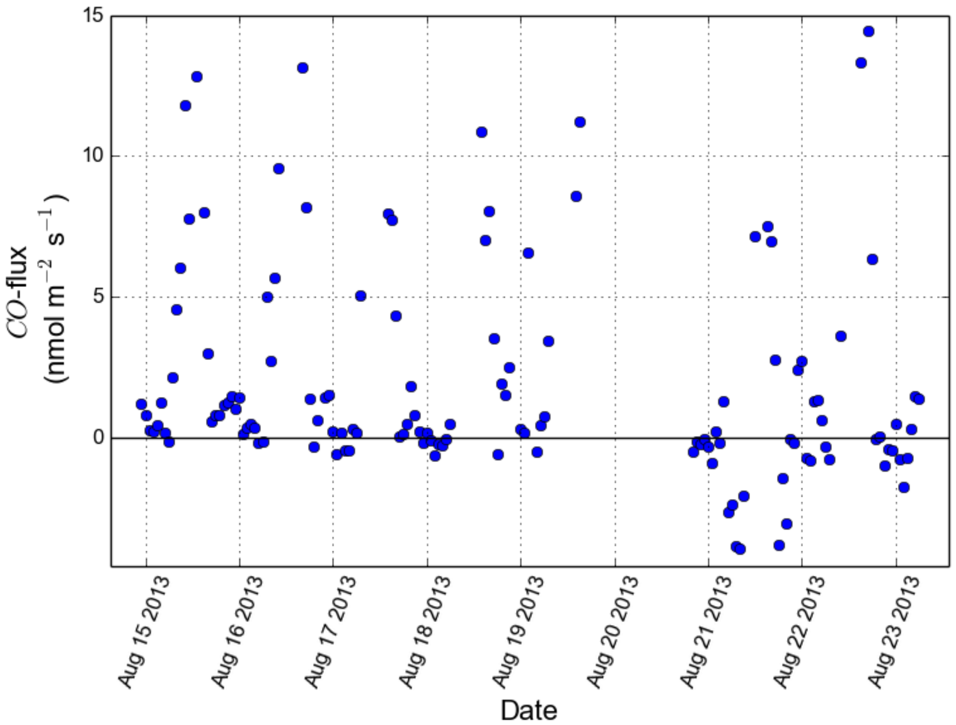
In this current form, the paper appears a bit too long. I find the data from eddy covariance and flux gradient less relevant to the questions on photo- and thermal degradation. I suggest the authors to cut down the related methods and results. One possibility is to briefly summarize the findings of these two methods in the materials and methods and move figure 1 to the supplementary materials.

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:

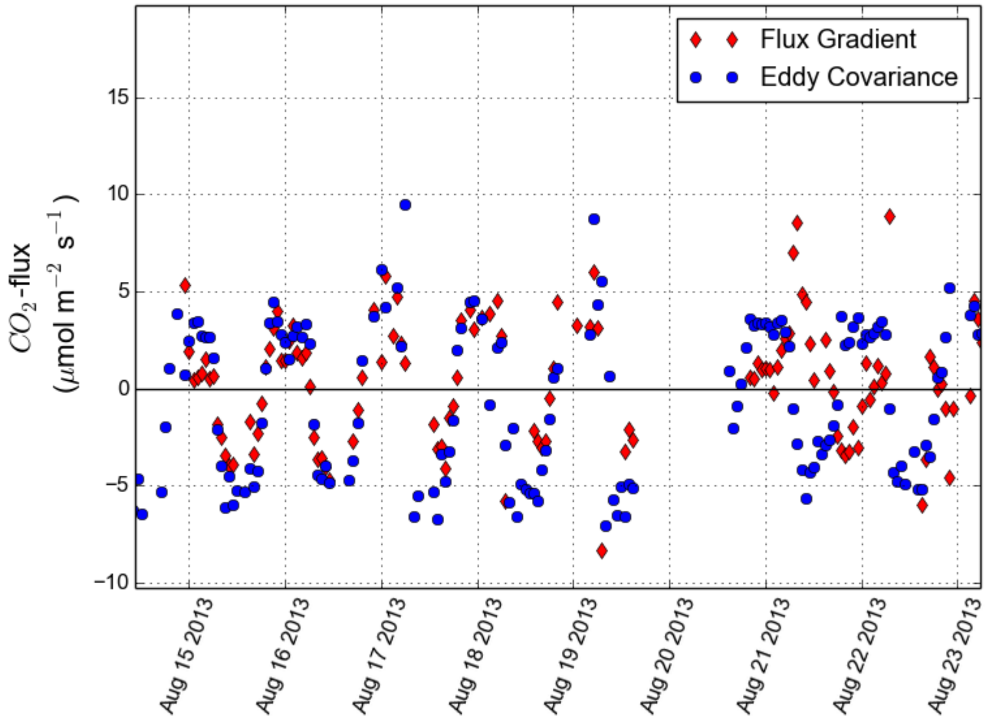
- show the comparability of the FG measurements to the EC measurements, which might be of interest when studying the FG CO flux measurements;
- show that the ecosystem was not (yet) in dormant state, wherefore direct comparison between chamber and FG (for the assessment of photodegradation) was not possible,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

<u>**Specific comments anonymous referee #2**</u>

The advised corrections have been taken over and implemented in the revised manuscript. Here we answer to the posed questions.

The authors consider the study site as an arid ecosystem. I find the site wetter than most arid ecosystems. Its annual precipitation was high, and CO_2 uptake can be found in the middle of the dry season.

The following information has been included in the limitation-discussion:

- The field site is located in a Mediterranean climate zone. The annual precipitation is 755 mm, however, this mostly falls in autumn and winter, causing the region to have arid characteristics in summer: no precipitation falls for several weeks, above ground vegetation dies or is in dormant state and the upper soil layers, especially the soil surface, are dried out.

What if this study was conducted in a drier ecosystem? Would photodegradation-induced flux be more prominent in drier environment, given that background soil respiration would be low? The authors should consider addressing these questions in the discussion.

The following information has been included in the limitation-discussion:

- The studied process, photodegradation, takes place at the surface. The surface in our ecosystem has the characteristics of an arid ecosystem (dry, constant radiation exposure, dead organic matter at the surface). Therefore we consider this ecosystem suitable and representative for measuring photodegradation in an arid ecosystem.

- The absolute amounts of photodegradation fluxes, which are taking place on the arid surface, are not influenced by the still existing respiration flux. The expected rates of photodegradation fluxes (as observed in earlier studies of 1 µmol m^{-2} s^{-1}) should have been detectable, even when mixed with respiratory fluxes.
- We agree that if deeper layers would have been dried out more, respiration would have been lower and therefore possible photodegradation fluxes would be more prominent, but this does not mean that the photodegradation fluxes cannot be measured otherwise.

P2436L8: Glass is not effective in transmitting UV radiation. Thus, radiation-induced fluxes (both photo- and thermal degradation) can be under-estimated. How was UV "transparency" measured? Any information on the spectrum of the transmitted radiation? Did glass transmit more UVB than UVA?

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.

P2437L21: Was the pair of chamber moved among the 6 chamber locations during the 3-day period? Indicate the dates that were included in the 3-day period.

This has been clarified in the Methodology section of the revised manuscript, the following information has been added:

- The chambers were not moved during the 3-day period, which was between 5-8 August. The days before (3-5), they were on the same locations, but then both still transparent.

P2438L13: How much radiation was received by samples? Several key details about the laboratory experiment were missing. How long were these experiments conducted at a given temperature? How were the laboratory chamber sealed? What were the dimensions of the chamber? Did grass/soil samples cover the entire chamber? What type of grass was used?

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.

Did photodegradation experiments include soil?

No, the photodegradation experiments did not include soil, for the following reasons:

- 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.

P2440L10: I would be very interested to see a figure with fluxes (transparent vs opaque) plotted against time during the 3-day period.

A plot of the fluxes during the 3-day period is shown below. The transparent chamber is indicated by the red squares. The chamber which was covered by aluminum foil, is indicated green before covering, and black after covering.

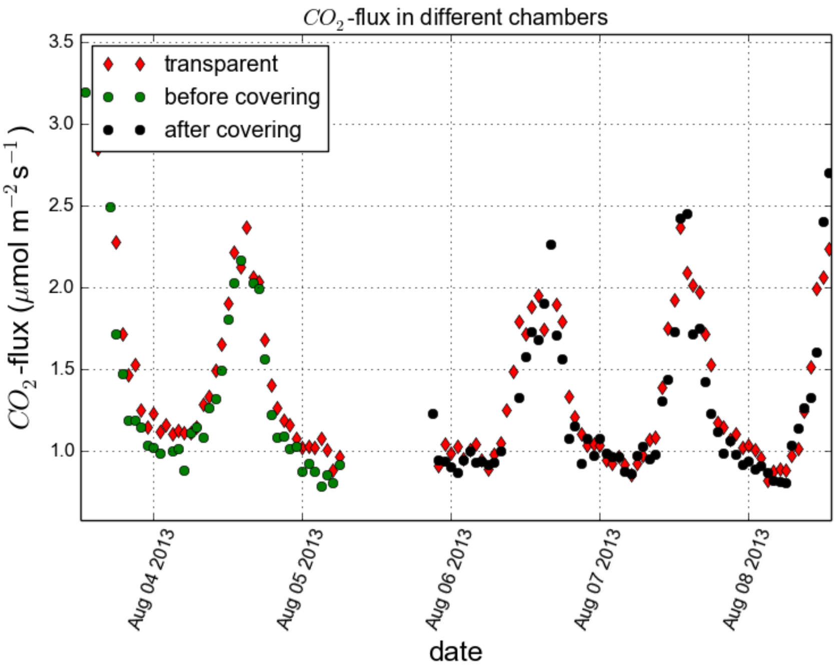


Figure: CO_2-flux data over 5 days. On 5th of August, one chamber was covered, this moment is indicated by change of color of markers.

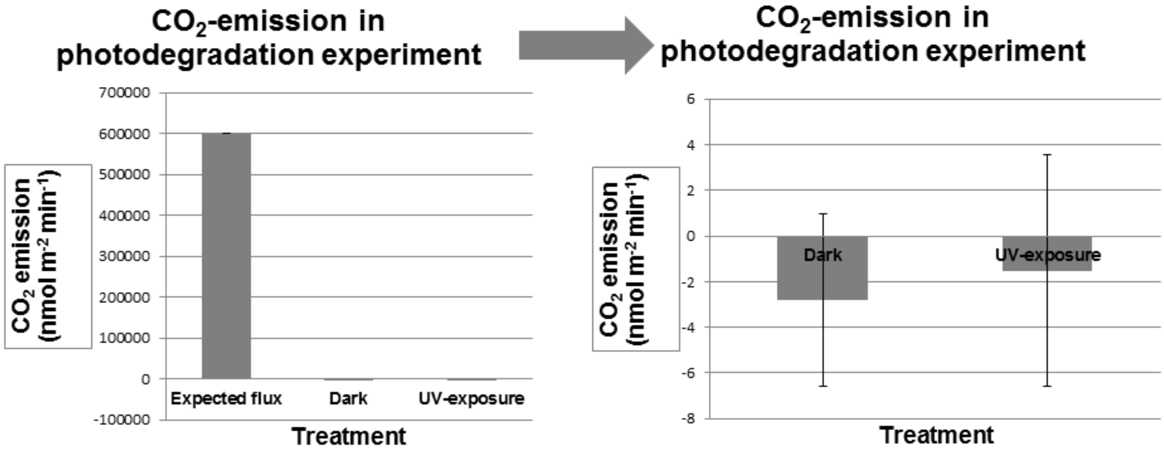
P2441L18-20: Data that supported this important finding were not presented. The laboratory experiment also manipulated the amount of samples and the type of radiation. However, none of these results were presented. Does it mean that neither factors had significant impacts?

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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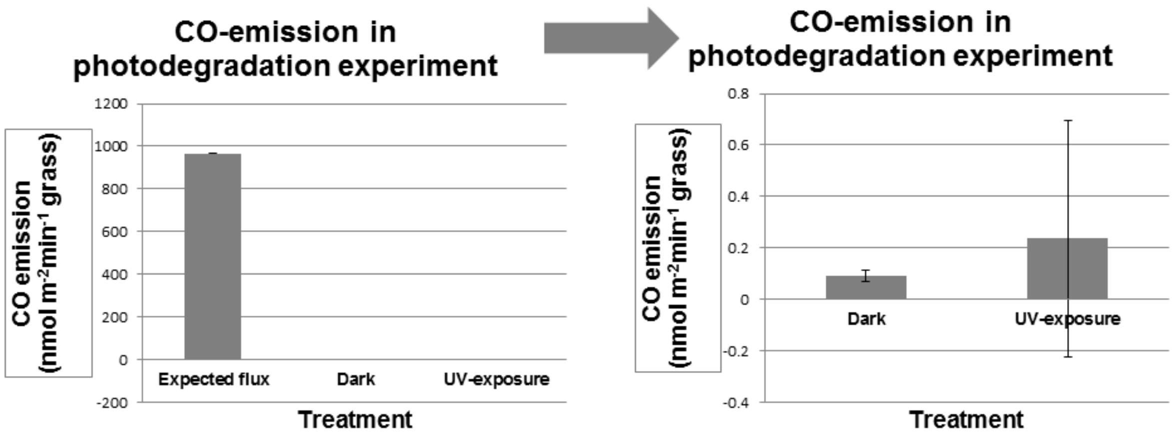

***Left figure**: Measured average CO emission under 'Dark treatment' (no radiation) or 'UV exposure' (UV-A and UV-B radiation) in comparison to expected photodegradation fluxes. Schade (1999) measured photodegradation CO fluxes of approximately 1.6 nmol m^{-2} s^{-1} ($100*10^9$ molecules cm^{-2} s^{-1}) 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.*

P2442L11: The increase of fluxes after rain events was not obvious to me. It appears that the first week of the field campaign had relatively low CO_2 production compared to the following weeks (Figure 2). Because these data were used to examine photodegradation, it could be important to discuss reasons for this phenomenon,

- Figure 2 shows a small increase in the chamber CO_2 fluxes after the rain event, which is not obvious during the day but clear during the night. Another observation is the increase in CO-uptake, which is enhanced after the rain event, indicating that the biological activity in the soil was restricted by soil water levels.
- A new Figure 1 and Figure 7 (Supplementary Materials) have been added to the manuscript and to this document. In Figure 7, FG CO_2 fluxes before and after the rain event are shown. It is visible that, after the rain event, the CO_2 respiration at night increases and that the net CO_2 uptake during the day is smaller (more buffered by respiration). It seems therefore that respiration was restricted by low soil water levels. Photosynthesis fluxes seem less dependent on low soil water levels, probably due to deep roots.
- An increase in soil CO uptake is also observed in the FG measurements (new Figure 1), indicating that the increased chamber soil CO uptake is not a spatial chamber shift artifact.

- The spatial and temporal heterogeneity was considered. When studying photodegradation, the locations measured with the opaque and transparent chamber were first analyzed for comparability, as can be seen in the third figure of this document. During these days (3-8 August) temporal variation is expected to be small since temperatures were stable and no precipitation had fallen (Figure 2).

- As the reviewer points out, Figure 2 shows lower fluxes in the beginning of the experiment (red markers). We hypothesize this is because of spatial differences. However, the second time the same location was measured, this was right after a large rain event, wherefore this theory cannot be validated.

P2443L10: What does the plus and minus sign mean?

The plus and minus notation is changed and an explanation is added to the manuscript:

- The plus and minus were used to indicate an estimate. The estimate was based on rough numbers (from Lee 2012), taking into account the type of material (C4-grass), the mass (2 grams) and the temperature and emission as read from Lee 2012 (graph 2A, 15 µmol m^{-2} min^{-1} at 55 °C). This results in approximately 125 nmol m^{-2} min^{-1}

P2443L22-25: Again, many citations here were not appropriate.

- The citations are checked and corrected.

P2444L5: both CO uptake and emission

- This has been corrected

P2444L17: an abiotic

- This has been corrected

P2445L25-: This paragraph repeated the results and can be reworked.

- This paragraph has been rewritten

2336L3-5: This one also seems repetitive.

- This paragraph has been rewritten

P2446L16-: This paragraph did not directly discuss thermal production of CO. The sentences on the FG vs FC comparisons could be merged with the paragraph at P2444L5-16.

This paragraph has been rewritten and merged with the limitation-discussion.