Hella van Asperen
University of Bremen
Otto-Hahn-Allee 1
D-28203 Bremen
v_asperen@iup.physik.uni-bremen.de

June 1, 2015

Dear Trevor Keenan,

Hereby we would like to submit the revised manuscript of ‘The role of photo- and thermal degradation for CO_2 and CO-fluxes in an arid ecosystem'

In the following PDF-document, the following information can be found:

- Authors response to Referee 1 (page 2-12)
- Authors response to Referee 2 (page 13-21)
- Track change document with LatexDif (page 22-54)

In the authors response parts, the issue raised by the referee is printed in **bold and small size**. The answers and proposed changes are given in normal font.

Since some issues were raised by both referee's, some parts of the text appear as well in 'Authors response to Referee 1' as in 'Authors response to Referee 2'.

Thank you for your consideration,
With kind regards,

Hella van Asperen (on behalf of the co-authors)

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

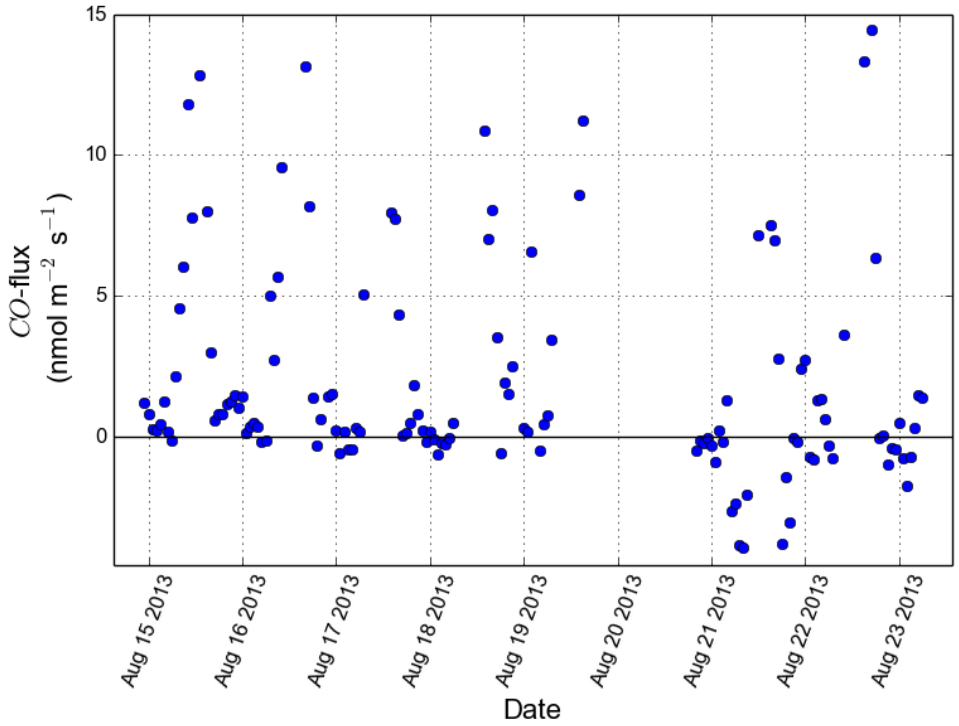
The paper is well written and summarises a lot of data from a range field and lab studies. It is novel in that is uses a range of CO_2 and CO measurement techniques to investigate photodegradation in the field (though only for three days) and the laboratory. The findings of the work are interesting and 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:

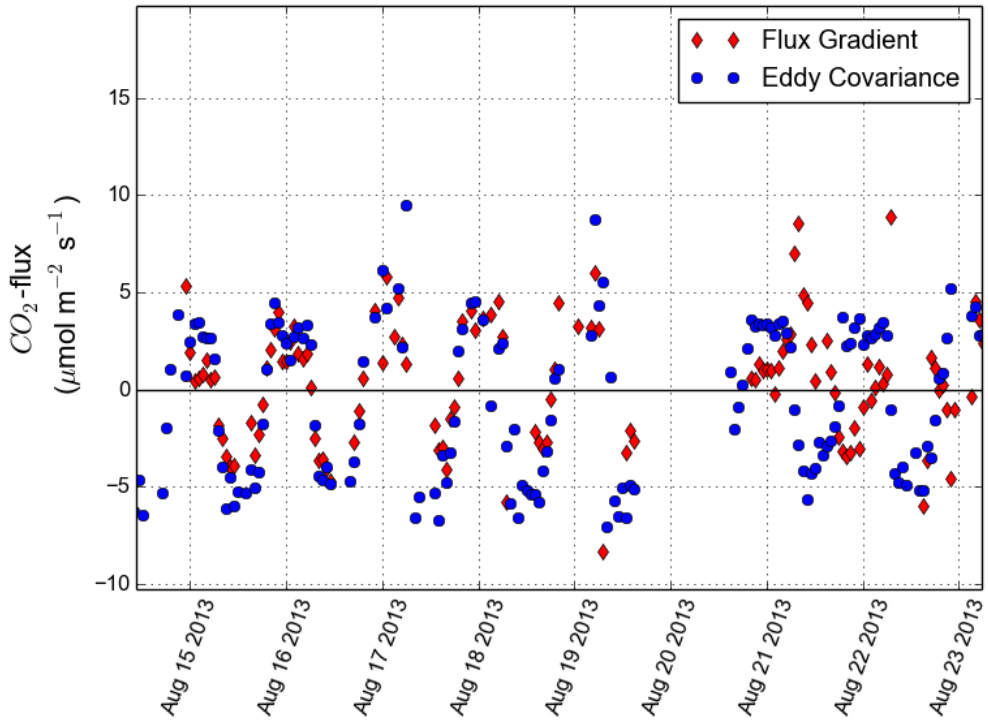
- show the comparability of the FG measurements to the EC measurements, which might be of interest when studying the FG CO flux measurements;
- show that the ecosystem was not (yet) in dormant state, wherefore direct comparison between chamber and FG (for the assessment of photodegradation) was not possible,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

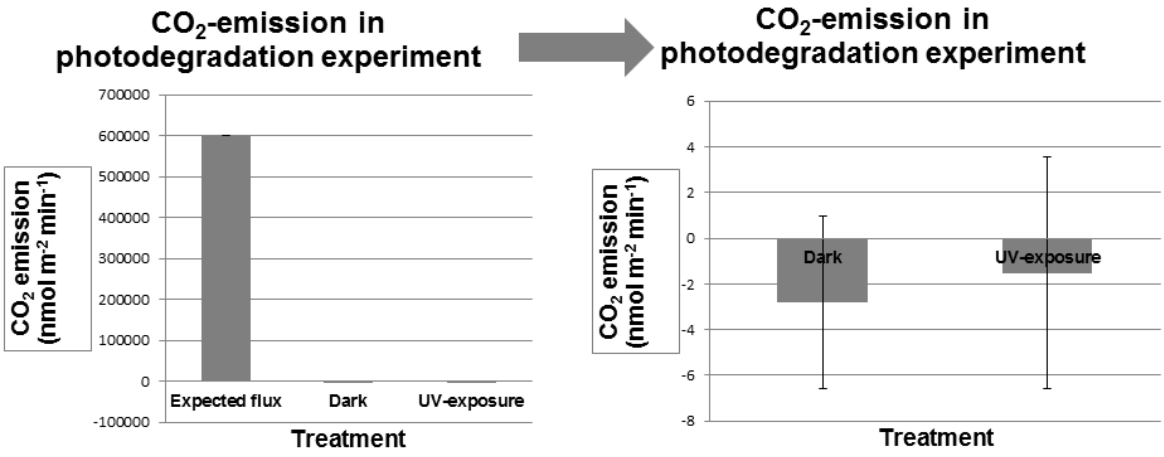
P2441 L17 Why is the data for the laboratory photodegradation experiment not shown? I would have liked to have seen the data for this. At the very least, "data not shown" should have been in this sentence.

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.

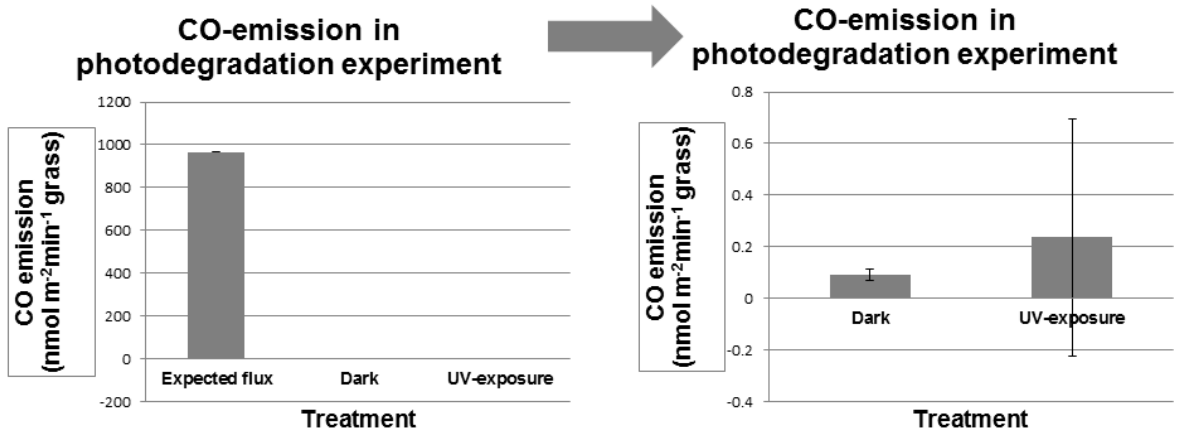
Below the figure, a comparison with expected values (based on previous studies) is made.

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.*
.



***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.

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.

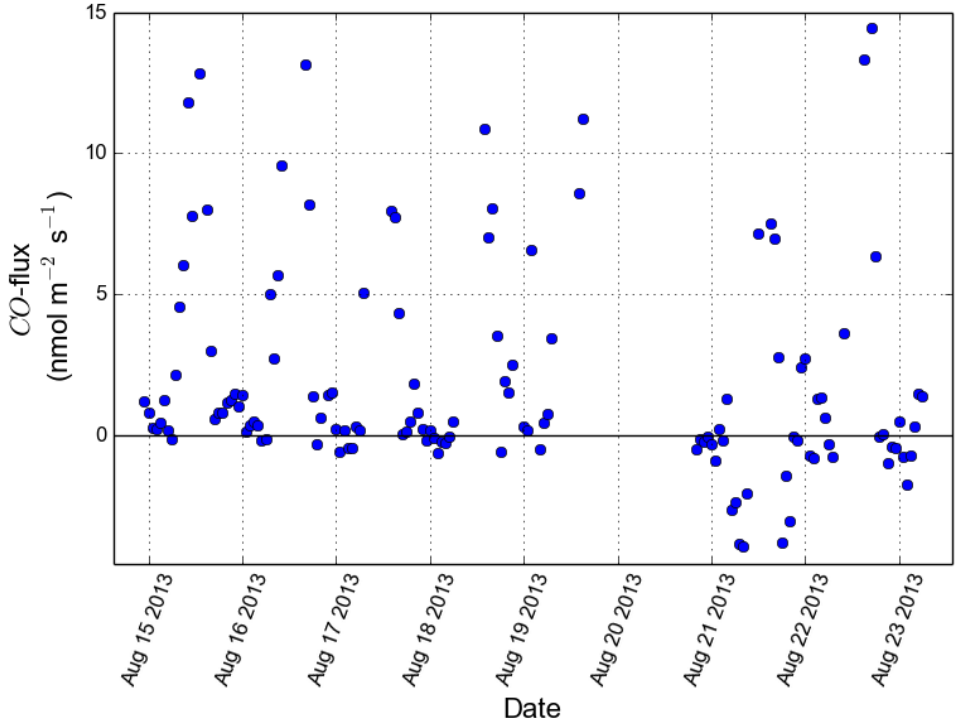
In this current form, the paper appears a bit too long. I find the data from eddy covariance and flux gradient less relevant to the questions on photo- and thermal degradation. I suggest the authors to cut down the related methods and results. One possibility is to briefly summarize the findings of these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

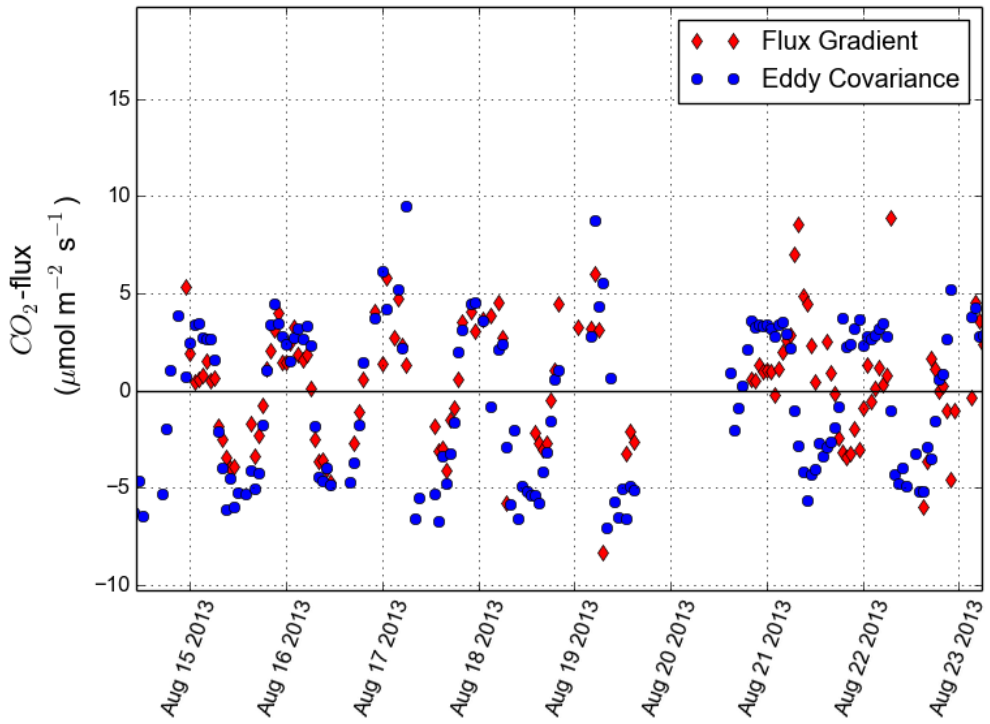
- show the comparability of the FG measurements to the EC measurements, which might be of interest when studying the FG CO flux measurements;
- show that the ecosystem was not (yet) in dormant state, wherefore direct comparison between chamber and FG (for the assessment of photodegradation) was not possible,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

Specific comments anonymous referee #2

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.

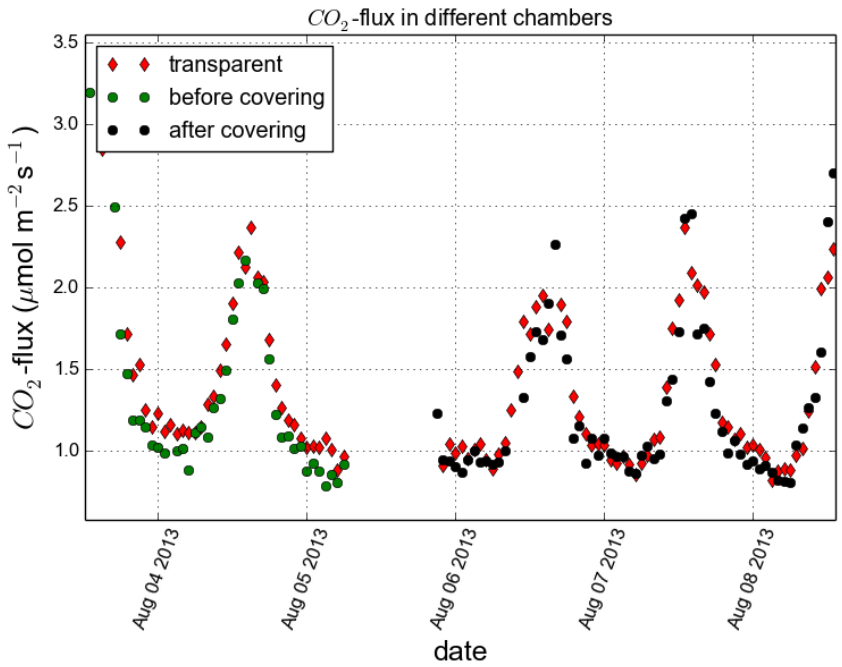


Figure: CO_2-flux data over 5 days. On 5th of August, one chamber was covered, this moment is indicated by change of color of markers.

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?

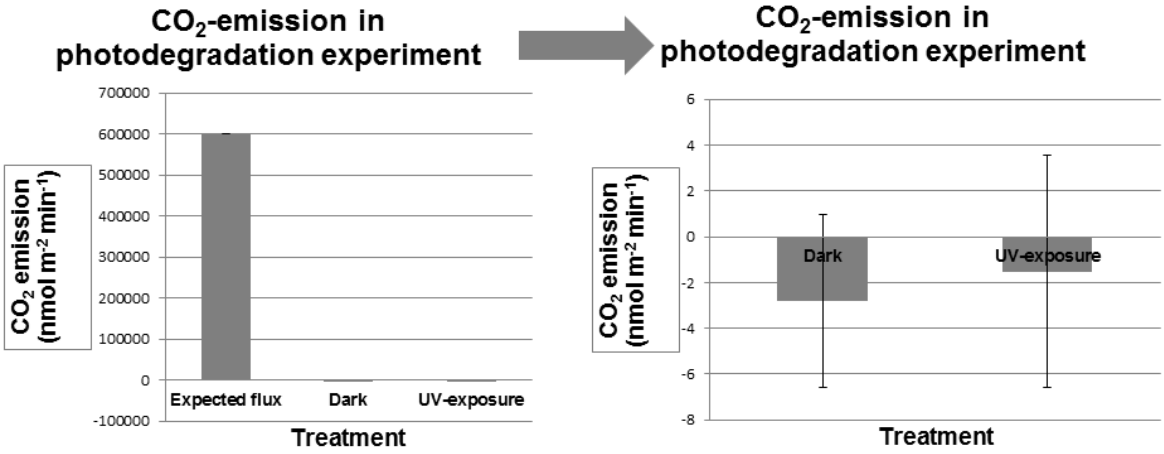
In this author's response, we have added graphs of the laboratory photodegradation measurements (see below).

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.

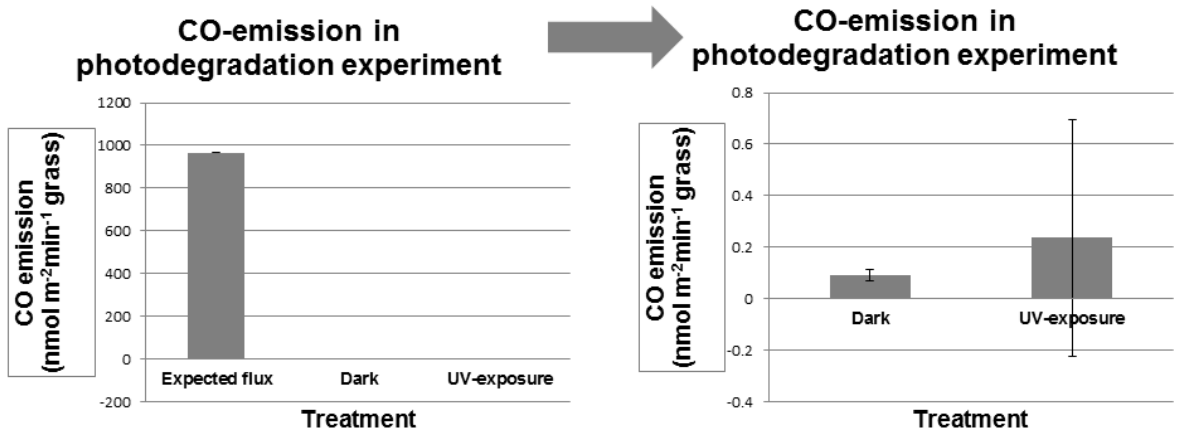
In the laboratory, no (significant) photodegradation fluxes were observed, independent of type of radiation (A or B) or the type of material (different grasses were tried, not shown). An increase in amount of grass increased the CO_2 emission both in dark and UV conditions, indicating a remaining respiration 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.*

.



***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.

Manuscript prepared for Biogeosciences Discuss.
with version 2014/09/16 7.15 Copernicus papers of the LaTeX class copernicus.cls.
Date: 2 June 2015

The role of photo- and thermal degradation for CO_2 and CO fluxes in an arid ecosystem

H. van Asperen[1], T. Warneke[1], S. Sabbatini[2], G. Nicolini[2,3], D. Papale[2], and J. Notholt[1]

[1]Institute of Environmental Physics, University of Bremen, Otto-Hahn-Allee 1, Bremen, 28359, Germany
[2]Department for innovation in biological agro-food and forest systems, University of Tuscia, via S. Camillo de Lellis s.n.c., 01100 Viterbo, Italy
[3]EuroMediterranean Center on Climate Changes – Impacts on Agriculture, Forest and Natural Ecosystem Division (IAFENT), 01100 Viterbo, VT, Italy

Correspondence to: H. van Asperen (v_asperen@iup.physik.uni-bremen.de)

Abstract

Recent studies have suggested the potential importance of abiotic degradation in arid ecosystems. In this study, the role of photo- and thermal degradation in ecosystem CO_2 and CO exchange is assessed. A field experiment was performed in Italy using a FTIR-spectrometer coupled to a flux gradient system and to flux chambers. In a laboratory experiment, field samples were exposed to different temperatures and radiation intensities.

No photodegradation-induced CO_2 and CO fluxes were found in the field ~~and~~ nor in the laboratory study. In the laboratory, ~~thermal degradation fluxes for~~ we measured CO_2 and CO ~~have been observed~~fluxes that were derived from thermal degradation. In the field experiment, CO uptake and emission have been ~~observed~~ measured and are proposed to be a result of biological uptake and abiotic thermal degradation-production.

We suggest that previous studies, ~~studying~~ addressing direct photodegradation, have overestimated the role of photodegradation and observed fluxes might be due to thermal degradation, which is an indirect effect of radiation. The potential importance of abiotic decompostion in the form of thermal degradation, especially for arid regions, should be considered in future studies.

1 Introduction

CO_2 is the main carbon species being exchanged between biosphere and atmosphere and the most important anthropogenic greenhouse gas. CO is a less abundant non-greenhouse gas but considered important in the climate debate due to its oxidation process with atmospheric OH^- (Stocker et al., 2013). Yearly, terrestrial ecosystems exchange approximately 120 Pg of carbon with the atmosphere (Stocker et al., 2013).

Arid ecosystems account for approximately 40 % of land area and 20 % of the soil carbon pool but are still an unknown factor in climate models (Lal, 2004). In recent studies, the possible importance of abiotic degradation for

arid regions, such as photo- and thermal degradation, has been recognized ~~(Rutledge et al., 2010; King et al., 2012; Austin and Vivanco, 2006)~~ (Austin and Vivanco, 2006; K

1.1 Ecosystem CO_2 fluxes; photo- and thermal degradation

Photodegradation is the direct breakdown of organic matter by radiation. Photodegradaton is known to be an important pathway in aquatic ecosystems (Zepp et al., 1998). Recently, the possible importance of photodegradation in terrestial ecosystems has been suggested ~~(Brandt et al., 2010; Rutledge et al., 2010; Friedlingstein et al., 2006; Austin and Vivanco, 2006)~~ (Photodegradation can play an important role in arid ecosystems, where microbial decomposition is restricted ~~(Austin and Vivanco, 2006; Brandt et al., 2010; Lee et al., 2012; Throop and Archer, 2009; Lin an~~ Rutledge (2010) estimated that in arid ecosystems, 19 % of the annual CO_2 flux is induced by photodegradation and, in dry summer conditions, even 92 % of daytime CO_2 emissions can be attributed to this process.

Photodegradation is attributed to UV as well as ~~well UV radiation as to visible radiation (Brandt et al., 2010; Austin and Vivanco, 2006; Bruhn et al., 2009)~~ visible radiation (Austin and Vivanco, 2006; Brandt et al., 2010; Bruhn et al., 2009) . The biochemical mechanisms behind photodegradation-induced carbon fluxes are not clear; it is proposed that solar radiative energy breaks down the bonds of carboxyl, directly producing CO_2 and other gas species (Lee et al., 2012). ~~Assumed is~~ It has been hypothesized that rates of photodegradation ~~are dependent~~ depend on plant and litter tissue type: lignin, one of the most recalcitrant tissue in plant material (to microbial decompostion), is expected to be most sensitive to photodegradation (Austin and Ballaré, 2010; King et al., 2012). However, while studies reporting photodegradation are multiple, recent studies, aiming to further investigate the process, were unable to observe ~~photodegradation-induced carbon fluxes (Lambie et al., 2014; Uselman et al., 2011; Kirschbaum et al., 2011)~~ the effects of photodegradation (Kirschbaum et al., 2011; Lambie et al., 2014; Uselman et al., 2011) . A reason for this discrepency has not yet been found ~~(Kirschbaum et al., 2011; Uselman et al., 2011; Lambie et al., 2014; Throop and Archer, 2007)~~ (K

It is important to notice that in literature, the term photodegradation is sometimes also used for the indirect effects of radiation on decomposition. One example is microbial faciliation: radiation breaks down organic compounds into smaller molecules, which are then easier degradable for microbes. For a review on studies done on photodegradation, please see King et al. (2012).

A less studied abiotic degradation pathway is thermal degradation, the temperature dependent degradation of carbon in absence of radiation and possibly oxygen ~~(Lee et al., 2012; Schade et al., 1999; Derendorp et al., 2011)~~ (Derendorp et al., 2011; Lee et al., However, photodegradation is considered the more dominant abiotic CO_2 producing process (Lee et al., 2012). Besides CO_2, ~~also~~ CO and CH_4 are also reported as products of photo- and thermal degradation ~~(Schade et al., 1999; Lee et al., 2012; Tarr et al., 1995; Derendorp et al., 2011; Vigano et al., 200~~

1.2 Ecosystem CO fluxes; photo- and thermal degradation

The role of CO in soils and ecosystems is not well understood. Soils are known for being sources as well as ~~well a source as a sink for~~ sinks of CO (Conrad, 1996). Most likely, the main cause for soil CO uptake is the oxidation of CO to CO_2 or CH_4 by soil bacteria or soil enzymes ~~(Ingersoll et al., 1974; Conrad, 1996; Spratt and Hubbard, 1981; Yonemura et al., 2000; Whalen e~~ Soil CO consumption is found to be dependent on atmospheric CO concentrations and the consumption rate is usually expressed in deposition velocity: the uptake rate divided by the CO concentration (Conrad and Seiler, 1982; Kisselle et al., 2002).

Soil CO emissions have also been reported and are thought to be of non-biological origin (Conrad and Seiler, 1980, 1982). For example, soil CO emissions were found in peatlands (Funk et al., 1994) and in arid soils (Conrad and Seiler, 1982). Living plants are also known to emit a small amount of CO ~~(Kirchhoff et al., 1990; Bruhn et al., 2013; Tarr et al., 1995)~~ (Bruhn et al., 2013; Kirchhoff et al., 19 However, senescent plant material has been shown to emit 5 to 10 times more ~~(Tarr et al., 1995; Schade et al., 1999; Derendorp et al., 2011) ; these~~ than

photosynthesising leaf material (Derendorp et al., 2011; Schade et al., 1999; Tarr et al., 1995). These fluxes, mostly determined in laboratory studies, were attributed to thermal degradation and, to a larger extent, ~~to~~ photodegradation (Derendorp et al., 2011; Lee et al., 2012; Schade et al., 1999).

1.3 Measurement of photo- and thermal degradation

Studying photodegradation is difficult due to the multiple (indirect) effects radiation has on total ~~(biological)~~ biological decomposition. For example, ~~UV radiation~~ UV-radiation is known to inhibit microbial processes, to change (senescent) tissue chemistry and to ~~shift~~ alter the dominating microbial and fungal communities, thereby affecting microbial decomposition rates in both directions ~~(Uselman et al., 2011; Formánek et al., 2014; Zepp et al., 1998; Williamson et al., 1997)~~ (Formán Differentiating photodegradation-induced fluxes from biological sources in field experiments can be achieved by comparison of different flux measurement techniques such as Eddy Covariance (EC) measurements vs. flux chamber measurements and/or soil gradient measurements, in ~~where~~ that one method does not receive solar radation (Rutledge et al., 2010). This approach requires that the areas or footprints sensed by the different techniques ~~(footprint)~~ are fully homogeneous, which is not often the case and hard to validate. To study ~~photodegradation, also flux chamber systems~~ the effects of photodegradation (in field or laboratory), also radiation filters can be used ~~, each with a different amount of radiation exposure (Lee et al., 2012; Brandt et al., 2010; Lin and King, 2014)~~ to expose samples to different types or amounts of radiation (Brandt et al., 2010; Lee et al., 2012; Lin and King, 2014) .

Studying the role of thermal degradation-induced carbon fluxes is challenging, especially for CO_2 due to the accompanying effect temperature has on microbial decomposition. To study thermal degradation-induced CO_2 production, microbial decomposition should be absent, which can only be achieved in laboratory studies (Lee et al., 2012).

Previous field and laboratory studies on the role of ~~(in)direct~~ direct or indirect abiotic degradation report very constrasting results

(King et al., 2012; Lambic et al., 2014; Rutledge et al., 2010; Kirschbaum et al., 2011; Uselman et al.,
More specific studies are thus needed to better understand this process and its role in the carbon cycle. In this study, we present the results of field and laboratory measurements aimed to evaluate the role of direct photodegradation and thermal degradation in an arid ecosystem.

2 Materials and methods

2.1 Study site

We performed a field experiment in a grassland (IT-Ro4, harvested cropland, approximately 250 m by 450 m, lat 42.37° N, long 11.92° E, 147 m a.s.l.), in the province of Viterbo, Italy. The climate is Mediterranean, with a typical drought period covering approximately 2 months during summer (July–August). Mean annual temperature is 14 °C and annual rainfall is 755 mm. Such climatic characteristics make the site suitable for abiotic degradation studies. The underlying material is Tuff, soil texture is clay loam and soils are classified as Eutric Cambisol. Yearly, the ~~fieldsite~~ field site is ploughed to a depth of 20 or 50 cm. Just before the experiment, oat and vetch were cultivated. During the experiment, vegetation was not managed and was a mix of invasive species such as *Amaranthus retroflexus*, *Chenopodium* spp., *Conyza Canadensis*, *Artemisia vulgaris*, *Cirsium* spp., *Mercurialis annua* and *Polygonum* spp. The field study was conducted in July–September 2013. At the beginning of the experiment, most vegetation was dried out, however, patches of active vegetation were observed. Temperature and rainfall during measurements were representative for the period (hot and dry) (Fig. 2), however, the preceding spring had been cold and rainy in respect to the average.

IT-Ro4 is an experimental site managed by the University of Tuscia (Viterbo). Continuous EC measurements of scalars and energy fluxes are performed (LI-7500 open path analyzer, Licor, Lincoln, Nebraska, USA; Windmaster Pro sonic anenomemeter, Gill, Hampshire, UK) along with meteorological and environmental measurements (CNR-1, Kipp & Zonen, Delft,

the Netherlands; soil water content, CS616, Campbell Scientific, North Logan, USA; soil temperature, CS107, Campbell scientific, North Logan, USA; soil heat flux, HFT3 Soil Heat Flux Plate, Campbell scientific, North Logan, USA).

2.2 Instrumentation and set up

The analyzer used in this study is based on a Fourier Transform Infrared (FTIR)-spectrometer (Spectronus, Ecotech), for details on the FTIR-analyzer, see Griffith (2012). A FTIR is capable of measuring air concentrations of CO_2, CH_4, N_2O, CO and $\delta^{13}CO_2$ simultaneously. Before being measured, air samples were dried by a nafion dryer and by a column of magnesium perchlorate. Measurements were corrected for pressure and temperature fluctuations and for cross-sensitivities (Hammer et al., 2013). Background measurements and a calibration routine using two standard gas cylinders were performed weekly. We designed an external manifold box which allowed us to connect the FTIR to a flux gradient (FG) setup and to 2 flux chambers (FC), simultaneously. Both methods provide air concentration data as well as flux data. In this paper, only CO_2 and CO flux data are presented.

2.3 Concentration and flux measurements

FG measurements were performed once per hour ~~. Air inlet heights were at 1.3~~ and ~~4.2. Air was sampled at 1. Sampling lines of stainless steel were used for the experiment. For 30, the airflows were led to air sampling bags, after that the bag inlet was closed until analysis. Before the analysis, the FTIR measurement cell was evacuated and flushed twice with measurement air before being filled. Per air sample, a 3-spectra (static) measurement was taken. FG measurements were~~ performed at the same ~~point as of the EC set-up (measurement height at 3.5). By FG method, fluxes can be calculated by:~~

$$F = K\frac{\delta C}{\delta z}$$

~~wherein δC is the difference in concentration of a gas species () between the two inlet heights (δz (m)) and K is the diffusion coefficient (), and F the flux ().K can be parameterized using the data of a sonic anemometer, based on the friction velocity (u-star), the Von Karman-constant, the effective height and the stability factor (ζ) (Foken, 2006) .~~

2.4 ~~The flux chamber technique~~

~~Soil~~ location as the EC tower. More information about the FG system can be found in the Supplementary Materials.

For FC measurements, six soil collars (50 cm × 50 cm) were inserted ~~until~~ to 10 cm depth a week before the start of the experiment. Positions of soil collars were checked for being undisturbed and representative. The two flux chambers (open dynamic chambers, 50 cm × 50 cm × 50 cm, produced by Karlsruhe Institute of Technology, Germany) consisted of a stainless steel frame, ~~glass walls (transparency in UV (280–400) ~ 50, transparency in visible light (400–700~~UV-transparent acrylic sides (Acryl Glass XT solar, 3mm, UV-transparent) ~~~ 90),~~ and a vent tube, and were tightened by use of clamps and rubber air strips. Transparency of the acrylic material was measured and reported to be > 90% in the UV and visible wavelength band (280-700 nm). Two fans per flux chamber were continuously running, insuring well-mixed headspace air. Automatic chamber closure (once per hour) was made possible by use of a pneumatic system regulated by the valve manifold box. Air flow from the flux chambers to the FTIR was initiated by a membrane pump placed behind the measurement cell, set to 1 L min^{-1}. Air flow was measured every 2 min continuously for 20 min in flow mode. Chamber opening and closure was ~~respectively~~ after 4 and 18 min, respectively. Sampling lines from the chambers were of equal size and material and were tested for leaks regularly. Chamber temperatures were recorded by temperature loggers (Voltcraft DL-1181THP). Fluxes were derived from concentration increases after chamber closure, by use of linear regression. Gas fluxes were calculated by:

$$F = \frac{VP}{RST}\frac{\delta C}{\delta t} \quad (1)$$

wherein V is the volume of the chamber (m^3), P the chamber air pressure (Pa), R the gas constant (8.314 m^3 Pa K^{-1} mol^{-1}), S the chamber surface area (m^2), T the chamber air temperature (K) and $\delta C/\delta t$ is the gas concentration change over time (mol mol^{-1} s^{-1}). For flux calculations, only the concentration increases between 2 and 10 min after closure were used. Concentration increases were checked for non-linear trends and, if found, not used. Flux standard deviations were derived from the propagated standard deviations of the regression slope.

When homogeneity in footprint can be assured, micrometeorological and FC methods can be compared and used to study the role of photodegradation. Flux chambers can be shielded from incoming radiation, preventing photodegradation-induced carbon production, while micrometeorological methods capture all fluxes. Comparing the two methods therefore gives an indication of the presence and the magnitude of photodegradation-induced carbon fluxes (Rutledge et al., 2010). The use of this method was planned for our field experiment, but could not be applied due to lack of conformity between flux methods footprints~~; sparse active vegetation (with photosynthetic activity) was only~~, because of sparse photosynthetically active vegetation present in the footprint of the FG technique, causing the methods to be incomparable.

To study photodegradation, two different flux chambers, one with and one without solar radiation exposure, were used. During this experiment, the flux chambers were measuring six fixed chamber locations, chambers were manually moved every few days. One flux chamber was made opaque by use of light excluding aluminium foil (on 5 August). On the days before (~~3–5~~28 July–5 August), ~~the~~ all positions were compared by measuring ~~both~~ the locations with transparent chambers~~; both~~. On 3–5 August, the same locations were measured (with transparent chambers) as on 5–8 August, when one of the two chambers was covered. Both locations showed very similar CO_2 and CO flux patterns. Unfortunately, on 8 August, a leak ~~was introduced~~ has formed in the opaque chamber system, ~~wherefore~~ therefore direct comparison between the two treatments is limited to 3 days. Flux measurements made by the opaque chamber after 8 August are not shown. With blank measurements, the flux chambers were tested for internal CO_2 and/or CO production. No

CO_2 production was found. Minor CO production was found during the day, negligible in comparison to field CO production: values presented in this paper are not corrected for this.

Studying thermal degradation-induced CO_2 production in the field is not possible due to the simultaneous temperature response of biological CO_2 production. For CO, no temperature dependent biological CO production is expected, wherefore measurement of thermal degradation-induced CO production in the field is possible. To study the role of thermal degradation in field CO exchange, chamber temperature sensors were installed, measuring air temperature every minute.

2.4 Laboratory experiment

Two different laboratory experiments were performed to study photo- and thermal degradation. Grass samples (senescent above ground grass material, mix of species as descibred in Methodology, pieces between 20-80 cm, not ground) for the laboratory experiment were taken from the field site~~(senescent above ground grass material) and mixed~~. Mixed soil material samples were taken from the upper 3 cm of the soil, soil samples were not sieved. Both sample types were dried at 35 °C for 72h, to assure microbial activity to be negligible (Lee et al., 2012).

Photodegradation of senescent grass material was studied with a ~~set up~~ system consisting of a metal ~~cylinder with a plexiglass cap~~cylinder, inner diameter=6.5 cm, height=25 cm, area=33 cm^2, with an acrylic cap, which could be closed by screws. Transmittance of cap was measured: 0.2% (250 nm), 6.1% (~~transparent to UV)below an~~ 260 nm), 35.9% (270 nm), 73.9% (280 nm), 89.6% (290 nm) and approximately 94% for larger wavelengths. The cylinders were placed beneath a high intensity (above natural values) UV-A and UV-B source (manufactor instrument: Isitec GmbH, Bremerhaven; UV-A lamp~~(~~: Phillips TL 60W/10R ~~,~~ (peak emission at 375 nm (~~±45~~45 $W\,m^{-2}\,nm^{-1}$)~~, UV-B lamp (~~), UV-B lamp: Phillips TL 40W/12RS ~~,~~ (peak emission at 310 nm (~~±30~~30 $W\,m^{-2}\,nm^{-1}$)~~Isitec GmbH, Bremerhaven). ~~). For comparison, approximate natural UV-A and UV-B levels are 1.2 and 0.6 $W\,m^{-2}\,nm^{-1}$ at these wavelengths respectively. During the experiment, different samples (empty ~~cilinder~~cylinder, 2 gram-sample and 4 gram-sample) were exposed to

different types/amounts of radiation (no radiation, UV-A and/or UV-B radiation). Grass in the cylinders was positioned so that at least 80% of the surface bottom was covered with grass material. During the experiments, air was continuously circulated from the cylinder to the FTIR and measured once per minute; emissions were derived from the measured concentration changes. Cylinder temperatures were monitored by an internal temperature probe (GTH 175/PT, Greisinger Electronics) and remained constant over the experiments (~~21 ± 0.3~~21, sd=0.15 °C). Every ~~experiment was performed twice.~~treatment was performed for 30 minutes and was duplicated.

To study thermal degradation, a glass flask (inner diameter= 6.7 cm, height=16 cm) was placed in a closed loop with the FTIR. For this experiment, only glass and stainless steel materials were used. ~~Grass samples (~~4 grass samples of 2 grams ~~) and soil samples (~~and 4 soil samples of 30 grams ~~)~~ were taken. The grass sample was distributed equally in the flask. The soil sample was not sieved and filled approximately 1 cm (height) of the glass flask. The samples were heated in temperature steps of 5° (20–65 °C) by use of a controlled temperature water bath. Temperature time steps were 20 minutes. During the experiments, air was circulated from the glass flask to the FTIR and measured once per minute~~; emissions~~ . After approximately 3 minutes, a stabilization in the CO production could be observed. Emissions were derived from the measured concentration changes. Glass flask air temperatures were manually measured to check if water bath temperature was representative for grass and soil material temperatures; after 5 min, the glass flask air temperature had reached the same temperature as the water. All experiments were performed in duplicate and in dark conditions.

In the results sections, the given regression coefficients from polynomial fits are the explained sum of squares divided by the total sum of squares.

3 Results

3.1 ~~Flux gradient measurements~~

During the field campaign (3 August–11 September, 2013), total precipitation was 15 mm and air temperatures ranged between 13 and 43 °C (see Fig. 2). Soil water content, measured at 10 cm depth was 18 % (VWC) and decreased less than 1 % over the experiment. ~~FG measurements were done at the same location as EC measurements. During day time, footprint analysis showed that 90 of the source area of the EC signal came from within 150, from within the grassland area. Since the FG method is measuring at the same location and height, it is expected that daytime FG fluxes mainly originate from the grassland area as well. During nighttime, footprint analysis showed fluxes mainly originating from outside the grassland.~~

3.1 Flux measurements

FG CO_2 fluxes ~~ranged between −7 and 8 (Fig. 1).~~ are shown in the Supplementary Materials. FG CO uptake (up to 1 nmol m^{-2} s^{-1}) and emission (up to 2 nmol m^{-2} s^{-1}) at night were ~~observed~~measured (Fig. 1). During the day, large ($\geq$ 10 nmol m^{-2} s^{-1}) CO emissions were ~~visible~~ recorded (Fig. 1). Based on the 31 days of FG measurements, ~~net ~ 42 (±30)~~on average net 42 nmol CO m^{-2} per day ~~is~~ was estimated to be emitted.

3.2 ~~Flux chamber measurements~~

~~Air temperatures,~~

FC CO_2 and FC CO fluxes of the transparent flux chamber can be seen in Fig. 2, rain events and incoming solar radiation are indicated. FC CO_2 fluxes showed a diurnal pattern with small emissions at night (1 µmol m^{-2} s^{-1}) and higher emissions during the day (up to 8 µmol m^{-2} s^{-1}). Large rain events on 20 and 27 August (6.6 and 2 mm) caused a short

increase in chamber CO_2 fluxes. Locations without organic surface material (indicated as 'bare soils' in Fig 2) showed slightly lower CO_2 ~~(~~and CO ~~)~~ fluxes.

At night, CO uptake of maximum 0.8 nmol m^{-2} s^{-1} was observed. During the day, emissions up to 3 nmol m^{-2} s^{-1} were observed. Over the course of the experiment, nightly CO uptake was continuously decreasing. The rain events caused a clear increase in nightly CO uptake, after which the decreasing continued (~~Fig.~~ Figs. 1 and 2). Based on 36 days of FC measurements, net ~~~ 8 (±1.2)~~on average net 8 nmol CO m^{-2} per day ~~is~~ was estimated to be emitted.

3.2 Photo- and thermal degradation

Photodegradation was studied by comparing opaque and transparent chamber measurements of three days (5–8 August) and by analysis of transparent FC data of a period in August (period with fixed location, stable weather conditions and no precipitation). Analysis of different periods (different locations with similar conditions) showed similar patterns.

Possible photo- and/or thermal degradation-induced CH_4 fluxes are not shown or evaluated here: FG CH_4 fluxes were too small for dependency analysis and CH_4 chamber fluxes mostly showed uptake, indicating a different process than ~~thermal- or photodegradation~~photo- or thermal degradation.

3.2.1 CO_2 fluxes

Figure 3 shows the CO_2 fluxes (of transparent and opaque chamber) vs. air temperatures (Fig. 3a) and chamber temperatures (after 6 min closure, Fig. 3c). FC measurements showed very weak dependency on soil temperatures at 10 cm (data not shown). Blocking radiation showed no distinguished impact on measured CO_2 fluxes. Chamber CO_2 fluxes correlate well with air temperatures and less with chamber temperatures (Fig. 3a and c). Chamber coverage had an effect on chamber temperatures; during daytime hours, the opaque chamber temperature differed up to 10 °C from the transparent chamber temperature.

3.2.2 CO fluxes

A clear effect of chamber coverage on CO fluxes was visible; transparent chamber fluxes were ~~significantly~~ higher during the day. FC CO fluxes correlate better with chamber temperatures than with air temperatures (Fig. 3b and d).

Figure 4 shows CO fluxes in the transparent chamber vs. air temperatures (Fig. 4a), chamber temperatures (after 6 min closure, Fig. 4b) and amount of solar radiation (Fig. 4c) for a period in August. Again, CO fluxes relate best to chamber temperatures, and less to air temperatures and amount of incoming radiation (Fig. 4).

A temperature dependent biological CO uptake curve was fitted over chamber temperature data from (cold) night conditions (when abiotic fluxes are assumed to be minimal) and extrapolated to warmer temperatures. For biological CO uptake, a Q10-value from literature of 1.8 was chosen (Whalen and Reeburgh, 2001). An abiotic thermal degradation Q10-curve was fitted, also based on chamber temperature data, with a fitted Q10-value of 2.1. The sum of both processes agrees well the observed field CO ~~emissions~~ fluxes ($R^2 = 0.85$, Fig. 5).

3.2.3 Laboratory experiment

In the laboratory, exposure of senescent plant material from the field site to high intensity ~~UV radiation~~ UV-radiation did not result in increased CO_2 or CO fluxes in comparison to measurements performed in dark conditions (data not shown).

Grass and soil material samples exposed to different temperatures, under dark conditions, showed significant CO_2 production during lower temperatures ($< 40\,^{\circ}C$) and displayed small CO_2 emissions at higher temperatures ($> 55\,^{\circ}C$) (Fig. 6a). For CO, clear thermal production was found, exponentially increasing with higher temperatures (Fig. 6b). A Q10-value of 2.14 ~~(senecest grass material)~~ for senescest grass material and 2.00 ~~(soil material)~~ for soil material was found to fit best to the observed laboratory thermal degradation CO fluxes (Fig. 6b).

4 Discussion

4.1 CO_2 fluxes

EC and FG measurements showed that the arid grassland was not yet in dormant state; significant CO_2 uptake was observed during the day (Fig. 7). FC CO_2 measurements, performed on locations without photosynthetic active vegetation, solely showed positive CO_2 fluxes, with peak emissions during the day up to $8\,\mu mol\,m^{-2}\,s^{-1}$. Figures 3a and 4a show that CO_2 fluxes mostly relate to air temperatures, and poorly relate to soil temperatures (not shown). Expected is that most CO_2 production takes place close to the surface where the temperature follows air temperatures closer than it follows soil temperatures at 10 cm depth. In the ~~flux chambers~~ecosystem, the rain events resulted in an increase in CO_2 production for several days, showing the typical water-dependent response of arid ecosystem respiration (Fig. 2 and 7).

Photo- and thermal degradation

~~The simultaneous use of opaque and transparent chambers was employed to study the effect of radiation on carbon fluxes in the field. Blocking radiation had no visible effect on field chamber fluxes (Fig. 3a and c). flux measurements performed on bare soil locations seemed lower than other locations; senescent surface material seemed to contribute to total fluxes (Fig. 2b). However, only 3of bare soil measurements are available and no opaque chamber measurements on bare soil are present, wherefore comparison is restricted.~~

In the thermal degradation laboratory experiment, CO_2 production from ~~senecest~~ senescest plant and soil material was observed during lower temperatures (20–40 °C), indicating remaining biological activity, even after drying. Above 50 °C, an increasing CO_2 production was observed with increasing temperatures, therefore expected to be (partly) of non-biological origin. Possible abiotic CO_2 production of ~~±3~~approximately 3 $nmol\,min^{-1}\,gr^{-1}$ for ~~senecest~~ senescest grass material was observed. Extrapolating the thermal production rates of the senescent grass material to field conditions (assuming

200 gr of ~~senecest~~ senescest plant material per m^2 at 55 °C), would result in a minor flux of 0.01 µmol m^{-2} s^{-1}~~(~~, in comparison to observed field fluxes of ~~> 1~~ > 1 µmol m^{-2} s^{-1}~~)~~. Based on the observations in the laboratory, it is expected that the soil material also produces thermal degradation-induced CO_2 fluxes. However, considering the relative cold and wet conditions of the ~~subsurface~~ *sub*surface soil material in the field~~(~~, compared to laboratory conditions and to surface temperatures~~), expected is~~ , it is expected that soil thermal degradation fluxes are minor in comparison to soil biological fluxes.

Other studies have observed thermal degradation-induced CO_2 fluxes with higher rates (~~±100~~approximately 125 nmol CO_2 gr^{-1} min^{-1} for C3-grass at 55 °C), but also at lower temperatures (Lee et al., 2012). We can not verify this observation for our field material. Based on our observations, we propose that under *natural* conditions, when soil surface temperatures and especially soil subsurface temperatures rarely exceed 55 °C, thermal degradation-induced CO_2 fluxes do not play an important role in comparison to biological production, even in arid regions such as our study area.

We observed that chamber design can ~~significantly~~ strongly influence chamber temperatures: during mid-day, the opaque and transparent chamber temperatures could differ up to 10 °C. As observed in the laboratory experiment, *unnatural* high temperatures might lead to abiotic thermal CO_2 production. A research ~~set up~~ methodology aiming at measuring photodegradation can unintentionally result in high surface temperature levels, which could lead to unrepresentative high abiotic CO_2 production estimates.

The simultaneous use of opaque and transparent chambers was employed to study the effect of radiation on carbon fluxes in the field. Blocking radiation had no visible effect on field chamber CO_2 fluxes (Fig. 3a and c). CO_2 flux measurements performed on bare soil locations (soils without organic surface material) seemed lower than other locations; senescent surface material seemed to contribute to total CO_2 fluxes (Fig. 2b). However, only 3 days of bare soil measurements are available and no opaque chamber measurements on bare soil are present, therefore comparison is restricted.

The flux chambers, which were used to assess photodegradation, had a transparency of 90% or higher in the UV-B, UV-A and visible wavelength band. For our field experiment, we can therefore conclude that no large direct photodegradation fluxes (as measured by Rutledge (2010) of 1 μmol m^{-2} s^{-1}) have been induced by natural sunlight intensities.
In the laboratory experiment, field site grass samples received above natural-intensity UV-radiation over the entire UV-wavelength band (280-400 nm). In this experiment, no direct photodegradation fluxes were observed from field site grass material. The results from the laboratory experiment support the conclusion from the field experiment that direct photodegradation fluxes in the field site are not as important as suggested by a previous study (Rutledge et al., 2010) .

The experiment was conducted on a field site situated in a Mediterranean climate. Based on annual precipitation and on measured respiration values, the ecosystem might seem too wet to be suitable to measure arid ecosystem processes. However, the climate is known for the precipitation free summers with high irradiation, causing the soil surface and surface materials to be fully dried out in summer. Since photodegradation is taking place at the soil surface, the ecosystem can be considered suitable for the assessment of this arid ecosystem process. The absolute amounts of possible photodegradation fluxes are not influenced by the respiration fluxes. The expected rates of photodegradation fluxes (of 1 μmol m^{-2} s^{-1}, (Rutledge et al., 2010)) should have been detectable, even when mixed with respiratory fluxes.

Similar as what has been found by Kirschbaum et al. (2011); Lambie et al. (2014); Uselman et al. (2011), we did not ~~find photodegradation-induced fluxes in the field as well as~~ observe the effects of photodegradation in field nor in the laboratory: no *direct* photodegradation-induced CO_2 fluxes have been observed. This is in contrast to other photodegradation ~~(field)~~ studies, which have ~~observed photodegradation fluxes (Lee et al., 2012; Rutledge et al., 2010; King et al., 2012)~~ reported photodegradation fluxes in field (Rutledge et al., 2010) or in the laboratory (Lee et al., 2012) . Potential explanations for this difference are: (a) the used field methodology in ~~previous studies~~

the previous study was not suitable for measuring ~~(direct)~~ direct abiotic degradation fluxes; (b) the role and significance of photodegradation differs per material and per field site or (c) studies might (partly) have misinterpreted thermal degradation fluxes as photodegradation fluxes. However, as shown, the magnitude and the potential importance of thermal degradation-induced CO_2 fluxes in arid ecosystems are still unknown.

4.2 CO fluxes

During the measurement period, both CO uptake ~~as emission has~~ and emission have been observed by the FG method (patches of green active vegetation inside the footprint) as well as by the FC method (no photosynthetic active vegetation contributing to the fluxes) (Figs. 1 and 2). CO exchange measurements from FG and FC differed largely, most likely caused by the difference in footprint.

During the night, uptake of up to $1\,\mathrm{nmol\,m^{-2}\,s^{-1}}$ of CO was observed, which is most likely caused by microbial oxidation to CO_2 or CH_4 ~~(Ingersoll et al., 1974; Conrad, 1996; Spratt and Hubbard, 1981; Yonemura et al., 2000; Whalen e~~ The CO uptake was decreasing over time but a rain event caused an enhanced uptake for some days (Figs. 1 and 2). Soil biota being responsible for the CO uptake seems plausible since the effect of drought (decreasing uptake over time) and the effect of the rain (enhanced uptake) indicate a biological process. Nevertheless, with solely biological CO uptake taking place, one would expect higher uptake during warmer temperatures and no CO emission~~should be observed. Expected is a abiotic counteracting production process taking place simultaneously , "buffering" the~~ . It is expected that an abiotic process occurs simultaneously with the biotic uptake of CO, leading to a "buffering" effect on CO uptake. For this reason, CO deposition velocities could not be calculated.

Photo- and thermal degradation

We propose that the observed CO emissions in the flux chambers are caused by thermal degradation.

FG measurements showed CO emissions during the day as well as during the night, indicating that CO is not (solely) produced by photodegradation (Fig. ~~1b~~1). By means of opaque chamber measurements, ~~significant~~ lower CO fluxes~~(~~, in comparison to transparent chamber measurements~~) were measured~~, were detected. However, as described before, FC temperatures were strongly affected by the blocking of solar radiation. Analysis of CO fluxes showed a strong correlation with FC temperatures, and no relationship with radiation input, indicating that not the absence of radiation, but the indirect effect on temperature caused the ~~significant~~ lower CO emissions (Figs. 3 and 4).

FC CO fluxes were ranging between -1 and $2.5\,\mathrm{nmol\,m^{-2}\,s^{-1}}$ and only originated from soil or surface litter, since photosynthetic active vegetation was absent. Measured CO emissions are higher than reported for CO emissions from living plants and similar to values found for ~~senecest plant material (Bruhn et al., 2013; Zepp et al., 1998; Schade et al., 1999; Derendorp et al., 2011; Lee et al., 201~~ plant material (Bruhn et al., 2013; Derendorp et al., 2011; Lee et al., 2012; Schade et al., 1999; Z However, the measurements are a cumulative signal of uptake and emission and can therefore not be compared directly to other studies.

In the laboratory experiment, ~~in~~ where grass from the ~~fieldsite~~ field site was exposed to above natural intensity ~~UV-radiation~~UV-radiation, no photodegradation-induced CO fluxes were observed. However, significant thermal degradation-induced fluxes from the ~~senecest field site~~ senescest grass and soil material were measured, ~~visible already~~ even measureable at low temperatures (20 °C). At 50 °C, a thermal CO production rate of ~~senecest~~ senescest grass material of $0.13\,\mathrm{nmol\,min^{-1}\,gr^{-1}}$ was found. Extrapolating this observation to field conditions (assuming 200 grams of ~~senecest~~ senescest plant material per m^2 at 50 °C), would result in a flux of ~~±0.4~~approximately 0.4 $\mathrm{nmol\,m^{-2}\,s^{-1}}$, which is approximately 5 times lower than the ~~measured (net)~~ net measured field CO fluxes. Ex-

trapolating the thermally-induced CO production rate of the soil material to field conditions would result in an estimated production of ~~1~~approximately 1 nmol m^{-2} s^{-1} ~~by~~ from the upper 3 cm of the soil during a summer day. However, while this estimate indicates that abiotic thermal soil CO production indeed might play a major role, for accurate estimates for net soil ~~CO~~ CO uptake or emission, more information about biological ~~CO~~ CO uptake and about the soil profile is needed.

The observed field chamber CO fluxes are suggested to be a cumulative signal of biological uptake ~~(taking place in the soil)~~ and abiotic thermal degradation~~(taking place in the soil and on the surface). The sum of both processes was~~ . Both processes were fitted over chamber temperatures~~($R^2 = 0.84$). For~~ . For the fitting of biological CO uptake, a Q10-value of 1.8 was ~~used (based on literature values). To reproduce the observed field chamber~~ chosen (Whalen and Reeburgh (2001) . To match the cumulative measured CO fluxes ~~, a~~ (purple diamonds in Fig. 5), a higher Q10-value ~~(~~of 2.1 ~~) for~~ for the abiotic thermal soil CO production was fitted ($R^2 = 0.85$).

The laboratory measurements were used to ~~experimentally~~ *experimentally* determine the Q10-value of thermal degradation-induced CO fluxes. Q10-values of 2.14 for senescent grass and 2.00 ~~were found which~~ for soil material were measured. These values are similar to the ~~fitted~~ Q10-value ~~for thermal degradation~~ which was fitted for the thermal degradation process to match the cumulative field measurements, as described in the previous paragraph (Fig. ~~5.~~5).

The soil CO uptake process, taking place below the surface, is subject to buffered chamber temperatures, and therefore the chosen Q10-value might be an underestimation. Also, the biological soil uptake is not expected to follow the Q10-temperature response at higher temperatures ($> 35\,^{\circ}C$). Nevertheless, the difference in temperature response (as a consequence of different Q10-values or as a consequence of buffered temperatures) causes biological CO uptake to be dominant during colder (chamber) temperatures, and thermal degradation to be dominant during warmer (chamber) temperatures. During our field experiment, thermal degradation started to be dominant from approximately 25 °C (chamber temperature) and followed an exponentional curve with higher temperatures

(Fig. 5).

~~Average net (uptake and emission)~~ 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 ~~exchange estimates from FG and FC measurements differed significantly. The difference is most likely caused by several factors. In the FG footprint, relatively more (higher) dead vegetation was present~~ 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 FG technique. FG CO emissions were higher, likely due to its footprint which contained relatively more dead vegetation (thermal degradating material) since, for practical reasons, the chambers were placed over ~~low~~ lower dead vegetation. Also, the FG footprint contained active vegetation, which is another possible CO emitting source (Bruhn et al., 2013).~~Furthermore, the flux chambers block some incoming radation (due to the frame and the glass, leading to lower exposure to radiation than in natural conditions) but also have shown to increase chamber air temperatures, with an unknown overall effect. Nevertheless,~~

Overall, the measurements show that the field site is a net source of CO during the summer months, affecting the atmospheric chemistry, at least at plant level, via OH^- depletion. More field measurements on ~~(annual)~~ annual CO exchange are needed to better understand the role of thermal degradation in CO ~~(~~and CO_2 ~~)~~ exchange in arid regions.

5 Conclusions

In our field and laboratory experiment, direct photodegradation-induced CO_2 and CO fluxes have not been observed. Based on laboratory experiments, the production of thermal

degradation-induced CO_2 is expected, but only significant under unnaturally high temperatures. In the laboratory, thermal degradation-induced CO fluxes were clearly observed, also at relatively low temperatures (20 °C). In the field, ~~as well~~ biological CO uptake as well as abiotic CO production was observed; abiotic CO production is assumed to be mainly a product of thermal degradation. The Q10-value of the CO producing thermal degradation process, as determined in the laboratory, agrees well with the fitted Q10-value for abiotic CO fluxes measured at the ~~fieldsite~~field site.

Not all litter types are reported to be sensitive to photodegradation, which could explain why we did not measure photodegradation-induced fluxes. Also, we realize that in field conditions, partitioning thermal degradation from photodegradation is challenging. We therefore do not exclude the existence of photodegradation. However, in our field experiment in an arid ecosystem, we were not able to observe any direct photodegradation-induced carbon fluxes, showing that direct photodegradation does not play a major role in this arid ecosystem. Previous studies suggesting the occurrence of major photodegradation fluxes might possibly have neglected thermal degradation fluxes, which is an indirect effect of radiation. The potential importance of abiotic decomposition in the form of thermal degradation, especially for arid regions, should be considered and be studied in more detail.

Acknowledgements. We are grateful for the support of InGOS (European Communitiy Seventh Framework Programme (FP7/2007-2013)) for funding the field experiment. Also, we would like to thank TTorch who supported the author in an exchange stay at University of Tuscia (TTORCH ESF Exchange Grant, part of the ESF "Tall Tower and Surface Research Network for Verification of Climate Relevant Emissions of Human Origin"-project). We would also like to thank the ESSReS Research School, part of the Helmholtz Centre for Polar and Marine Research. We thank Alessio Boschi, Michele Tomassucci and Sipko Bulthuis for their help during the field experiment. Furthermore, we would like to thank Tommaso Chiti for his help taking the soil samples, Stefano Ponziani for providing field data and Annika Wieferich for her additional experiments in the laboratory. Thanks is also extended to the two anonymous reviewers whose comments helped improve our manuscript.

6 Supplementary materials

Flux Gradient method

FG measurements were performed once per hour. Air inlet heights were at 1.3 and 4.2 m. Air was sampled at 1 L min^{-1}. Sampling lines of stainless steel were used for the experiment. For 30 min h^{-1}, the airflows were led to air sampling bags, after that the bag inlet was closed until analysis. Before the analysis, the FTIR measurement cell was evacuated and flushed twice with measurement air before being filled. Per air sample, a 3 min-spectra (static) measurement was taken. FG measurements were performed at the same point as of the EC set-up (measurement height at 3.5 m). During day time, footprint analysis showed that 90 % of the source area of the EC signal came from the grassland area within 150 m. Since the FG method is measuring at the same location and height, it is expected that daytime FG fluxes mainly originate from the grassland area as well. During nighttime, footprint analysis showed fluxes mainly originating from outside the grassland. FG CO_2 fluxes agreed well with EC fluxes and ranged between -7 and 8 µmol m^{-2} s^{-1} (Fig. 7)
By using the FG method, fluxes can be calculated by:

$$F = K\frac{\delta C}{\delta z} \tag{2}$$

wherein δC is the difference in concentration of a gas species (mol m^{-3}) between the two inlet-heights (δz (m)) and K is the diffusion coefficient (m^2 s^{-1}), and F the flux (mol m^{-2} s^{-1}). K can be parameterized using the data of a sonic anemometer, based on the friction velocity (u-star), the Von Karman-constant, the effective height and the stability factor (ζ) (Foken, 2006) .

References

Austin, A. T. and Ballaré, C. L.: Dual role of lignin in plant litter decomposition in terrestrial ecosystems, P. Natl. Acad. Sci. USA, 107, 4618–4622, 2010.

Austin, A. T. and Vivanco, L.: Plant litter decomposition in a semi-arid ecosystem controlled by photodegradation, Nature, 442, 555–558, 2006.

Bartholomew, G. and Alexander, M.: Microbial metabolism of carbon monoxide in culture and in soil., Appl. Environ. Microb., 37, 932–937, 1979.

Brandt, L., King, J., Hobbie, S., Milchunas, D., and Sinsabaugh, R.: The role of photodegradation in surface litter decomposition across a grassland ecosystem precipitation gradient, Ecosystems, 13, 765–781, 2010.

Bruhn, D., Mikkelsen, T. N., Øbro, J., Willats, W. G. T., and Ambus, P.: Effects of temperature, ultraviolet radiation and pectin methyl esterase on aerobic methane release from plant material, Plant Biol., 11, 43–48, 2009.

Bruhn, D., Albert, K. R., Mikkelsen, T. N., and Ambus, P.: UV-induced carbon monoxide emission from living vegetation, Biogeosciences, 10, 7877–7882, doi:10.5194/bg-10-7877-2013, 2013.

Conrad, R.: Soil microorganisms as controllers of atmospheric trace gases (H_2, CO, CH_4, OCS, N_2O, and NO), Microbiol. Rev., 60, 609–640, 1996.

Conrad, R. and Seiler, W.: Role of microorganisms in the consumption and production of atmospheric carbon monoxide by soil, Appl. Environ. Microb., 40, 437–445, 1980.

Conrad, R. and Seiler, W.: Arid soils as a source of atmospheric carbon monoxide, Geophys. Res. Lett., 9, 1353–1356, 1982.

Derendorp, L., Quist, J., Holzinger, R., and Röckmann, T.: Emissions of H_2 and CO from leaf litter of *Sequoiadendron giganteum*, and their dependence on UV radiation and temperature, Atmos. Environ., 45, 7520–7524, 2011.

Foken, T.: Angewandte Meteorologie, Springer, Berlin, Heidelberg, 2006.

Formánek, P., Rejšek, K., and Vranová, V.: Effect of elevated CO_2, O_3, and UV radiation on soils, The Scientific World Journal, 730149, doi:10.1155/2014/730149, 2014.

Friedlingstein, P., Cox, P., Betts, R., Bopp, L., Von Bloh, W., Brovkin, V., Cadule, P. Doney, S., Eby, M., Fung, I., Bala, G.,John, J.,Jones, C., Joos F., Kato, T., Kawamiya, M., Knorr, W., Lindsay, K., Matthews, H. D., Raddatz, T., Rayner, P., Reick, C., Roeckner, E., Schnitzler, K.-G., Schnur, R., Strassman, K., Weaver, A. J., Yoshikawa, C., and Zeng, J.: Climate-carbon cycle feedback analysis: Results from the C4MIP model intercomparison, J. Climate, 19, 3337–3353, 2006.

Funk, D. W., Pullman, E. R., Peterson, K. M., Crill, P. M., and Billings, W.: Influence of water table on carbon dioxide, carbon monoxide, and methane fluxes from taiga bog microcosms, Global Biogeochem. Cy., 8, 271–278, 1994.

Griffith, D. W. T., Deutscher, N. M., Caldow, C., Kettlewell, G., Riggenbach, M., and Hammer, S.: A Fourier transform infrared trace gas and isotope analyser for atmospheric applications, Atmos. Meas. Tech., 5, 2481–2498, doi:10.5194/amt-5-2481-2012, 2012.

Hammer, S., Griffith, D. W. T., Konrad, G., Vardag, S., Caldow, C., and Levin, I.: Assessment of a multi-species in situ FTIR for precise atmospheric greenhouse gas observations, Atmos. Meas. Tech., 6, 1153–1170, doi:10.5194/amt-6-1153-2013, 2013.

Ingersoll, R., Inman, R., and Fisher, W.: Soil's potential as a sink for atmospheric carbon monoxide, Tellus, 26, 151–159, 1974.

King, J. Y., Brandt, L. A., and Adair, E. C.: Shedding light on plant litter decomposition: advances, implications and new directions in understanding the role of photodegradation, Biogeochemistry, 111, 57–81, 2012.

Kirchhoff, V. W., Da Silva, I., and Browell, E. V.: Ozone measurements in Amazonia: dry season versus wet season, J. Geophys. Res.-Atmos., 95, 16913–16926, 1990.

Kirschbaum, M. U., Lambie, S. M., and Zhou, H.: No UV enhancement of litter decomposition observed on dry samples under controlled laboratory conditions, Soil Biol. Biochem., 43, 1300–1307, 2011.

Kisselle, K. W., Zepp, R. G., Burke, R. A., de Siqueira Pinto, A., Bustamante, M., Opsahl, S., Varella, R. F., and Viana, L. T.: Seasonal soil fluxes of carbon monoxide in burned and unburned Brazilian savannas, J. Geophys. Res.-Atmos., 107, LBA–18, 2002.

Lal, R.: Carbon sequestration in dryland ecosystems, Environ. Manage., 33, 528–544, 2004.

Lambie, S., Kirschbaum, M., and Dando, J.: No photodegradation of litter and humus exposed to UV-B radiation under laboratory conditions: No effect of leaf senescence or drying temperature, Soil Biol. Biochem., 69, 46–53, 2014.

Lee, H., Rahn, T., and Throop, H.: An accounting of C-based trace gas release during abiotic plant litter degradation, Glob. Change Biol., 18, 1185–1195, 2012.

Lin, Y. and King, J. Y.: Effects of UV exposure and litter position on decomposition in a California Grassland, Ecosystems, 17, 158–168, 2014.

Rutledge, S., Campbell, D. I., Baldocchi, D., and Schipper, L. A.: Photodegradation leads to increased carbon dioxide losses from terrestrial organic matter, Glob. Change Biol., 16, 3065–3074, 2010.

Schade, G. W., Hofmann, R.-M., and Crutzen, P. J.: CO emissions from degrading plant matter, Tellus B, 51, 889–908, 1999.

Smith, W. K., Gao, W., Steltzer, H., Wallenstein, M., and Tree, R.: Moisture availability influences the effect of ultraviolet-B radiation on leaf litter decomposition, Glob. Change Biol., 16, 484–495, 2010.

Spratt, H. G. and Hubbard, J. S.: Carbon monoxide metabolism in roadside soils, Appl. Environ. Microb., 41, 1192–1201, 1981.

Stocker, T. F., Qin, D., Plattner, G.-K., Tignor, M., Allen, S. K., Boschung, J., Nauels, A., Xia, Y., Bex, V., and Midgley, P. M.: Climate change 2013: The Physical Science Basis, Intergovernmental Panel on Climate Change, Working Group I Contribution to the IPCC Fifth Assessment Report (AR5), Cambridge Univ. Press, New York, 2013.

Tarr, M. A., Miller, W. L., and Zepp, R. G.: Direct carbon monoxide photoproduction from plant matter, J. Geophys. Res.-Atmos., 100, 11403–11413, 1995.

Throop, H. L. and Archer, S. R.: Interrelationships among shrub encroachment, land management, and litter decomposition in a semidesert grassland, Ecol. Appl., 17, 1809–1823, 2007.

Throop, H. L. and Archer, S. R.: Resolving the dryland decomposition conundrum: some new perspectives on potential drivers, in: Progress in Botany, Springer, Berlin, Heidelberg, 171–194, 2009.

Uselman, S. M., Snyder, K. A., Blank, R. R., and Jones, T. J.: UVB exposure does not accelerate rates of litter decomposition in a semi-arid riparian ecosystem, Soil Biol. Biochem., 43, 1254–1265, 2011.

Vigano, I., van Weelden, H., Holzinger, R., Keppler, F., McLeod, A., and Röckmann, T.: Effect of UV radiation and temperature on the emission of methane from plant biomass and structural components, Biogeosciences, 5, 937–947, doi:10.5194/bg-5-937-2008, 2008.

Whalen, S. and Reeburgh, W.: Carbon monoxide consumption in upland boreal forest soils, Soil Biol. Biochem., 33, 1329–1338, 2001.

Williamson, C. E., Metzgar, S. L., Lovera, P. A., and Moeller, R. E.: Solar ultraviolet radiation and the spawning habitat of yellow perch, *Perca flavescens*, Ecol. Appl., 7, 1017–1023, 1997.

Yonemura, S., Kawashima, S., and Tsuruta, H.: Carbon monoxide, hydrogen, and methane uptake by soils in a temperate arable field and a forest, J. Geophys. Res.-Atmos., 105, 14347–14362, 2000.

Zepp, R. G., Callaghan, T., and Erickson, D.: Effects of enhanced solar ultraviolet radiation on biogeochemical cycles, J. Photoch. Photobio. B, 46, 69–82, 1998.

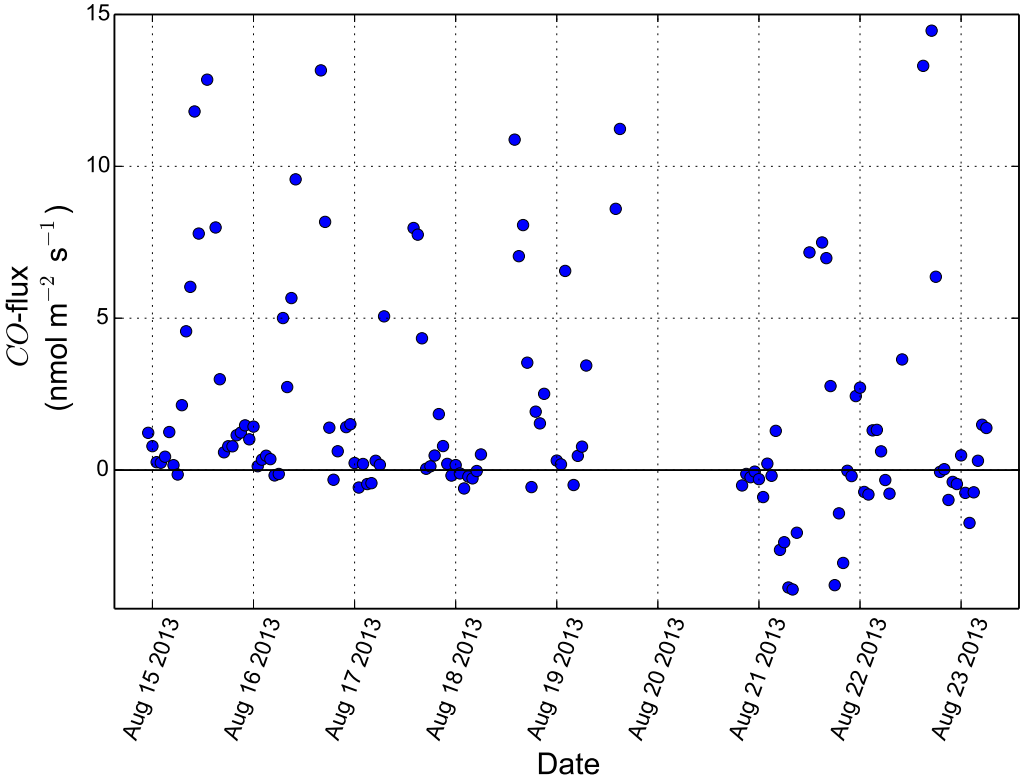


Figure 1. Flux Gradient CO measurements over 8 days in August. A large rain event took place on 20 August.

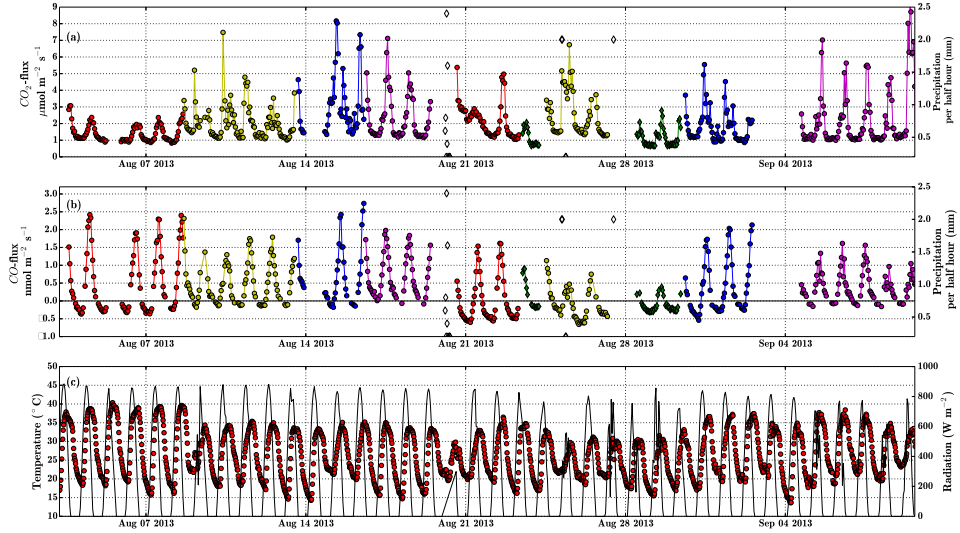


Figure 2. **(a, b)** Chamber CO_2 and CO fluxes with (errorbars with SD of flux are included but not visible due to low value) during field experiment, different colors are different locations. The two bare soil locations (soils without organic surface material) are both presented with green diamonds. Rain events (open diamonds) are indicated. Presented data is from transparent flux chamber measurements; **(c)** Air temperature (°C) (red circles) and radiation (W m^{-2}) (black line).

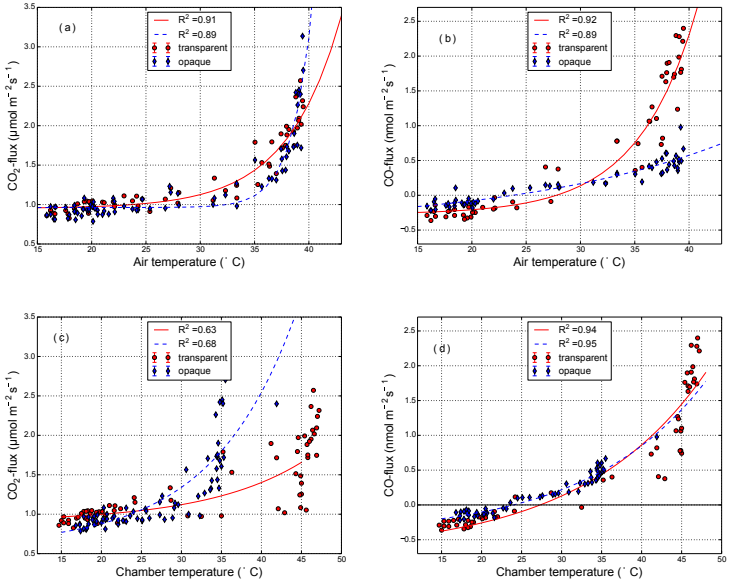


Figure 3. Transparent and opaque flux chamber CO_2 fluxes (left) and CO fluxes (right) vs. air temperature **(a, b)** and chamber temperature after 6 min closure **(c, d)**. Regression coefficients of polynomial fits are given in the legends.

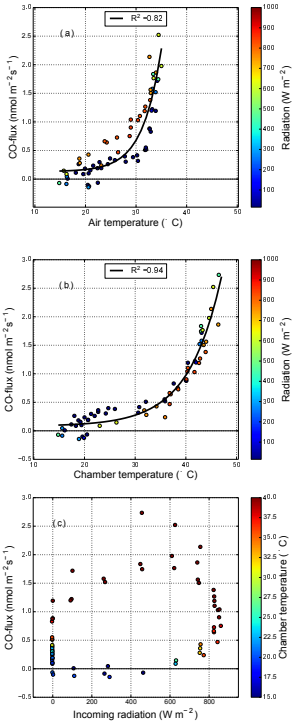


Figure 4. Transparent flux chamber CO fluxes for 15–19 August vs. air temperature **(a)**, chamber temperature after 6 min closure **(b)** and solar radiation **(c)**. Regression coefficients of polynomial fits are given in the legends.

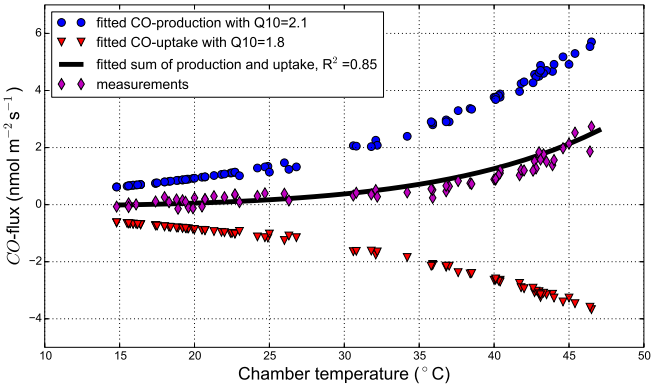


Figure 5. Fitted CO fluxes for 15–19 August (black line) for measured field CO fluxes (purple diamonds)($R^2 = 0.85$). The cumulative fitted CO flux is a sum of fitted CO uptake (with Q10 = 1.8, based on literature Whalen and Reeburgh, 2001) and fitted CO production (with Q10 = 2.1) based on chamber temperature (after 6 min closure).

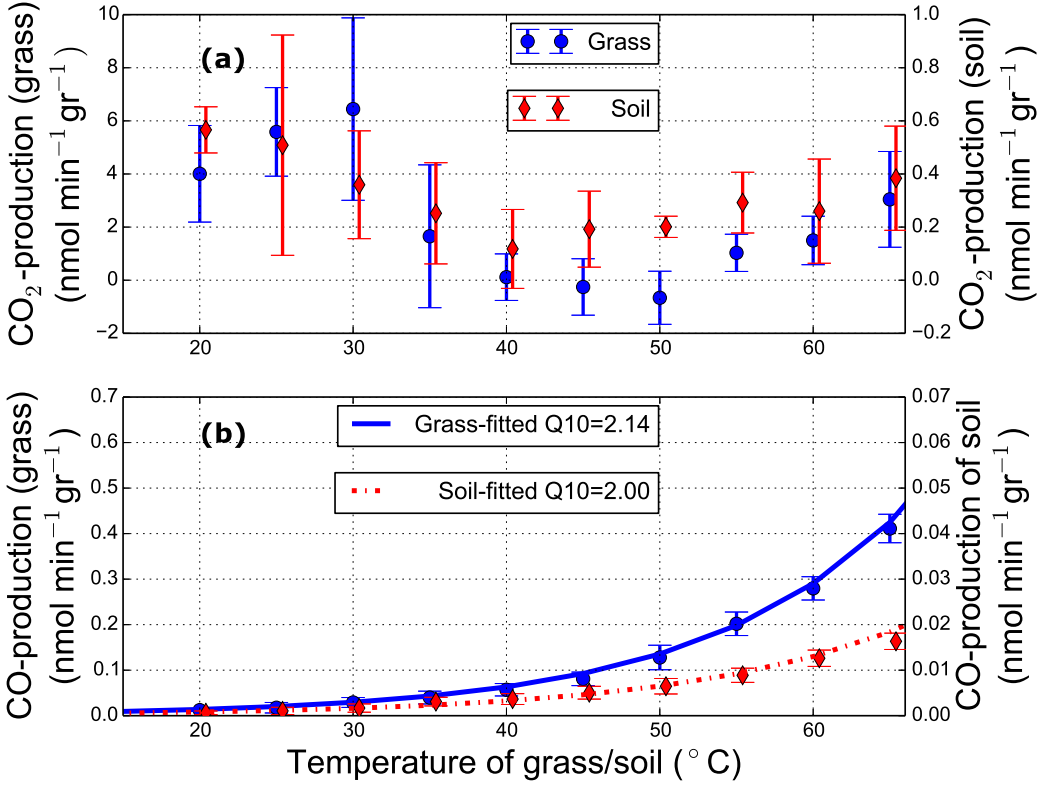


Figure 6. **(a)** Average CO_2 production of grass and soil material (nmol min^{-1} gr^{-1}) over different temperatures in the laboratory experiment; **(b)** Average CO production of grass and soil material (nmol min^{-1} gr^{-1}) over different temperatures in the laboratory experiment, with fitted Q10-value.

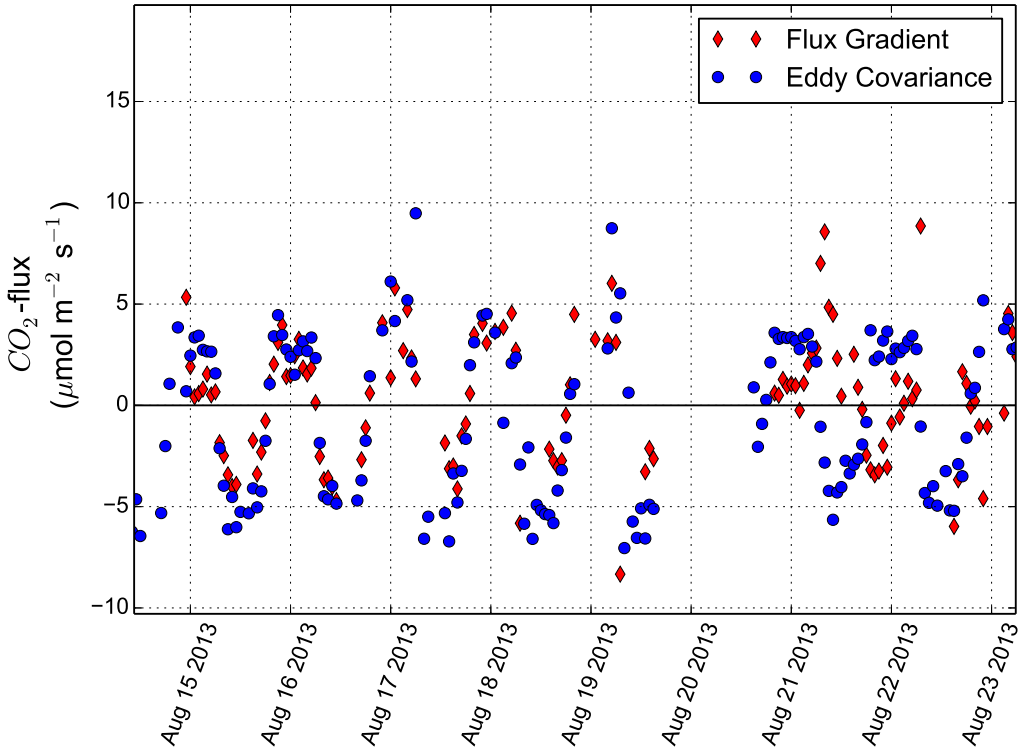


Figure 7. Comparison of Flux Gradient- and Eddy Covariance-CO_2 flux measurements over 8 days in August. On 20 August was a large rain event.