

Author response to the referee #1 comments

We want to sincerely thank the reviewer for detailed and constructive comments and suggestions that certainly have improved the manuscript. We acknowledge the expert input and deep understanding of the topic, and we feel privileged to have had him/her as a reviewer. We have now carefully addressed all the comments.

You can find our response below (in blue) to each of the reviewer comments. In the corrected manuscript version attached below, we have colored the changes in red. We have not marked each small change (e.g. missing commas, changed words etc), but mostly highlighted the significant changes.

on behalf of all co-authors,
Mari Pihlatie

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Second review by referee #1

General comments

Literature review should go partly from Discussion to Introduction.

The N₂O flux data is still a little bit misplaced in the manuscript. In the results some N₂O flux patterns are described, but only after reading the discussion it becomes clear to the reader WHY the authors want to study N₂O fluxes in combination with CO fluxes, and suddenly in the Conclusions, it becomes one of the main findings. I agree with the authors that some process understanding and previous studies should be known by the readers, but since the link between CO and N₂O is not so well known, I would add a few lines in the introduction as well. So, part of what is written in Discussion should also/only appear in the Introduction.

We have added short description of N₂O process understanding and potential links between CO and N₂O fluxes to the introduction (P 2, lines 14-16). In the end of the introduction (P 4, lines 7-13), we also added a sentence to describe what we expect based on the current understanding of the links between N₂O and CO fluxes. We have also modified the discussion accordingly, not to repeat what was written in the introduction.

The same remark counts for the NEE/CO₂ literature review. In the last sentence of the Introduction, the authors state that they will focus on CO₂, and don't mention NEE. It should be clear to the reader earlier why this is of interest. So, part of the NEE-CO relationship literature review should appear earlier in the manuscript.

In the introduction (P 2, lines 10-17) we write that the "Understanding of the biological processes leading to CO release and the importance of these sources in terrestrial ecosystems are poorly understood (Moxley and Smith, 1998; King and Crosby, 2002; Vreman et al., 2011; He and He, 2014)." We list biological processes, which have been found to release CO, and give references therein, but we also state that the importance of biological CO forming processes in the net CO exchange and, in general, to the global CO budget still remain largely unknown.

In the end of the introduction (P 4, lines 7-13), we now write: "Based on previous studies, we expect that the diurnal and seasonal variations in F_{CO} are strongly dependent on radiation and temperature. On the other hand, we do not expect strong relationships between F_{CO} and NEE, or F_{CO} and N₂O fluxes due to the limited information available on the involvement of biological processes in F_{CO} , and challenges in separating between parallel abiotic and biotic drivers of F_{CO} . We hypothesize that a negative correlation between F_{CO}

and NEE can indicate an involvement of a biological component in CO production, and that a positive correlation between night-time F_{CO} and N_2O flux may indicate an involvement of nitrifiers in CO consumption.”

Concerning the NEE-CO discussion, it would be good if the authors are a little more careful with their conclusions. They state that a negative correlation between F_{CO} and NEE indicates biological CO formation (page 14, line 21-22). Here no reference is given, is this a conclusion of the authors themselves? While I agree that the negative correlation CAN be an indicator for the biological CO formation, it can also be caused by other indirect effects (some environmental factors are closely related to NEE, and could also be a driving factor for F_{CO}). It would be good if the authors give a reference here, or shortly elaborate why they are sure about this statement.

We have now rewritten this part of the text in the Discussion (P 15, lines 16-28) to avoid drawing too strong conclusions on the issue. Now it states: “Although we cannot separate between biotic and abiotic CO formation at the RCG field site, our findings of the negative correlation between daytime F_{CO} and NEE ($r = -0.469$) during early summer (days 146-160), the period of maximum NEE, indicate that some CO may also be formed via plant physiological processes. This early summer CO emission period (days 146-160) coincides with the steepest slope in CO_2 uptake (more negative NEE), supporting the findings of Wilks (1959), Bruhn et al. (2013) and Fraser et al. (2015) that CO can be emitted not only from dead plant matter but also from living green leaves. The observed daytime CO emissions during early summer can have also been formed through abiotic processes, which also occur in living plants (Tarr et al., 1995; Erickson et al., 2015). King et al. (2012) suggested that the CO emissions from photodegradation generally decrease with increasing leaf area index, and Tarr et al. (1995) and Erickson et al. (2015) found that the CO photoproduction efficiency is lower for living plants compared to senescent or dead vegetation. These studies support our findings of lower daytime CO emissions from fully developed crop during the summer (days 205-240) compared to CO emissions during the spring (days 110-145), when the ground was covered by the dead plant litter. Still the role of biological CO formation in living green plants and the forming processes remain unresolved and call for further process-studies.”

Footprint analyses

Footprint analyses are now well explained, just a minor comment. In the introduction it is made clear that CO fluxes are pretty dependent on environmental factors such as ground water. Considering this, are there any elevation changes in your footprint? Wet or dry spots? Or does this not play any role? A sentence can be added to clarify this for the reader.

P 4, lines 26-27: We added a sentence specifying that there is a slight slope in the footprint and the wettest area lies in the northern corner of the footprint. During the snow melt there is always standing water in the northern corner of the field, however, there is no standing water during the growing season. We did not perform any measurements on the moisture gradient at the field.

Figure 2, 3 and 4.

The figure which was added to the Authors response (so not in manuscript) is very useful. Is it possible to plot the soil temperature inside the manuscript as well? I see that the authors decided to write 'not shown' but I think there is no need for a new figure, it could be easily added to Figure 3. This would help for the statement that thermal degradation probably doesn't play a role in the early morning hours (page 14, line 10-15). A small remark on this point. It seems unlikely that thermal degradation is ever fully absent. However, considering the previous studies who found exponential curves with temperature, and that the fieldsite is located in a cold climate, the fluxes are probably very small. Therefore, I would rephrase your sentence like 'we expect it to be negligible'.

We made all the suggested changes to the Figures and to the text concerning the role of thermal degradation. We also changed all the figures to black and white improve readability when printed black and white.

Figure 2: It would be good to draw a black line on the 0-line, to clearly divide uptake and emission periods. Also, in this figure, could you indicate the moment of sunset and sunrise?

Figure 2. We added 0-line, and the moment of sunrise and sunset.

Figure 3: As said, the addition of soil temperature here would be very nice and insightful.

Figure 4: Maybe also here indicate the moment of sunrise and sunset.

Figure 3. We added soil temperature

Figure 4. We added the moment of sunrise and sunset

Tables 1 and 2 (and explanation in text)

Table 1 and 2, and the explanation in the text, need quite some improvement. In the current form, it takes a lot of effort from the reader to interpret each column, and especially the values in Table 2 are quite a puzzle without a good explanation. This could be easily improved by adding a few lines either in the text, or besides the column.

We clarified the Tables 1 and 2, and explanation in the text. We followed the suggestions below to make the reading easier. See in detail below.

Table 1

Table 1, please check the description and maybe clarify methods. As I understand, first 'mean' column takes average of FCO when $h_{sun} > 0$, second 'mean' column takes average of FCO when $h < 0$. But the last 'mean' column is not explained. The reader probably assumes it is the mean over all FCO data, but it is better to clarify this.

In Table 1, the last column (net FCO) is now explained as “a net flux over all F_{CO} data (net F_{CO}) for the six measurement periods”.

Table 2

Table 2: I think the use of FCO is confusing here. In Table 1, FCO is meant for the actual measured flux (right?). In Table 2, you state 'gross FCO', but I think you actually mean 'estimated production during daytime', right? In the text, it is more clear because you define it as emissions (page 9, line 24). However, using 'gross FCO' is confusing, since F stands for flux, and flux is usually the net result of uptake and emission. So, if the authors indeed mean production, please rename this term and call it 'gross CO production during the day' or something similar. Gross FCO will confuse the readers.

We agree that the use of FCO was misleading here. We renamed the 'gross FCO' to 'gross daytime CO emission'. We wanted to use the word 'emission' instead of production as the word 'emission' better explains that we measure net emission, whereas 'production' refers to the production process, while there can be simultaneous consumption of CO.

The first columns of Table 2 'Gross FCO' are explained in the Table-text in the last sentence (Gross CO fluxes refer to the difference between.... presented in Table 1). Please add such a sentence for all 3 'mean' values (for 'gross FCO-day', for 'uptake $FCO_{day}(Q10,1.8)$ ', for 'gross $FCO_{day}(Q10, 1.8)$ '), and elaborate. For example:

Gross CO fluxes (gross FCO_{day}) refer to the difference between daytime fluxes (FCO_{day}) and

nighttime fluxes (FCO_night) presented in Table 1. With other words, this is the estimated net production of CO with an assumed constant CO uptake, based on measured uptake rates at night.

Uptake CO fluxes (uptake FCO_day(Q10, 1.8)) refers to the estimated CO uptake taking place during the day, based on measured CO uptake values at night. The value is extrapolated from averaged measured night time CO uptake (Table 1), and extrapolated with a Q10 of 1.8 to day time temperatures (Whalen and Rheebug).

Estimated CO production/emission fluxes (gross F_CO_day) values are based on column 1 from Table 1, minus column 6 from Table 2. Etc.

In the Table-text of Table 2, we write now: The estimated gross daytime CO emission is calculated in two ways: 1) assuming a constant CO uptake, and 2) assuming temperature dependent CO uptake. Gross daytime CO emission based on a constant CO uptake (way 1, Chapter 2.4) refers to the difference between daytime fluxes (FCO_day) and night-time fluxes (FCO_night) presented in Table 1. The temperature corrected gross daytime CO emission (Gross daytime CO emission (Q10, 1.8)) refers to the difference between daytime fluxes (FCO_day) (Table 1.) and daytime CO uptake (Q10, 1.8). The daytime CO uptake (Daytime CO uptake (Q10, 1.8)) is calculated by extrapolating the night-time CO fluxes (FCO_night) to daytime using the difference between day and night soil temperatures (2.5 cm depth) (Δt_{soil}) and the Q10-value of 1.8 (Whalen and Reeburgh, 2001), as described in Chapter 2.4.

You could also refer to page 9, line 24 here, where you describe the 2 'ways' of estimation. You could clearly state you refer to the first 'way' here. So link the text (at page 9, line 24) better with your values in Table 2.

In the Table-text, we added a reference to the Chapter 2.4 (instead of giving page and line numbers), as it is difficult to give specific page and line numbers, when (and if) this manuscript is accepted as a publication.

Again, even if the information is probably findable in the text, it should be more clear since in this form, it takes too much effort of the reader to interpret this table.

We agree and we hope the description is now clarified. We have also modified the description of the calculations in Chapter 2.4 (Pages 8-9, lines 24-), and therein we refer to the Table 2.

Specific comments

P1, line 15: 'However'.. I have the feeling this sentence does not contradict the previous one, so better not use 'however'. Maybe choose another word. 'In general, soils are considered as.....'

P1, lines 14-15: We changed the order of two sentences, stating now that "Soils are generally considered as a sink of CO due to microbial oxidation processes, while emissions of CO have been reported from a wide range of soil-plant systems."

P1, line 16, micrometeorological eddy--> the micrometeorological eddy

Corrected.

P1, line 18: as well as relevant--> as well as to relevant

Corrected.

P1, line 20-21, you mention that mid-April to mid June the field is a net source, the rest of the measurement period (July-Nov) was a net sink, but you exclude the end of June in this sentence. This

is not the maintenance period, right? I would rephrase.

We rewrote this sentence as follows: "The reed canary grass crop was a net source of CO from mid-April to mid-June, and a net sink throughout the rest of the measurement period from mid-June to November 2011, excluding a measurement break in July."

P1, line 22: and an emission--> and a net CO emissions

Corrected.

P2, Line 17: reference to Funk 1994 is not in bibliography. Please check all your references once more

All the references were checked, and Funk 1994 was added to the reference list.

P2, Line 17: Emissions of CO from water logged soils have often been attributed to anaerobic production of CH₄.

The paper of Funk only says that the occurrence of CO fluxes correspond with the occurrence of CH₄ fluxes. This paper mostly underlines the UTILIZATION of CO for producing CH₄. Furthermore, the paper of Varella doesn't measure or mention any CH₄. Please remove or correct this statement, and refer to the correct papers.

P2, line 19-23: We modified the sentence accordingly: "Although microbial CO formation may occur in anaerobic conditions (Funk et al., 1994; Rich and King, 1999), most often the CO production has been related to abiotic processes such as thermal, UV- or visible light-induced degradation of organic matter or plant material..."

P2, Line 18: 'such as thermal or UV- or visible light' change to 'such as thermal, UV- or visible light'

Corrected.

P2-3, Line 26- Line 1: In the current form, the sentence is incorrect grammatically. Either divide into two sentences (split before 'while' and check commas), or rephrase.

P3, lines 5-9: We split the sentence, and it is now written: "Thermal degradation is identified as the temperature-dependent degradation of carbon in the absence of radiation and possibly oxygen (Derendorp et al., 2011; Lee et al., 2012; van Asperen et al., 2015). The separation between CO formation through thermal degradation and photodegradation is very challenging because they both can take place simultaneously and the indirect photodegradation may occur even in the absence of solar radiation if adequate thermal energy is present (Lee et al., 2012)."

P3, line 1-3: What is described here is also sometimes referred to as indirect photodegradation. Can you merge this with page 2, line 23?

The description of indirect photodegradation was now merged in one place, and can be found in P2-3, line 25 onwards.

P3, line 9: 'are needed for CO is formation'--> remove 'is'

P3, lines 11-17: this chapter dealing with biological CO formation was rewritten.

P3, line 15: remove extra bracket

Corrected.

P 3, line 17, add white space before 'with a tendency'

Corrected.

P3, line 16-20: Here the statement is made that higher CO uptake is reported from natural and dry soils, followed by many references. Do these references all support this statement, or you state this fact yourself after reading these articles? Or do these articles only support the first part of the sentence (the reported -2 to 2 nmol m² s)? Please clarify

P3, lines 23-26: we modified this part so that it more clearly states what is supported by the literature. We also removed part of the text to focus on the relevant information related to our study, and to give a general view of the reported CO flux rates. More details of the differences between ecosystem types is discussed in the Discussion (P13, lines 7-12).

P3, line 19-22. Same statement here. Now it seems that all these papers support this statement. I assume that you observed this gradient yourself after reading these papers? Maybe clarify this.

P3, lines 24-26: now we write that: "Based on the available literature, there is a tendency of south to north gradient with higher CO emissions from tropical and Mediterranean environments compared to boreal and temperate ecosystems."

P3, line 25: 'and in North'--> change to 'and in the North'

Corrected.

P3, line 28: 'using micrometeorological'--> change to 'using the micrometeorological'

Corrected.

P4, line 1, 'as well as relevant' change to 'as well as with relevant'

Corrected.

P4, line 6, sentence has unlogical order. Change to something like:
The measurements were conducted on a mineral agricultural field located in Eastern Finland (63..., 27...), cultivated with a perennial reed canary grass (RCG, Ph.....)

P4, lines 16-17: Corrected as follows: "The measurements were conducted on a mineral agricultural field located in Eastern Finland (63°9'48.69" N, 27°14'3.29" E), cultivated with a perennial reed canary grass (RCG, *Phalaris arundinaceae*, L. cv. Palaton)."

P4, line 10, sentence has unlogical order. Change to something like:
In 2011 in the beginning of the growing season (23 May), the crop was fertilized with an N-P-K-S fertilizer.....

P4, line 20: Corrected as follows: "In 2011 in the beginning of the growing season (23 May, day 143), ..."

P4, line 11: Be consistent with dates. Sometimes you write 23 May, other places 28 OF april.

Furthermore, in line 12, you add the day number (day 118). That is quite useful, since you continue using that the rest of the manuscript. Maybe also do that for page 4, line 11.

We modified the date formats to be consistent, and added the day number when it was suitable.

P4, line 20-22, 'within the ploughing layer from the surface to about 30 cm'--> does this count for as well the soil pH as the soil organic matter? Unclear from this sentence. Also the last part of the sentence seems to lack a verb. Please check.

P 5, lines 3-4: We modified this text, and now it reads: "Within the ploughing layer from the surface to about 30 cm, soil pH varies from 5.4 to 6.1, and soil organic matter content varied between 3 and 11%, respectively."

P5, line 7: reduces footprint extent--> reduces the footprint extent

Corrected.

P5, line 9. Why is referred to figure 1 c. Do you mean 1d?

Corrected.

P5, line 17, please add day numbers after April to November 2011 (Like you did in line 18)

Corrected.

P 5, lines 20-21. This sentence seems to assume that the reader knows about the Rannik paper. Please rephrase, something like:

The AR-CW-QCL and LGR-CQ-QCL were the same as used in the study of Rannik (2015) wherein four laser based fast response gas analyzers to measure N₂O were compared (or something similar).

P 5, lines 2-4: the sentence was corrected as suggested.

P 5, line 22, add day number

Corrected.

P6, line 21. 'Sa' is not defined in text.

P 7, line 3: now Sa is defined.

P6, line 23-26. The despiking process is well described. However, which percentage of your data was replaced? Can you state this in the text?

We consider that this information is not relevant for the reader. The despiking is performed to the high frequency rawdata (10 Hz timeseries). The number of spikes for each half-hour is saved in the output, and if there are more than 300 sec of spikes in one half-hour, that flux value is marked as a missing value.

P7, line 27, add coma after 'the fluxes', makes reading more smooth

P7, line 10: A comma was added.

P7, line 28. Groups of days well described. Just a suggestion, is it possible to add real dates between

brackets? Easier for reader to interpret the groups.

P7, lines 11-13: real dates were added.

P8, line 22: the term 'cumulative CO flux' is introduced as cum FCO. The text says it shows that the site is a net sink of CO. Where is that shown? I assume that cumulative stands for the total measurement period of 7 months? Is this the same term as 'net FCO' for days 110-325 in table 1? If so, you can refer to Table 1, and clarify that cumulative is the same as net FCO for the period 'all' in Table 1.

P9, lines 12-14: We modified the text to better explain how the cumulative flux was obtained, as follows "Cumulative CO flux (cum FCO) curves, calculated by cumulating the half-hourly fluxes, show that the site was a net sink of CO over the 7-month measurement period (Fig. 1f)." Hence, the cumulative flux is not literally the same as net FCO for days 110-325, which is a mean of all the half-hourly CO fluxes over the period of days 110-325.

P9, line 9, The autumn was characterized by decreasing FCO..... Statement too vague. By 'the autumn' do you mean A+LA (so days 241 to 325)? And, which FCO is meant here? Net FCO during the day or night or net? Or estimated production in Table 2? Please clarify

P9, lines 24-27: This sentence was clarified and states now: "The autumn (A, LA) was characterized by decreasing daytime F_{CO} (F_{CO_day}) and slowly dropping air and soil temperatures, decreasing radiation intensity, and decreasing photosynthetic activity of the crop (less negative NEE) (Fig. 1)."

Page 10, line 2, add white space

Added.

Page 11, lines 19: over the whole measurement period → over the whole 7 month measurement period.

Corrected.

Page 12, line 5-7. sentence unclear. Maybe: were rather low, crop was not yet → were rather low and the crops were not yet....

P 12, line 29: Corrected as suggested.

Page 12, line 10. Decreasing amount of--> decreasing amounts of

Corrected as suggested.

page 12, line 25: to calculate and annual--> to calculate an annual

Corrected as suggested.

Page 12, line 25: when stating the number -0.25, please refer to Table 1, so reader knows where the number comes from

P 13, line 20: this reference to Table 1 was added.

Page 13, line 7-11. I would refer here to the same papers as in Table 5, to be consistent to the reader

P 14, lines 2-5: Many of the referred papers here are process studies, and as this chapter / sentence refers to the processes, and to observations of the processes, we preferred to keep these references. In Table 5, most of the studies are field studies reporting net CO fluxes, and many of these papers do not focus on processes.

Page 13, line 14. You introduce Mco here, and introduce the abbreviation. However, if you dont use this term anymore afterwards, I think there is no need to introduce an abbreviation.

P 14, lines 7-8: We agree with this comment, however, as MCO is presented now in the correlation tables 3 and 4, we left also the abbreviation in the text, as it is shown in the tables. Now the text reads: "We did not find correlation between daytime or night-time CO concentration (MCO) and FCO (Tables 3 and 4),..."

Page 13, line 15: In line 12 you state that you expect CO emission also exists during the day. In line 15, you state 'if existing'. I would phrase your doubt less strong, more like
In our site the estimated/assumed daytime CO consumption is overruled by.....

P 14, line 9-10: Corrected as suggested. "In our site the estimated daytime CO consumption is overruled by a simultaneous strong CO production..."

Page 13, line 26: drives → drive

Corrected.

Page 13, line 29. You state that a supporting factor includes the high C to N ratio. However, since it is an important point, I would add the accompaying reference right after this point. Now it is at the end of the sentence and unclear for the reader which reference belongs to which supporting factor. Or you could take this point out of this sentence and merge it with the next sentence, since you elaborate there anyway.

P 14, lines 24-29: We merged the text with the text where we elaborated with factors supporting CO formation via abiotic degradation processes. Now the text reads: "Factors supporting the CO production through abiotic photodegradation and thermal degradation processes include high C to N ratio of the plant material (King et al., 2012), presence of oxygen (Tarr et al., 1995; Lee et al., 2012), greater solar radiation exposure (no shading) (King et al., 2012), and litter area to mass ratio (King et al., 2012; Lee et al., 2012). As the dead plant material in our measurement site has a high C to N ratio (mean \pm stdev: 66 ± 6.3), and as this dry plant material was well exposed to radiation in the spring, we expect that the conditions were suitable for CO formation through abiotic degradation processes."

Page 14, line 15-16: Is thermal degradation not by definition temperature dependent? No need for reference here.

References removed.

Page 14, line 21: Based on understanding of biological CO formation, a negative correlation between FCO and NEE....

This is nice information, but it would be good if the reader is aware of this assumed relationship before. Could this expected relationship be stated and explained in Introduction? This might help the reader understand the flow and content of the paper better. Also, as mentioned in general comments, please elaborate on this negative correlation, can this only mean biological formation, or

can this correlation also be caused by something else.

We have addressed this topic shortly in the Introduction (P 3, lines 10-17) and in the Discussion (P 15, lines 16-28). We agree that it is good to write open our assumptions and expectations as early as possible in the manuscript. As there is very little information available on the connections between FCO and NEE, and in general, on the biological CO formation processes, we have now minimized speculations based on our data. We do acknowledge that some CO may be formed in plant physiological processes, however, we also state that our data does not allow drawing conclusions on the involvement of biological (or abiotic) processes.

Page 14, line 25-26: at the RCG crop--> at the RCG field site/arable land/....

This sentence was deleted as the chapter was reorganized and compressed.

Page 15, line 6-7: verb missing. Maybe: net CO emission also--> net CO emissions occurring also

This sentence was deleted as the chapter was reorganized and compressed.

Page 15, line 14: verb too much, remove 'remain'

Corrected.

Page 15, line 14-16: incorrect/unclear sentence. Rephrase to something like:
A study by K&C (2002) demonstrated the lack of understanding in sink-source dynamics of CO, and showed that plant roots are capable of producing CO, which rate/source can be as high as the current.....

This sentence was deleted due to the efforts in minimizing speculations of biological CO formation at our site.

Page 15, line 17. Also stated in general comments. This expected strong relationship should already be clear in Introduction.

We elaborate the relationship between night-time FCO and N2O fluxes in the Discussion at Page 16, lines 3-13. We also added a sentence in the beginning of the Introduction (P 2, lines 14-16) stating that "A diverse group of soil microbes are capable of oxidizing CO. They include carboxydrotrophs, methanotrophs, and nitrifiers (Ferenci et al., 1975; Jones and Morita, 1983; Bender and Conrad, 1994; King and Weber, 2007), hence potentially linking CO fluxes to the exchange of CH₄ and N₂O." Additionally, in the end of the Introduction (P4, lines 7-13) we state that "Based on previous studies, we expect that the diurnal and seasonal variations in F_{CO} are strongly dependent on radiation and temperature. On the other hand, we do not expect strong relationships between F_{CO} and NEE, or F_{CO} and N₂O fluxes due to the limited information available on the involvement of biological processes in F_{CO}, and challenges in separating between parallel abiotic and biotic drivers of F_{CO}. We hypothesize that a negative correlation between F_{CO} and NEE can indicate an involvement of a biological component in CO production, and that a positive correlation between night-time F_{CO} and N₂O flux may indicate an involvement of nitrifiers in CO consumption."

Page 16, line 6: the smaller emissions of CO..... Do you refer to literature here or to your own data?
Rephrase/clarify

This sentence was deleted to make the Discussion more concise and avoid overlapping. The role of biotic vs. abiotic processes in CO formation are discussed now on Page 15, lines 16-28.

Figures

Figure 1. If the manuscript is printed in black/white, the lines are hard to differentiate. Could the lines have different patterns?

We changed all the figures to black and white to avoid problems in differentiating the lines.

Very minor comments, but why are there different types of blue used in figure 5, in comparison to previous figures?

Now and the figures are presented in black and white.

Tables

Table 2, please add white space before (Q10, 1.8) (two times)

White space added.

Table 5, The authors have explained why they keep the table in this form, and have elaborated in the text about which study measured at daytime, and which diurnal. This is fine, but it would help if the header and table would be more self-explanatory. Elaborate column 4 by for example: 'Data Period, measurement frequency, and moment of measurement'. In the current form the header 'diurnal cycle' doesn't really cover the content of the column

Table 5. We changed the column 4 to 'Data Period, measurement frequency, and moment of measurement' as suggested.

Seasonal and diurnal variation in CO fluxes from an agricultural bioenergy crop

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Abstract. Carbon monoxide (CO) is an important reactive trace gas in the atmosphere, while its sources and sinks in the biosphere are only poorly understood. Soils are generally considered as a sink of CO due to microbial oxidation processes, while emissions of CO have been reported from a wide range of soil-plant systems. We measured CO fluxes by the micrometeorological eddy covariance method from a bioenergy crop (reed canary grass) in Eastern Finland over April to November 2011. Continuous flux measurements allowed us to assess the seasonal and diurnal variability, and to compare the CO fluxes to simultaneously measured net ecosystem exchange of CO₂, N₂O and heat fluxes as well as to relevant meteorological, soil and plant variables in order to investigate factors driving the CO exchange.

The reed canary grass crop was a net source of CO from mid-April to mid-June, and a net sink throughout the rest of the measurement period from mid-June to November 2011, excluding a measurement break in July. CO fluxes had a distinct diurnal pattern with a net CO uptake in the night and a net CO emission during the daytime with a maximum emission at noon. This pattern was most pronounced during the spring and early summer. During this period the most significant relationships were found between CO fluxes and global radiation, net radiation, sensible heat flux, soil heat flux, relative humidity, N₂O flux and net ecosystem exchange. The strong positive correlation between CO fluxes and radiation suggests towards abiotic CO production processes, whereas, the relationship between CO fluxes and net ecosystem exchange of CO₂, and night-time CO fluxes and N₂O emissions indicate towards biotic CO formation and microbial CO uptake, respectively.

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The study shows a clear need for detailed process-studies accompanied with continuous flux measurements of CO exchange to improve the understanding of the processes associated with CO exchange.

1 Introduction

Carbon monoxide (CO) is an important reactive trace gas in the atmosphere where it participates in the chemical reactions with hydroxyl radicals (OH), potentially leading to the production of the strong greenhouse gas ozone (O₃). The reactions of CO and OH decrease the atmospheric capacity to oxidize atmospheric methane (CH₄), hence indirectly affecting the lifetime of this important greenhouse gas. Although CO itself absorbs only little infrared radiation from the Earth, the cumulative indirect radiative forcing of CO may even be larger than that of a third powerful greenhouse gas nitrous oxide (N₂O) (Myhre et al., 2013). Anthropogenic activities related to burning of fossil fuel and biomass (e.g. forest fires) and photochemical oxidation of CH₄ and non-methane hydrocarbons are the main sources of CO (Duncan et al., 2007), while the reaction with OH is the major sink of CO in the atmosphere (Duncan and Logan, 2008). Soils are globally considered as a sink for CO due to microbial oxidation processes in the soil (Conrad and Seiler, 1982; Potter et al., 1996; Whalen and Reeburgh, 2001; King and Weber, 2007). According to Conrad and Seiler (1980) the soil consumption of CO is a microbial process, it follows first-order kinetics and can take place in both aerobic and anaerobic conditions. **A diverse group of soil microbes are capable of oxidizing CO. They include carboxydrotrophs, methanotrophs, and nitrifiers (Ferenci et al., 1975; Jones and Morita, 1983; Bender and Conrad, 1994; King and Weber, 2007), hence potentially linking CO fluxes to the exchange of CH₄ and N₂O.** In addition to CO consumption, production of CO has been found from a wide range of soils (Moxley and Smith, 1998; Gödde et al., 2000; King, 2000; Varella et al., 2004; Galbally et al., 2010; Bruhn et al., 2013; van Asperen et al., 2015), plant roots (King and Crosby, 2002; King and Hungria, 2002), living and degrading plant material (Tarr et al., 1995; Schade et al., 1999; Derendorp et al., 2011; Lee et al., 2012) and degrading organic matter (Wilks, 1959; Conrad and Seiler 1985b). **Although microbial CO formation may occur in anaerobic conditions (Funk et al., 1994; Rich and King, 1999),** most often the CO production has been related to abiotic processes such as thermal, UV- or visible light-induced degradation of organic matter or plant material (Conrad and Seiler, 1985b; Tarr et al., 1995; Schade et al., 1999; Derendorp et al., 2011; Lee et al., 2012; van Asperen et al., 2015; Fraser et al., 2015). Photodegradation involves direct and indirect photodegradation of e.g. litter or organic material (King et al., 2012). In the direct photodegradation, a molecule (e.g. lignin) has absorbed radiation and undergoes direct changes such as fragmentation, intramolecular rearrangement or electron transfer from or to the molecular (King et al., 2012). In the indirect photodegradation, certain photosensitizers absorb the incoming radiation and

transfer the energy to other molecules such as triplet oxygen, forming reactive intermediates such as singlet oxygen, hydroxyl radical or hydrogen peroxide, which further can change the chemistry of another non-light-absorbing molecule (e.g. cellulose) or part of the same molecule where the photosensitizer resided (King et al., 2012). Indirect photodegradation may also refer to radiation induced stimulation of microbial degradation through breaking down organic compounds making them easily available for microbial degradation (see King et al. 2012). Thermal degradation is identified as the temperature-dependent degradation of carbon in the absence of radiation and possibly oxygen (Derendorp et al., 2011; Lee et al., 2012; van Asperen et al., 2015). The separation between CO formation through thermal degradation and photodegradation is very challenging because they both can take place simultaneously and the indirect photodegradation may occur even in the absence of solar radiation if adequate thermal energy is present (Lee et al., 2012).

Understanding of the biological processes leading to CO release and the importance of these sources in terrestrial ecosystems are poorly understood (Moxley and Smith, 1998; King and Crosby, 2002; Vreman et al., 2011; He and He, 2014). Formation of CO from living green plants under illumination and the presence of oxygen was found already in the late 1950's by Wilks (1959) and Siegel et al. (1962). More recently, CO has been found to be formed e.g. in plant roots (King and Crosby, 2002), in stressed plants (He and He, 2014), during heme oxidation (Engel et al., 1972; Vreman et al., 2011), in aromatic amino acid degradation processes (Hino and Tauchi, 1987), and in lipid peroxidation reactions (Wolff and Bidlack, 1976). However, the importance of these biological CO forming processes in the net CO exchange and, in general, to the global CO budget still remain largely unknown (King and Crosby, 2002).

Most of the reported CO flux measurements are either short-term field experiments (e.g. Conrad and Seiler 1985a; Funk et al, 1994; Zepp et al., 1997; Kuhlbusch et al., 1998; Moxley and Smith 1998; Schade et al., 1999; Varella et al., 2004; Bruhn et al., 2013; van Asperen et al., 2015), or laboratory incubations with specific treatments of the soil or plant material (Tarr et al., 1995; King and Crosby 2002; Lee et al., 2012). Both CO uptake and emissions are reported from soil-plant systems in different climatic regions, and mostly the CO fluxes range between -2 and 2 nmol m⁻² s⁻¹ (Conrad et al., 1988; Khalil et al., 1990; Funk et al., 1994; Zepp et al., 1997; Moxley and Smith, 1998; Schade et al., 1999; King, 2000; King and Hungria, 2002; Varella et al., 2004; Galbally et al., 2010). Based on the available literature, there is a tendency of south to north gradient with higher CO emissions from tropical and Mediterranean environments compared to boreal and temperate ecosystems (e.g. Zepp et al., 1997; Kuhlbusch et al., 1998; King, 2000; Varella et al., 2004; Galbally et al., 2010; Constant et al., 2008; Bruhn et al., 2013; van Asperen et al., 2015). However, the high variation between CO uptake and emission rates does not allow yet to classify the ecosystem types or climatic regions. Tall tower (Andreae et al., 2015) and airborne

measurements have indicated source areas of CO both in the Amazon basin (Harriss et al., 1990) and in the North American tundra (Ritter et al., 1992; 1994) suggesting a connection between high plant biomass and biological CO forming processes. To our understanding this is the first study to report long-term and continuous field measurements of CO fluxes (F_{CO}) using the micrometeorological eddy covariance (EC) method. We measured F_{CO} above a boreal perennial grassland ecosystem, reed canary grass, over a 7-month snow-free period in 2011 by two parallel laser absorption spectrometers. We compared the F_{CO} with simultaneously measured fluxes of carbon dioxide (CO_2), net ecosystem exchange of CO_2 (NEE), nitrous oxide (N_2O), heat and energy as well as with relevant soil, plant and meteorological variables. Based on previous studies, we expect that the diurnal and seasonal variations in F_{CO} are strongly dependent on radiation and temperature. On the other hand, we do not expect strong relationships between F_{CO} and NEE, or F_{CO} and N_2O fluxes due to the limited information available on the involvement of biological processes in F_{CO} , and challenges in separating between parallel abiotic and biotic drivers of F_{CO} . We hypothesize that a negative correlation between F_{CO} and NEE can indicate an involvement of a biological component in CO production, and that a positive correlation between night-time F_{CO} and N_2O flux may indicate an involvement of nitrifiers in CO consumption.

2 Materials and methods

15 2.1 Measurement site

The measurements were conducted on a mineral agricultural field located in Eastern Finland (63°9'48.69" N, 27°14'3.29" E), cultivated with a perennial reed canary grass (RCG, *Phalaris arundinaceae*, L. cv. Palaton). The measurements covered a period from snow-melt to the new snowfall, from April to November 2011. Long-term (reference period 1981-2010) annual mean air temperature in the region is 3.2°C and the annual precipitation is 612 mm (Pirinen et al., 2012). The crop was cultivated in the beginning of June 2009. In 2011 in the beginning of the growing season (23 May, day 143), the crop was fertilized with an N-P-K-S fertilizer containing 76 kg N ha⁻¹ ($NO_3-N : NH_4-N = 47:53$). The crop from the previous season was kept at the site over the winter (Burvall, 1997), and was harvested on 28 April (day 118) (Lind et al., 2016). The spring and early summer (days 118-160) was characterized by fast growing crop with the crop height increasing from about 10 cm in mid-May to 1.7 m in late June (day 180), reaching the maximum height of 1.9 m in early July. The field was 6.3 ha in size and from the sampling location of the EC measurement system the footprint was homogenous in all directions, extending 162, 137, 135 and 178 m to N, E, S and W, respectively. There is a slight south to north slope in the field and the wettest area lies in the northern corner of the footprint, which has often standing water during the period of snow-melt (April).

The soil at the site is classified as a Haplic Cambisol/Regosol (Hypereutric, Siltic) (IUSS Working Group WRB, 2007) and the texture of the topsoil (0–28 cm) varied from clay loam to loam based on the US Department of Agriculture (USDA) textural classification system. Within the ploughing layer from the surface to about 30 cm, soil pH varies from 5.4 to 6.1, and soil organic matter content varied between 3 and 11%, respectively. The average C/N ratio in the ploughing layer was 14.9 (ranging from 14.1 to 15.7).

We performed footprint analysis in order to identify the source area of the flux measurements. Two limiting cases were analysed: first, a low crop representing the beginning of the campaign, and second, canopy with 1.9 m height representing the RCG canopy after mid-summer. The measurement heights 2.2 and 2.4 m were used in the analysis, respectively. In the first case, we represented the low canopy as the surface with aerodynamic roughness 0.04 m (determined from measurements), in the second case, a canopy with leaf area distribution characteristic to RCG crops was represented by a beta distribution. In both cases the sources were assumed at the soil surface. Such an assumption was made due to limited information on source-sink behaviour (see Sect. 3 below), and also in order to obtain more conservative footprint estimates. Three stability classes representing unstable (the Obukhov length $L = -10$ m), near-neutral ($L = -100$ m) and stable ($L = +10$ m) conditions were considered. The footprint evaluation was performed by using the Lagrangian stochastic trajectory simulations (e.g. Rannik et al., 2003). The upwind distance contributing 80% of the flux was identified for low/high canopy as follows: 53/23 m, 83/34 m, and 166/60 m for unstable, near-neutral, and stable stratifications, respectively. The conducted footprint analysis reveals that the presence of a canopy significantly reduces the footprint extent. Note that the conservative footprint scenario with no canopy is applicable only for a short period of time due to fast canopy growth in the beginning of the campaign (see Fig. 1d). Considering that prevailing wind direction during the measurement period was from SE and SSW directions, and the wind direction interval 110-315° contributed 90% of the half-hour periods used in the analysis, the footprint analysis hence confirms that the footprint was sufficient and the measurements well represent the RCG canopy.

2.2 CO flux measurements

The EC measurements were made as a part of the ICOS (Integrated Carbon Observation System) Finland program during April to November 2011. Here we report the results of F_{CO} calculated from the concentration measurements by two continuous-wave quantum cascade lasers: AR-CW-QCL (model CW-TILDAS-CS Aerodyne Research Inc., see e.g. Zahniser et al., 2009) and LGR-CW-QCL (model N2O/CO-23d, Los Gatos Research Inc., see e.g. Provencal et al., 2005). The measurements by AR-CW-QCL extended the whole measurement period from April to November 2011 (days 110-325),

whereas for LGR-CQ-QCL data is available from later summer to the end of the measurement period (days 206-330). Fluxes by the two analyzers are compared, however, due to the longer data coverage, the diurnal and seasonal variation in F_{CO} is assessed using data from AR-CW-QCL only. **The AR-CW-QCL and LGR-CQ-QCL were the same as used in the study of Rannik et al. (2015) wherein four laser-based fast-response gas analyzers to measure nitrous oxide (N_2O) fluxes were compared.**

The measurement height was 2.2 m until 30 June 2011 (day 181) when the height was raised to 2.4 m due to the growth of RCG. The gas inlets of the closed-path analyzers were located 10 cm below a sonic anemometer (USA-1, Metek Germany GMBH, respectively) used for measuring turbulent wind components. In addition, CO_2 and H_2O fluxes were measured at the site by an infrared gas analyzer (LI7000 – Li-Cor Inc., Lincoln, NE, USA) connected to a sonic anemometer (R3-50, Gill Solent Ltd., UK). The closed-path gas analyzers were located in an air conditioned cabin at about 15 m east from the air inlet and the anemometers. This wind direction (50-110° sector) was therefore discarded from further analysis due to possible disturbances to flux measurements. Sample lines (PTFE) were shielded and heated slightly above ambient air temperature. Sample lines were 16 meters in length, their inner diameters were 4 and 8 mm, the sample air flow rates were 13.2 and 11.6 LPM (Rannik et al., 2015). Based on material testing with LGR-CW-QCL, the PTFE tubing was found inert with respect to CO in a constant-flow setup and flow rate of 2.5 LPM (unpublished data). The EC measurements were sampled at 10 Hz frequency. Further details on the EC set-up, instrument specifications and data acquisition, can be found in Rannik et al. (2015) and Lind et al. (2016).

2.3 Supporting measurements

A weather station located at the site monitored continuously several meteorological and soil parameters such as air temperature (T_{air}) and relative humidity (RH) (model: HMP45C, Vaisala Inc.), precipitation (P_r) (model: 52203, R.M. Young Company), global (R_{glob}) and net radiation (R_{net}) (model: CNR1, Kipp&Zonen B.V.), photosynthetically active radiation (PAR, model: SKP215, Skye instruments Ltd.), soil heat flux at 7.5 cm depth (G) (model: HPF01SC, Hukseflux), soil temperatures at 2.5, 5, 10, 20 and 30 cm depths (T_{soil}) (model: 107, Campbell Scientific Inc.), and soil water content at 2.5, 5, 10 and 30 cm depths (SWC) (model: CS616, Campbell Scientific Inc.). All meteorological data were recorded as 30 min mean values and stored using a datalogger (model: CR 3000, Campbell Scientific Inc.).

Leaf area index (LAI) was measured at approximately weekly intervals during the main crop growth period using a plant canopy analyser (model: LAI-2000, LiCor). Green area index (GAI) was estimated on weekly basis from plots adjacent to the LAI measurements according to Wilson et al. (2007) and Lind et al. (2016). The GAI measurements were conducted from three locations (1 x 1 m²) and within each from three spots (8 x 8 cm²) by counting a number of green stems (S_n) and green leaves (L_n) per unit area and measuring the green area of leaves (L_a) and stems (S_a). The GAI was calculated as

$$GAI = (S_n S_a) + (L_n L_a) .$$

2.4 Data processing and analysis

The EC data processing was performed with post-processing software EddyUH (Mammarella et al., 2016). Filtering to eliminate spikes (Vickers and Mahrt, 1997) was performed according to an approach, where the high frequency EC data were despiked by comparing two adjacent measurements. If the difference between two adjacent concentration measurements of CO was greater than 20 ppb, the following point was replaced with the same value as the previous point.

The spectroscopic correction due to water vapour impact on the absorption line shape was accounted for along with the dilution correction. LGR-CW-QCL automatically corrected the water vapour effect by a built-in module in the LGR data acquisition software. The same spectroscopic correction was applied to AR-CW-QCL after a software update in July 2011. Prior to this software update, the respective dilution and spectroscopic corrections to AR-CW-QCL high-frequency CO mole fraction data were performed during the post-processing phase according to Rannik et al. (2015) with the instrument specific CO spectroscopic coefficient ($b=0.28$) determined in the field.

Prior to calculating the turbulent fluxes, a 2-D rotation (mean lateral and vertical wind equal to zero) of sonic anemometer wind components was done according to Kaimal and Finnigan (1994) and all variables were linearly detrended. The EC fluxes were calculated as 30 min co-variances between the scalars and vertical wind velocity following commonly accepted procedures (e.g. Aubinet et al., 2000). Time lag between the concentration and vertical wind speed measurements induced by the sampling lines was determined by maximizing the covariance. Due to the larger inner diameter (8 mm) of the sampling line in LGR-CW-QCL, the resulting lag time was 4.2 sec compared to that of 0.91 sec for AR-CW-QCL with the sampling line inner diameter of 4 mm. The final processing was, however, done by fixing the time lag to avoid unphysical variation of lag occurring due to random flux errors. Spectral corrections were applied to account for the low and high frequency attenuation of the covariance. The first order response times of the EC systems were determined to be 0.07 and 0.26 sec for

the AR-CW-QCL and LGR-CW-QCL systems, respectively, following the method by Mammarella et al. (2009). This resulted in different flux correction factors mainly due to tube damping: For AR-CW-QCL the 5 and 95 percentile values of flux underestimation were 2.1 and 12.2% and for LGR-CW-QCL 5.7 and 21.4%, respectively. Data quality screening was performed according to Vickers and Mahrt (1997) to ensure exclusion of the system malfunctioning as well as unphysical and/or unusual occasions in measurements. We chose to perform tests on single time series to ensure quality of measurements used in the analysis and did not use the flux stationarity test (Foken and Wichura, 1996) because the CO fluxes are frequently small and respectively with large relative random errors. In such cases the tests based on relative errors are not expected to perform well (e.g. Rannik et al., 2003). After quality screening, 66.0% of the F_{CO} data (AR-CW-QCL) was available, with data coverage of 59.2% during the daytime and 75.9% during the night-time. For details of the data processing and quality screening see Rannik et al. (2015).

To evaluate in detail the seasonal changes in F_{CO} and factors affecting the fluxes, the data was divided into six periods (days 110-145 (20 April – 25 May) = spring (S), days 146-160 (25 May – 9 June) = early summer (ES), days 161-181 (10 June – 30 June) = mid-summer (MS), days 205-240 (24 July – 28 August) = late summer (LS), days 241-295 (29 August – 23 October) = autumn (A), and days 296-325 (24 October – 21 November) = late autumn (LA)). The division into these periods was based on seasonal changes in crop growth and development, or changes in F_{CO} and temperature, while the lengths of the periods were kept as similar in length as possible. Also, F_{CO} were not measured during an instrumental break between days 181 and 204. To compare diurnal changes in the F_{CO} , the data was further divided into daytime (F_{CO_day}) and night-time (F_{CO_night}) data. We used sun elevation angle $h < 0$ for night-time and $h > 0$ for daytime. Pearson correlations between daytime and night-time half-hour average fluxes and other measured parameters were determined. Data processing was performed with Matlab version R2014a (The MathWorks, Inc., United States) and the statistical testing with IBM SPSS statistics (IBM Corporation, United States).

To evaluate the gross CO emission during daytime (gross daytime CO emission), we calculated the gross daytime CO emission in two ways 1) by assuming an equivalent CO uptake for daytime and night-time (constant uptake), and 2) by taking into account temperature dependency (Q_{10} of 1.8) in CO uptake according to Whalen and Reeburgh (2001). Based on a constant CO uptake, the gross daytime CO emission was calculated by subtracting the night-time F_{CO} (F_{CO_night}) from the daytime F_{CO} (F_{CO_day}), presented in Table 1. The uptake CO fluxes refers to the estimated CO uptake taking place during the day, based on measured CO uptake values at night. The temperature corrected daytime CO uptake (Daytime CO uptake, (Q_{10}

1.8)) is calculated by extrapolating the measured night-time CO fluxes (F_{CO_night}) (table 1) to using the difference between day and night soil temperatures (2.5 cm depth) (Δt_{soil}) and the Q_{10} -value of 1.8 (Whalen and Reeburgh, 2001). The temperature dependent daytime CO uptake ($R2$) was solved from the equation

$$Q_{10} = \frac{\left(\frac{R2}{R1}\right)^{10}}{(T2-T1)},$$

5 where Q_{10} is 1.8 (Whalen and Reeburgh, 2001), $R1$ is the night-time F_{CO} (net F_{CO_night}) ($\text{nmol m}^{-2} \text{s}^{-1}$), and $T2-T1$ is the temperature difference between daytime ($T2$) and night-time ($T1$) soil temperature at 2.5 cm depth ($^{\circ}\text{C}$), respectively. The temperature corrected gross daytime CO emissions (Gross daytime CO emission ($Q_{10} 1.8$)) was estimated by subtracting the temperature corrected daytime CO uptake (Daytime CO uptake, ($Q_{10} 1.8$)) from the daytime F_{CO} (F_{CO_day}). These gross CO emission and uptake rates were estimated for each of the six measurement periods and are presented in Table 2.

10 3 Results

3.1 Seasonal variation

The RCG field was a net source of CO from mid-April in the spring to mid-June (days 110-160), after which the site turned to a net sink until the end of the measurement period in November 2011 (days 161-325) (Fig. 1f). **Cumulative CO flux (cum F_{CO}) curves, calculated by cumulating the half-hourly fluxes, show that the site was a net sink of CO over the 7-month measurement period (Fig. 1f).** During daytime, the net CO fluxes (F_{CO_day}) were positive during the spring and early summer (days 110-160) and again during late summer (days 205-240). These daytime emissions were highest during the spring (Table 1). Night-time CO fluxes (F_{CO_night}) were negative (CO uptake) throughout the whole measurement period with a trend of increasing CO consumption towards late autumn (Table 1).

The spring emission period (days 110-145) covered a time (days 110-118) with a standing dry crop from the previous year. The old crop was harvested on 28 of April (day 118), after which the ground consisted mainly of short dead plant material and litter, and a slowly sprouting new RCG. The second emission period in early summer (days 146-160) was characterized by fast growing RCG crop, high and fertilizer-induced N_2O emissions (Shurpali et al., 2016), increasing air and soil temperatures, growing leaf area and increasing NEE (Fig. 1). After the crop had reached its maximum height of 1.9 m in mid-June (around day 160), the site started to act as a net sink of CO, followed by a period of net daytime emissions during late summer in July-August (days 205-240). **The autumn (A, LA) was characterized by decreasing daytime F_{CO} (F_{CO_day}) and**

slowly dropping air and soil temperatures, decreasing radiation intensity, and decreasing photosynthetic activity of the crop (less negative NEE) (Fig. 1).

5 Comparison of the two gas analyzers, AR-CW-QCL and LGR-CW-QCL, during the period when both were operational (days 205-325), shows that the measured F_{CO} agree reasonably well (Fig. 1f). A correlation scatter plot of the F_{CO} from LGR-CW-QCL against F_{CO} of AR-CW-QCL results a correlation coefficient of 0.95 and a slope of 0.96 (data not shown). According to this comparison, LGR-CW-QCL shows slightly (4%) smaller fluxes compared to AR-CW-QCL, however, the difference between the two analyzers is very small, giving us confidence in the use of either of the analyzer in further analysis.

10 3.2 Diurnal variation

The F_{CO} had a distinct diurnal pattern with an uptake in the night-time and an emission during the daytime with maximum emissions at noon (Fig. 2). This pattern was most pronounced during the spring, days 110-145, when the maximum daytime CO emissions reached $2.7 \text{ nmol m}^{-2} \text{ s}^{-1}$ (Fig. 2). The net F_{CO} was positive (emission) during the spring and early summer, after which the night-time uptake dominated making the site as a net sink of CO (Fig. 2, Table 1.). Night-time F_{CO} show a
15 near constant uptake of CO over the whole measurement period with a mean of $-0.77 \text{ nmol m}^{-2} \text{ s}^{-1}$ over the whole measurement period (Fig. 2, Table 1.).

The diurnal F_{CO} over the six measurement periods followed closely the daily pattern of R_{glob} with a maximum F_{CO} (emission) at around noon and minimum F_{CO} (highest uptake) at midnight (Figs. 2 and 3). The highest radiation intensity was reached during the early summer (days 146-160), while the maximum F_{CO} were observed during the spring (days 110-145) (Figs. 2
20 and 3). Diurnal variation in soil temperature was highest during the spring and early summer, and always peaked during the afternoon (Fig. 3).

Compared to the F_{CO} , the diurnal variation in CO_2 exchange, expressed here as NEE, was very small during the spring (days 110-145) (Fig. 4). A rapid increase in LAI and GAI at around day 150 (Fig. 1d) lead to an increase in CO_2 uptake during daytime, which is seen in a distinct diurnal pattern with high CO_2 uptake (negative NEE) during daytime and a small positive
25 NEE during night-time (Fig. 4). Maximum NEE values were reached during mid-June (days 161-181) after which the NEE slowly decreased and the CO_2 uptake disappeared by mid-October (day 290) (Figs. 1 and 4).

During early summer, the fluxes of N_2O followed a similar daily pattern as that of F_{CO} with higher daytime N_2O emissions compared to night-time fluxes (Shurpali et al., 2016). This period of high N_2O emissions (days 143-158) was a direct

response to the N-P-K-S fertilizer application on 23 May, and it lasted for about 15 days. After this, an opposite diurnal pattern was observed during which the N₂O emissions were on average 50% higher during the night than during the day (Shurpali et al., 2016).

The gross daytime CO emissions were estimated in two ways: 1) assuming an equal CO uptake during day and night (constant uptake), and 2) accounting for temperature dependent CO uptake according to Whalen and Reeburgh (2001). The gross CO emissions calculated in either way, show that in the daytime the site emitted CO throughout the whole measurement period with the highest emissions during the spring and late summer (Table 2). During mid-summer and autumn the daytime emissions were markedly smaller, and less than half of the emissions during the spring. The smallest gross CO emissions were measured in late autumn (Table 2). When the temperature dependency in the CO uptake was taken into account, using a Q₁₀ value of 1.8 (Whalen and Reeburgh, 2001), both the daytime CO uptake (Daytime CO uptake (Q₁₀, 1.8)), and the daytime emission (Daytime CO emission (Q₁₀, 1.8)) were almost twice as high as the rates without the temperature correction (Table 2).

3.3 Driving factors for CO fluxes

The most pronounced relationships between F_{CO} and other measured scalars were found for the daytime data (sun elevation h>0) during the two emission periods in the spring and early summer (Table 3, Figure 5). Furthermore, the strongest correlations were found during the spring between F_{CO_day} and R_{glob} (r=0.760, p<0.01), R_{net} (r=0.760, p<0.01), H (r=0.729, p<0.01) and G (r=0.575, p<0.01). These positive correlations remained significant but became weaker towards the end of the measurement period (Table 3, Figure 5). Strong negative correlations were found during the spring between F_{CO_day} and RH (r=-0.537, p<0.01), and during the early summer with NEE (r=-0.469, p<0.01), while the correlation between daytime F_{CO} and M_{CO}, F_{N2O} or ecosystem respiration (RESP) were very weak throughout the 7-month measurement period (Table 3). Night-time (h<0) F_{CO} (F_{CO_night}) correlated weakly with F_{N2O} (r=-0.336, p<0.01), H (r=0.315, p<0.01), and LE (r=-0.241, p<0.05) in the spring and with M_{soil} (r=0.308, p<0.01) during early summer (Table 4). A strong negative correlation was found between F_{CO_night} and F_{N2O} during mid-summer (r=-0.607, p<0.01) and late autumn (r=-0.514, p<0.01), and a positive correlation between F_{CO_night} and LE (r=0.459, p<0.05) during mid-summer (Table 4).

4 Discussion

Based on the 7-month EC flux measurements at the RCG crop, we demonstrate that the EC method is suitable for measuring CO fluxes (F_{CO}) from a perennial agricultural crop. We show that the soil-plant system acted as a net source of CO during the spring and early summer and a net sink of CO over the late summer and autumn, and that the F_{CO} had a clear diurnal pattern with net CO emissions during daytime and net CO uptake during the night. This source-sink pattern existed over the whole measurement period with decreasing net emissions towards the end of the autumn. To our knowledge, similar long-term and continuous F_{CO} data series measured by the EC method over any ecosystem type does not exist, and hence this study is unique in bringing new insight to the understanding of short-term diurnal and long-term seasonal F_{CO} dynamics at ecosystem-level. Combining the continuous F_{CO} data with simultaneously measured CO_2 , N_2O and energy fluxes as well as meteorological and soil variables allowed us to distinguish driving variables of the F_{CO} , and demonstrate the suitability of the EC method to analyze ecosystem-level CO exchange dynamics. Due to the fact that the EC method measures net fluxes, we cannot directly separate between different processes, such as CO production and consumption. However, based on process understanding and our data, we made an assumption that most of the CO production takes place during daytime and that the night-time CO uptake is due to microbial activity. After these assumptions, we divided the data into daytime and night-time periods in order to analyse seasonal changes in dependencies between CO emissions and uptake and their driving variables. Cumulative CO fluxes (cum F_{CO}) over the whole 7-month measurement period showed that the RCG crop was a net sink of CO. This cum F_{CO} estimation may be biased due to the instrumental break during July (days 181-205), during which we do not have an estimate of the CO fluxes. Also, due to the fact that the data processing removed more daytime values (40.8% removed) compared to night-time data (24.1% removed), the night-time CO uptake is weighing more in the cumulative flux estimation, potentially leading to smaller and more negative net fluxes than estimated based on an equal number of flux data from daytime and night-time. We tested a simple statistical gap-filling method to obtain a balanced number of daytime and night-time data, however, as this gap-filling did not change the interpretation of the results, and as we do not have an appropriate process model to account for uptake and emission processes, we decided not to present these results. Based on the seasonal variation, we could divide the F_{CO} to a distinct emission period and an uptake period. During the “emission” period (days 110-160), the soil-plant system was a strong source of CO during daytime and a small sink during night-time. Furthermore, the emission period was divided into a spring emission period (days 110-145) and an early summer emission period (days 146-160), which differed from each other based on the daytime CO emission rates and relationships with other measured variables such as radiation and NEE. The highest CO emissions were observed soon after the snow melt during the spring in April to early May **when the air and soil temperatures were rather low and the crop was not yet** actively

photosynthesizing (low LAI, low NEE), while the radiation intensity was already rather high. As suggested by King (2000), the elevated spring-time CO emissions probably resulted from the degradation of the readily available last year's crop and litter, which has been shown to be a significant source of CO (King, 2000; King et al., 2012; Lee et al., 2012). Decreasing amounts of this readily degradable litter also partly explains the decreasing trend in CO emissions during spring and early summer (King, 2000).

In general, the F_{CO} rates from the RCG crop in this study fall into the same range as those reported from different natural and managed ecosystems across the different climatic regions (Table 5). **There is a tendency of higher CO emissions from tropical and Mediterranean ecosystems compared to northern and boreal ecosystems. The data comparison also indicates net CO uptake from forest ecosystems (Zepp et al., 1997; King, 2000; Kuhlbusch et al., 1998), CO emissions from savanna and croplands ecosystems (King, 2000; Kisselle et al., 2002; Varella et al., 2004; Galbally et al., 2010), and variation between CO uptake and emission from grassland ecosystems (Constant et al., 2008; Bruhn et al., 2013; van Asperen et al., 2015; Table 5).** When comparing daytime fluxes, the mean daytime F_{CO} at the RCG of $0.21 \text{ nmol m}^{-2} \text{ s}^{-1}$ is at the lower end of the emissions reported in grasslands or croplands (King, 2000; Bruhn et al., 2013; van Asperen et al., 2015), however, the strong seasonality and higher CO emissions during the spring ($0.91 \text{ nmol m}^{-2} \text{ s}^{-1}$) are very similar to the fluxes measured in tropical pastures and croplands (King, 2000; Varella et al., 2004; Galbally et al., 2010). The comparison of reported CO fluxes to our results is challenged by the differences in temporal resolution of the flux measurements. As most of the reported studies are conducted during daytime only and with biweekly to monthly intervals, possible diurnal and seasonal variation in the fluxes are neglected (e.g. King, 2000; Varella et al., 2004; Galbally et al., 2010; van Asperen et al., 2015).

To calculate an annual CO balance of the RCG site, we used a mean F_{CO} over the whole measurement campaign of $-0.25 \text{ nmol m}^{-2} \text{ s}^{-1}$ (Table 1) to apply for the missing period from day 326 to day 109 (22 November 2011 - 18 April 2012). This annual cumulative F_{CO} of $-111 \text{ mg CO m}^{-2} \text{ yr}^{-1}$ naturally has a high uncertainty due to the missing measurements. However, we expect that the F_{CO} are minimal during the snow-cover period in December-February. Whereas, for the spring period during the snow-melt in March-April, the assumption of small F_{CO} does not necessarily hold as the amount of radiation and temperature increase and the soil surface is freed from the snow allowing the old previous year's crop residues to decompose. Hence, we expect that the use of the mean F_{CO} from the measurement period probably underestimates the F_{CO} during the early spring period.

Similar to our findings from the emission period, soils from boreal to tropical regions have been found to have a clear diurnal pattern with emissions in the noon and uptake during the night (Conrad and Seiler, 1985a; Schade et al., 1999; Kisselle et al., 2002; Constant et al., 2008; van Asperen et al., 2015). The existing literature suggests that the net CO exchange involves

simultaneous production and consumption processes occurring in a variety of soil-plant systems. While the consumption is suggested to be a microbial process in the soil (Conrad and Seiler, 1980), the production of CO has been mostly linked with abiotic photodegradation or thermal degradation of soils, organic matter and vegetation (Conrad and Seiler 1985a; 1985b; Moxley and Smith 1998; Lee et al., 2012; Bruhn et al., 2013; Fraser et al., 2015) or to a minor extent to anaerobic microbial activity in wet soils (Funk et al., 1994; Bender and Conrad, 1994). In our study, the net CO uptake during night-time indicates that there is a microbial sink of atmospheric CO. We expect that this CO consumption also exists during daytime, and it may be increased due to temperature dependency of the consumption (King, 2000; Whalen and Reeburgh, 2001). We did not find correlation between daytime or night-time CO concentration (M_{CO}) and F_{CO} (Tables 3 and 4), indicating that M_{CO} is not limiting CO consumption at our site. In our site the estimated daytime CO consumption is overruled by a simultaneous strong CO production, creating the observed diurnal pattern in the spring and early summer. Assuming a temperature dependent CO uptake (Whalen and Reeburgh, 2001), we estimated that the daytime CO uptake (mean of $-1.79 \text{ nmol m}^{-2} \text{ s}^{-1}$) is over two times that in the night (mean $-0.77 \text{ nmol m}^{-2} \text{ s}^{-1}$) (Tables 1 and 2). When this was taken into account in gross daytime CO emissions, also daytime CO emission was estimated markedly higher compared to the daytime CO emission without the temperature corrected CO uptake. These gross rate calculations result slightly higher CO uptake and smaller emission compared to what van Asperen et al. (2015) reported from a Mediterranean grassland. van Asperen et al. (2015) reported night-time CO uptake up to $-1.0 \text{ nmol m}^{-2} \text{ s}^{-1}$ and daytime emissions of around $10 \text{ nmol m}^{-2} \text{ s}^{-1}$ by a flux gradient method. They also reported night-time minimum chamber fluxes of $-0.8 \text{ nmol m}^{-2} \text{ s}^{-1}$ and daytime maximum chamber fluxes of up to $3 \text{ nmol m}^{-2} \text{ s}^{-1}$, both measured over about one month period. Other reported diurnal CO fluxes are mostly over 24-hours only, hence mainly demonstrating the potential variation in the CO exchange over one day (Zepp et al., 1997; Kisselle et al., 2002; Constant et al., 2008).

Strong correlations between daytime F_{CO} and R_{glob} (and other radiation components) especially in the spring and early summer indicate that the direct or indirect effects of radiation drive the CO emissions. During the spring period, the strongest correlations were observed between daytime F_{CO} and solar radiation (R_{glob} , R_n), sensible heat flux and soil heat flux, all indicating a close connection between F_{CO} and radiation and heat transfer. Factors supporting the CO production through abiotic photodegradation and thermal degradation processes include high C to N ratio of the plant material (King et al., 2012), presence of oxygen (Tarr et al., 1995; Lee et al., 2012), greater solar radiation exposure (no shading) (King et al., 2012), and litter area to mass ratio (King et al., 2012; Lee et al., 2012). As the dead plant material in our measurement site has a high C to N ratio (mean \pm stdev: 66 ± 6.3), and as this dry plant material was well exposed to radiation in the spring, we expect that the conditions were suitable for CO formation through abiotic degradation processes. Correlation between F_{CO}

and soil heat flux (G), and that between F_{CO} and T_{air} indicate that also thermal degradation plays an important role in daytime CO formation. As the correlation between F_{CO} and T_{soil} was poor (at maximum $r=0.355$), the T_{soil} at the depth of 2.5 cm does not seem to reflect the location of CO formation via thermal degradation. However, a better correlation between F_{CO} and T_{air} indicates that most likely majority of thermal degradation or indirect photodegradation takes place on the soil surface or in (dead) plant material on top of the soil where temperature and degradation processes are directly influenced by radiation. A close look at the diurnal pattern of F_{CO} during the autumn and summer days in Figure 2 during the time of sunrise or sunset reveals that the F_{CO} starts to increase before the sun rise at around 9 am (late autumn, days 296-325), and the F_{CO} in the afternoon continues to decrease after the sun set at around 20 pm (late summer, days 205-240). These phenomena could be explained by temperature driven CO consumption, which according to soil temperatures should have a minimum soon after sunrise, hence affecting to the diurnal variation of the net F_{CO} (Figure 3). As the abiotic thermal degradation is temperature dependent, we do not expect thermal degradation to be responsible for increased CO production during early morning hours before the sunrise, however, this process may have contributed to the prolonged CO formation after the sunset during late summer. Our data does not allow for deeper process-level interpretation, however, these findings also indicate that direct photodegradation is probably not the sole source of CO at the site, and that also indirect photodegradation, thermal degradation or biological processes may play roles in the CO formation.

Although we cannot separate between biotic and abiotic CO formation at the RCG field site, our findings of the negative correlation between daytime F_{CO} and NEE ($r=-0.469$) during early summer (days 146-160), the period of maximum NEE, indicate that some CO may also be formed via plant physiological processes. This early summer CO emission period (days 146-160) coincides with the steepest slope in CO_2 uptake (more negative NEE), supporting the findings of Wilks (1959), Bruhn et al. (2013) and Fraser et al. (2015) that CO can be emitted not only from dead plant matter but also from living green leaves. The observed daytime CO emissions during early summer can have also been formed through abiotic processes, which also occur in living plants (Tarr et al., 1995; Erickson et al., 2015). King et al. (2012) suggested that the CO emissions from photodegradation generally decrease with increasing leaf area index, and Tarr et al. (1995) and Erickson et al. (2015) found that the CO photoproduction efficiency is lower for living plants compared to senescent or dead vegetation. These studies support our findings of lower daytime CO emissions from fully developed crop during the summer (days 205-240) compared to CO emissions during the spring (days 110-145), when the ground was covered by the dead plant litter. Still the role of biological CO formation in living green plants and the forming processes remain unresolved and call for further process-studies.

Based on our data, we suggest that a poor correlations between F_{CO} and ecosystem respiration (RESP) throughout the measurement campaign indicates that microbial and plant respiratory activity does not play an important role in the CO formation. With respect to F_{N_2O} and F_{CO} , we do not expect a strong relationship due to the difficulties in separating between overlapping abiotic CO production, microbial CO consumption (Conrad and Seiler, 1980; Moxley and Smith 1998), and microbial N_2O production/uptake in the soil. As nitrifiers are among the diverse microbial community oxidizing CO in soils (Jones and Morita, 1983; Bender and Conrad, 1994; King and Weber, 2007), a high nitrification activity may be reflected in higher CO consumption in the soil. In the field, this could be visible during night-time when the CO consumption is expected to dominate the net CO fluxes, while in most of the year during daytime the CO production overrides the consumption. If a large fraction of the CO uptake was due to nitrification activity, we should be able to see this in negative correlation between night-time F_{N_2O} and F_{CO_night} . In fact, we found significant negative correlations between F_{N_2O} and F_{CO_night} in the spring ($r=-0.336$), mid-summer ($r=-0.607$) and late autumn ($r=-0.514$). These correlations were significant but much weaker during the daytime (Table 3). These findings hint towards the role of nitrifiers in CO consumption at the reed canary grass site. However, we have no process data from the site showing the link between nitrifiers and CO consumption.

This is the first study to apply EC based techniques to measure long-term variation in F_{CO} at any ecosystem type in the world. In addition to the long-term seasonal variability in the F_{CO} , we were able to identify the driving variables and processes at ecosystem level, findings that have previously been shown with plot scale chamber measurements or in the laboratory. The high diurnal and seasonal variability over the 7-month measurement period shows that there is an urgent need for continuous and long-term assessment of F_{CO} . The limitations of the EC method, such as inability to separate between CO production and consumption processes, naturally increase uncertainties in the interpretation of the results. However, despite these limitations, the data allowed us to distinguish between the daytime and night-time processes involved and to link the diurnal and seasonal variability to abiotic and biotic processes. Also, the EC method has clear advantages over the traditional enclosure methods such as measuring non-disturbed ecosystem fluxes and avoiding surface reactions with measurement material, both supporting the application of the EC method to measure F_{CO} in different ecosystems.

5 Conclusions

Long-term and continuous EC based measurements of F_{CO} over an arable reed canary grass showed clear seasonal variation with net emissions during the spring and early summer, and net uptake of CO during the late summer and autumn. Daytime emissions of CO and night-time uptake of CO demonstrate the dynamic nature of parallel consumption and production

processes. Based on daytime and night-time separation of F_{CO} , and correlation analysis between F_{CO} and radiation, T_{soil} , T_{air} , heat fluxes (H, LE), NEE and ecosystem respiration, and F_{N_2O} the daytime CO emissions were suggested to be driven mainly by direct and indirect effects of radiation such as heat fluxes and temperature, while the night-time CO uptake was found to be connected to N_2O emissions. Although, the measurement approach does not allow to separate between different CO forming and consuming processes, CO emissions are suggested to mainly result from abiotic photo- and thermal degradation of plant material and soil organic matter, whereas the night-time CO uptake was expected to be microbial. This study demonstrates the applicability of the EC method in CO flux measurements at ecosystem scale, and shows the potential in linking the short-term F_{CO} dynamics to its environmental drivers. In order to fully understand the source-sink dynamics and processes of CO exchange, continuous and long-term F_{CO} measurements in combination with process-based studies are urgently needed.

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1 Table 1. Mean, median and 25-75th percentiles of the CO fluxes (F_{CO} , $\text{nmol m}^{-2} \text{s}^{-1}$) measured in a read canary grass (RCG) crop at Maaninka. The fluxes are separately
 2 calculated for daytime (F_{CO_day} , sun elevation, $h_{sun} > 0$) and night-time (F_{CO_night} , $h_{sun} < 0$), and as a net flux over all F_{CO} data (net F_{CO}) for the six measurement periods (S =
 3 spring, ES = early summer, MS = mid-summer, LS = late summer, A = autumn, LA = late autumn), and over the full measurement period (All) from April to November 2011.
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Period, days	F_{CO_day}				F_{CO_night}				net F_{CO}			
	mean	median	25 th -75 th percentile		mean	median	25 th -75 th percentile		mean	median	25 th -75 th percentile	
S, 110-145	0.97	0.68	-0.15	2.00	-0.64	-0.56	-0.97	-0.20	0.41	0.09	-0.57	1.28
ES, 146-160	0.24	0.08	-0.29	0.57	-0.67	-0.49	-0.72	-0.33	0.03	-0.10	-0.45	0.43
MS, 161-181	-0.07	-0.08	-0.40	0.24	-0.67	-0.52	-0.86	-0.22	-0.22	-0.18	-0.55	0.16
LS, 205-240	0.36	0.30	-0.07	0.87	-0.76	-0.49	-0.96	-0.19	-0.09	-0.04	-0.53	0.49
A, 241-295	-0.12	-0.18	-0.48	0.13	-0.66	-0.61	-0.90	-0.32	-0.44	-0.44	-0.77	-0.10
LA, 296-325	-0.62	-0.59	-0.94	-0.26	-1.05	-1.01	-1.37	-0.65	-0.92	-0.89	-1.25	-0.49
All, 110-325	0.21	0.01	-0.41	0.55	-0.77	-0.66	-1.06	-0.33	-0.25	-0.34	-0.79	0.17

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1 Table 2. Mean, median and 25-75th percentiles of the estimated gross daytime CO emission (Gross daytime CO emission, nmol m⁻² s⁻¹), temperature corrected daytime CO
 2 uptake (Daytime CO uptake, (Q₁₀ 1.8)), and temperature corrected gross daytime CO emission (Gross daytime CO emission (Q₁₀ 1.8)) calculated for the read canary grass
 3 (RCG) crop at Maaninka. The CO emission and uptake rates are calculated for six measurement periods (S = spring, ES = early summer, MS = mid-summer, LS = late
 4 summer, A = autumn, LA = late autumn), and over the full measurement period (All) from April to November 2011. The estimated gross daytime CO emission is calculated
 5 in two ways: 1) assuming a constant CO uptake, and 2) assuming temperature dependent CO uptake. Gross daytime CO emission based on a constant CO uptake (way 1,
 6 Chapter 2.4) refers to the difference between daytime fluxes (F_{CO,day}) and night-time fluxes (F_{CO,night}) presented in Table 1. The temperature corrected gross daytime CO
 7 emission (Gross daytime CO emission (Q₁₀, 1.8)) refers to the difference between daytime fluxes (F_{CO,day}) (Table 1.) and daytime CO uptake (Q₁₀, 1.8). The daytime CO
 8 uptake (Daytime CO uptake (Q₁₀, 1.8)) is calculated by extrapolating the night-time CO fluxes (F_{CO,night}) to daytime using the difference between day and night soil
 9 temperatures (2.5 cm depth) (Δt_{soil}) and the Q₁₀-value of 1.8 (Whalen and Reeburgh, 2001), as described in Chapter 2.4.

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Period, DOY	Gross daytime CO emission				Δt_{soil}	Daytime CO uptake (Q ₁₀ , 1.8)				Gross daytime CO emission (Q ₁₀ , 1.8)			
	mean	median	25 th -75 th percentile		T _{day} -T _{night}	mean	median	25 th -75 th percentile		mean	median	25 th -75 th percentile	
S, 110-145	1.61	1.24	0.83	2.20	2.1	-1.24	-1.09	-1.89	-0.39	2.22	1.76	1.74	2.39
ES, 145-160	0.91	0.57	0.43	0.91	1.2	-1.27	-0.92	-1.36	-0.63	1.51	1.00	1.06	1.20
MS, 160-181	0.59	0.45	0.46	0.46	0.7	-1.23	-0.96	-1.58	-0.41	1.15	0.89	1.18	0.65
LS, 205-240	1.12	0.79	0.89	1.07	0.9	-1.42	-0.91	-1.78	-0.36	1.77	1.21	1.71	1.24
A, 240-295	0.54	0.42	0.41	0.45	1.0	-1.24	-1.13	-1.68	-0.59	1.11	0.95	1.19	0.72
LA, 295-325	0.42	0.42	0.43	0.39	0.3	-1.90	-1.84	-2.49	-1.18	1.28	1.25	1.56	0.92
ALL, 110-325	0.98	0.68	0.65	0.88	3.5	-1.58	-1.37	-2.19	-0.68	1.79	1.38	1.78	1.23

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5 Table 3. Pearson correlation matrix for half-hour daytime CO fluxes (F_{CO_day}) during six periods (S = spring, ES = early summer, MS = mid-summer, LS = late summer, A = autumn, LA = late autumn) at the reed canary grass crop in Maaninka. M_{CO} = CO mixing ratio, NEE = net ecosystem exchange, RESP = ecosystem respiration, F_{N_2O} = N_2O flux, H = sensible heat flux, LE = latent heat flux, T_{air} = air temperature, R_{glob} = global radiation, R_{net} = net radiation, G = soil heat flux, T_{soil} = soil temperature at 2.5 cm, SWC = soil water content at 2.5 cm.

	F_{CO_day} S, 110-145		F_{CO_day} ES, 146-160		F_{CO_day} MS, 161-180		F_{CO_day} LS, 205-240		F_{CO_day} A, 241-295		F_{CO_day} LA, 296-325							
		n		n		n		n		n		n						
M_{CO}	0.080	*	711	0.128	**	510	-0.116	*	436	-0.074		488	0.038		851	-0.284	**	288
NEE	-0.188	**	711	-0.469	**	510	-0.308	**	436	-0.488	**	488	-0.237	**	850	-0.25	**	288
RESP	0.015		711	0.274	**	510	0.272	**	436	0.257	**	488	0.198	**	850	0.077		288
F_{N_2O}	-0.219	**	669	0.000		453	-0.293	**	426	-0.026		478	-0.085	*	850	-0.172	**	287
H	0.729	**	711	0.329	**	510	0.234	**	436	0.427	**	488	0.132	**	851	-0.076		288
LE	0.402	**	418	0.398	**	401	0.514	**	224	0.625	**	307	0.317	**	573	0.289	**	185
RH	-0.537	**	711	-0.176	**	510	-0.303	**	436	-0.434	**	488	-0.081	*	851	-0.179	**	288
T_{air}	0.425	**	711	0.344	**	510	0.36	**	436	0.433	**	488	0.241	**	851	0.073		288
R_{glob}	0.760	**	711	0.498	**	510	0.373	**	436	0.549	**	488	0.265	**	851	0.256	**	288
R_{net}	0.760	**	711	0.515	**	510	0.376	**	436	0.558	**	488	0.277	**	851	0.218	**	288
G	0.575	**	711	0.473	**	510	0.406	**	436	0.485	**	488	0.247	**	851	0.033		288
T_{soil}	0.191	**	711	0.282	**	510	0.318	**	436	0.358	**	488	0.206	**	851	0.071		288
M_{soil}	-0.099	**	711	0.033		510	0.095	*	436	0.086		488	-0.105	**	851	0.095		288

** . Correlation is significant at the 0.01 level (2-tailed).

* . Correlation is significant at the 0.05 level (2-tailed).

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5 Table 4. Pearson correlation matrix for half-hour night-time CO fluxes (F_{CO_night}) during six periods (S = spring, ES = early summer, MS = mid-summer, LS = late summer, A = autumn, LA = late autumn) at the reed canary grass crop in Maaninka. M_{CO} = CO mixing ratio, NEE = net ecosystem exchange, RESP = ecosystem respiration, F_{N_2O} = N_2O flux, H = sensible heat flux, LE = latent heat flux, T_{air} = air temperature, R_{glob} = global radiation, R_{net} = net radiation, G = soil heat flux, T_{soil} = soil temperature at 2.5 cm, SWC = soil water content at 2.5 cm.

	F_{CO_night} S, 110-145		F_{CO_night} ES, 146-160		F_{CO_night} MS, 161-180		F_{CO_night} LS, 205-240		F_{CO_night} A, 241-295		F_{CO_night} LA, 296-325	
		n		n		n		n		n		n
M_{CO}	-0.045	380	-0.043	142	-0.279 **	134	-0.165 **	324	-0.110 **	1149	-0.041	700
NEE	0.069	380	-0.167 *	142	-0.118	134	-0.049	324	0.024 **	1149	0.025	700
RESP	0.056	380	0.015	142	-0.006 **	134	0.125 **	324	0.062 *	1149	0.072	700
F_{N_2O}	-0.336 **	350	0.034	120	-0.607 **	126	-0.197 **	307	0.009	1140	-0.514 **	696
H	0.315 **	380	0.170 *	142	0.002	134	0.051	324	-0.021 **	1149	0.080 *	700
LE	-0.241 *	74	0.099	72	0.459 *	20	-0.078	62	0.135 **	453	0.161 **	279
RH	0.027	380	-0.016	142	-0.057	134	-0.12 **	324	-0.033	1149	-0.041 **	700
T_{air}	0.107 *	380	-0.013	142	0.092	134	0.249 **	324	0.138 **	1149	0.098 **	700
R_{glob}	0.077	380	0.118	142	-0.096	134	-0.02	324	-0.001	1149	-0.041 **	700
R_{net}	0.011	380	0.111	142	0.026	134	0.087	324	0.043	1149	-0.053 **	700
G	0.050	380	0.029	142	0.121	134	0.207 **	324	0.175 **	1149	0.162 **	700
T_{soil}	0.075	380	-0.146	142	-0.035	134	0.167 **	324	0.038	1149	0.117 **	700
M_{soil}	0.043	380	0.308 **	142	0.212 *	134	0.138 *	324	0.093 **	1149	0.008	700

** . Correlation is significant at the 0.01 level (2-tailed).

* . Correlation is significant at the 0.05 level (2-tailed).

Table 5. Reported CO fluxes measured in different ecosystems and climatic regions, using chambers (transparent or dark), micrometeorological flux gradient or eddy covariance methods, and the reported data period, measurement frequency and the moment of the measurements.

Reference	Ecosystem, climate, country	Measurement method	Data period, measurement frequency, moment of measurement	F_{CO} (nmol m ⁻² s ⁻¹)
Zepp et al., 1997	Black spruce forest, boreal, Manitoba, Canada	Chambers, transparent	3 months, weekly, daytime	-1.06
Zepp et al., 1997	Jack pine forest, boreal, Manitoba, Canada	Chambers, transparent	3 months, weekly, daytime	-0.58
King, 2000	Pine forest, Northeast, Walpole, Maine, USA	Chambers, dark	1.3 years, biweekly, daytime	1.12
King, 2000	Mixed hardwood-coniferous forest, Walpole, Maine, USA	Chambers, dark	1.3 years, biweekly, daytime	0.62
King, 2000	Pine forest, Griffin, Georgia, USA	Chambers, dark	1 year, bimonthly, daytime	-0.21
King, 2000	Pine forest, Tifton, Georgia, USA	Chambers, dark	1 year, bimonthly, daytime	-0.95
Kuhlbusch et al., 1998	Black spruce, boreal, Manitoba, Canada	Chambers, dark	1 year, bimonthly, daytime	-1.11
Galbally et al. 2010	Mallee, Eucalyptus sp. Ecosystem, tropical, Australia	Chambers, transparent	1 year, bimonthly, daytime	0.61
Kisselle et al., 2002	Cerrado, campo sujo, tropical, Brazil	Chambers, transparent	1 year, monthly, daytime	3.16
Kisselle et al., 2002	Cerrado, stricto sensu, tropical, Brazil	Chambers, transparent	1 year, monthly, daytime	2.66
Varella et al., 2004	Natural cerrado, tropical, Brazil	Chambers, transparent	1.5 years, monthly, daytime	1.91
Varella et al., 2004	Pasture (<i>Brachiaria brizantha</i>), tropical, Brazil	Chambers, transparent	1.5 years, monthly, daytime	1.20
King, 2000	Cropland, corn, Walpole, Maine, USA	Chambers, dark	1.3 years, biweekly, daytime	2.19
King, 2000	Cropland, sorghum/wheat, Griffin, Georgia, USA	Chambers, dark	1 year, bimonthly, daytime	1.16
King, 2000	Cropland, cotton/peanuts/winter wheat, Tifton, Georgia, USA	Chambers, dark	1 year, bimonthly, daytime	1.03
Galbally et al. 2010	Cropland, wheat, tropical, Australia	Chambers, transparent	1 year, bimonthly, daytime	0.98
Constant et al., 2008	Grassland, boreal, Quebec, Canada	Flux gradient	1 year, diurnal cycle	-2.11
Bruhn et al., 2013	Grassland, temperate, Denmark	Chambers, dark	2 months, monthly, daytime	-0.78
Bruhn et al., 2013	Grassland, temperate, Denmark	Chambers, transparent	2 months, monthly, daytime	0.36
van Asperen et al., 2015	Grassland, Mediterranean, Italy	Chambers, transparent	5 weeks, summer, diurnal cycle	0.35
van Asperen et al., 2015	Grassland, Mediterranean, Italy	Flux gradient	1 month, 30-min, diurnal cycle	1.74
this study	Grassland, reed canary grass, boreal, Finland	Eddy covariance	7 months, 30-min, diurnal cycle	-0.25

Figure captions

5 Figure 1. (a) Daily mean air and soil temperatures, (b) global radiation sum (R_{glob}), (c) daily precipitation sum (P_r) and soil water content (SWC), (d) weekly leaf area index (LAI) (black) and green area index (GAI) (grey), (e) net ecosystem exchange of CO_2 (NEE), and (f) cumulative CO fluxes calculated from half-hour mean CO fluxes (cum F_{CO} ; black lines) and daytime mean CO fluxes ($F_{\text{CO_day}}$; grey) over the 7-month measurement period in a reed canary grass crop. Measurement periods (S = spring, ES = early summer, MS = mid-summer, LS = late summer, A = autumn, LA = late autumn) are separated by solid lines.

10 Figure 2. Diurnal cycle of half-hour mean CO fluxes (F_{CO} , $\text{nmol m}^{-2} \text{s}^{-1}$) from the reed canary grass crop from six distinct periods during the April to November 2011. Grey areas indicate the moment of sunrise and sunset, and the vertical bars indicate ± 1 standard deviation of the fluxes.

Figure 3. Diurnal cycle of half-hour mean global radiation (R_{glob} , W m^{-2}) (black) and soil temperature at 2.5 cm depth (grey) at the reed canary grass crop from six distinct periods during the April to November 2011. The vertical bars indicate ± 1 standard deviation of the fluxes and temperatures.

15 Figure 4. Diurnal cycle of half-hour mean net ecosystem exchange of CO_2 (NEE, $\mu\text{mol CO}_2 \text{m}^{-2} \text{s}^{-1}$) from the reed canary grass crop from six distinct periods during the April to November 2011. Grey areas indicate the moment of sunrise and sunset, and the vertical bars indicate ± 1 standard deviation of the fluxes.

Figure 5. Daytime half-hour average CO fluxes (F_{CO}) against global radiation (R_{glob}), sensible heat flux (H) and net ecosystem exchange of CO_2 (NEE) measured over two emission periods (Spring, days 110-145, Early Summer, days 146-160) at the reed canary grass crop in Maaninka. The bin averages with ± 1 standard deviation are presented in black line.

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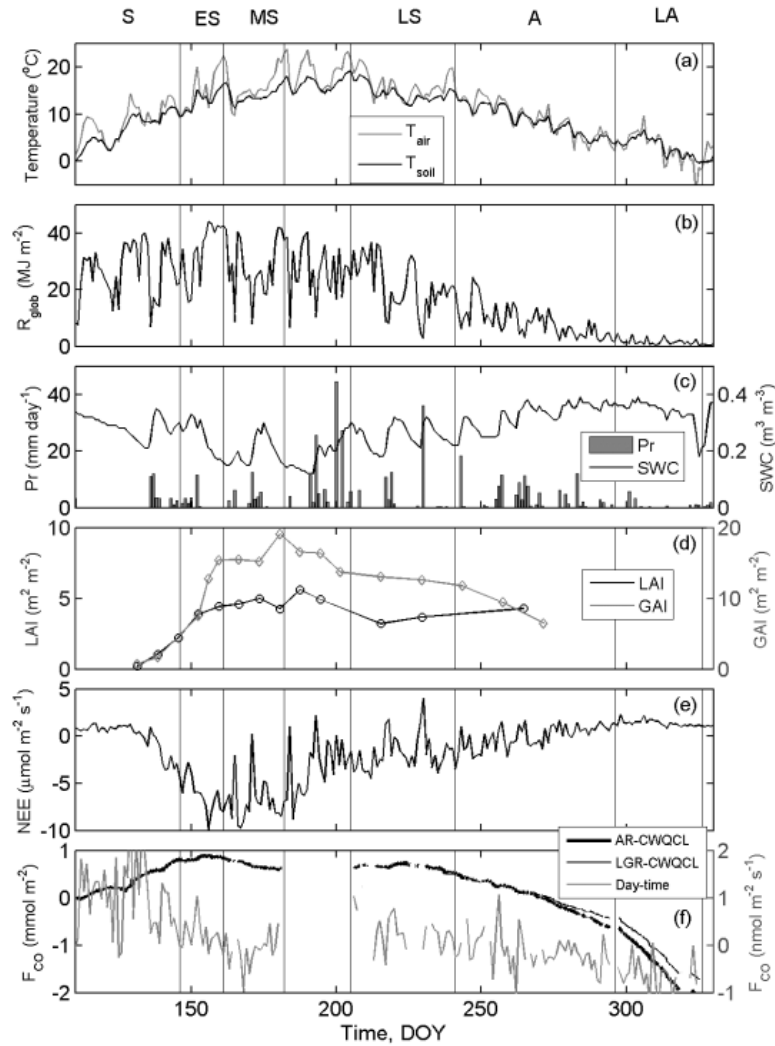


Figure 1. (a) Daily mean air and soil temperatures, (b) global radiation sum (R_{glob}), (c) daily precipitation sum (P_r) and soil water content (SWC), (d) weekly leaf area index (LAI) (black) and green area index (GAI) (grey), (e) net ecosystem exchange of CO₂ (NEE), and (f) cumulative CO fluxes calculated from half-hour mean CO fluxes (cum F_{CO} ; black lines) and daytime mean CO fluxes (F_{CO_day} ; grey) over the 7-month measurement period in a reed canary grass crop. Measurement periods (S = spring, ES = early summer, MS = mid-summer, LS = late summer, A = autumn, LA = late autumn) are separated by solid lines.

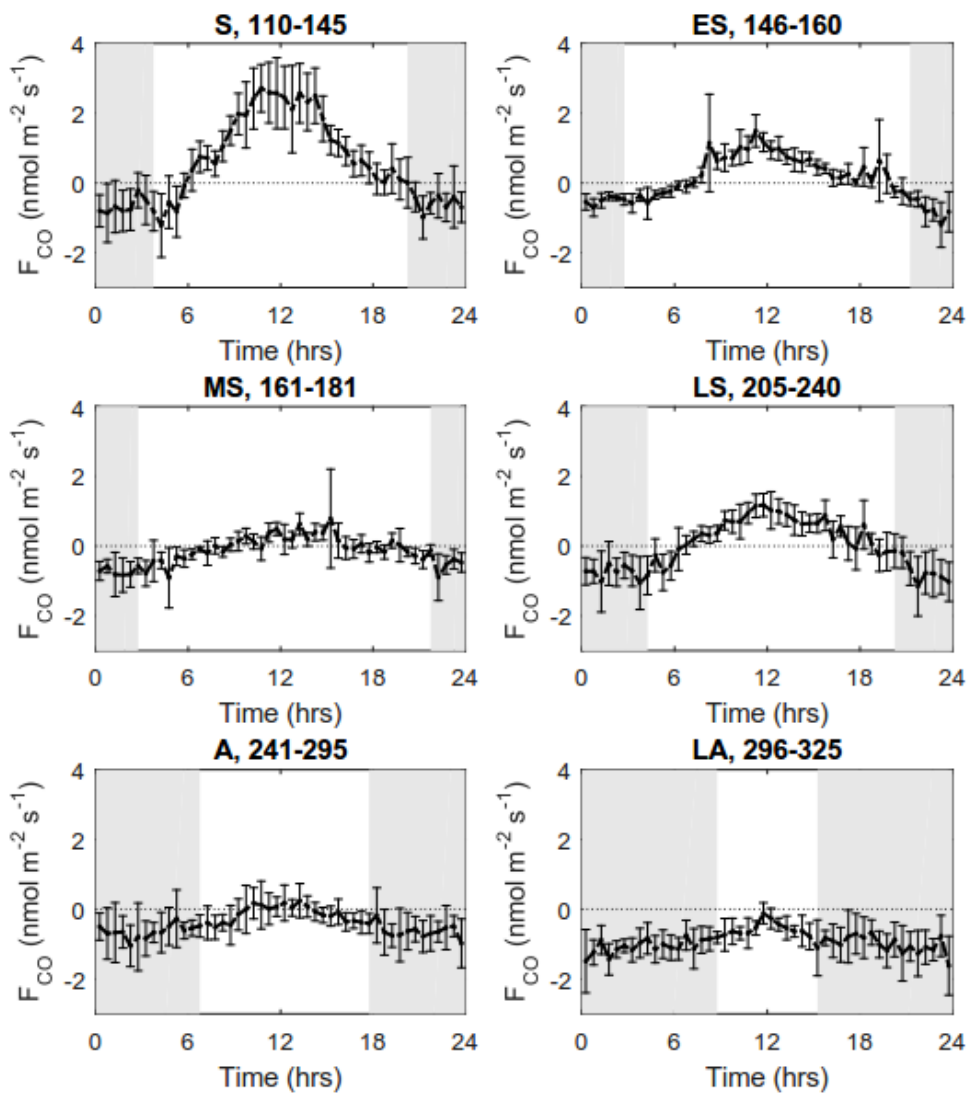


Figure 2. Diurnal cycle of half-hour mean CO fluxes (F_{CO} , $\text{nmol m}^{-2} \text{s}^{-1}$) from the reed canary grass crop from six distinct periods during the April to November 2011. Grey areas indicate the moment of sunrise and sunset, and the vertical bars indicate ± 1 standard deviation of the fluxes.

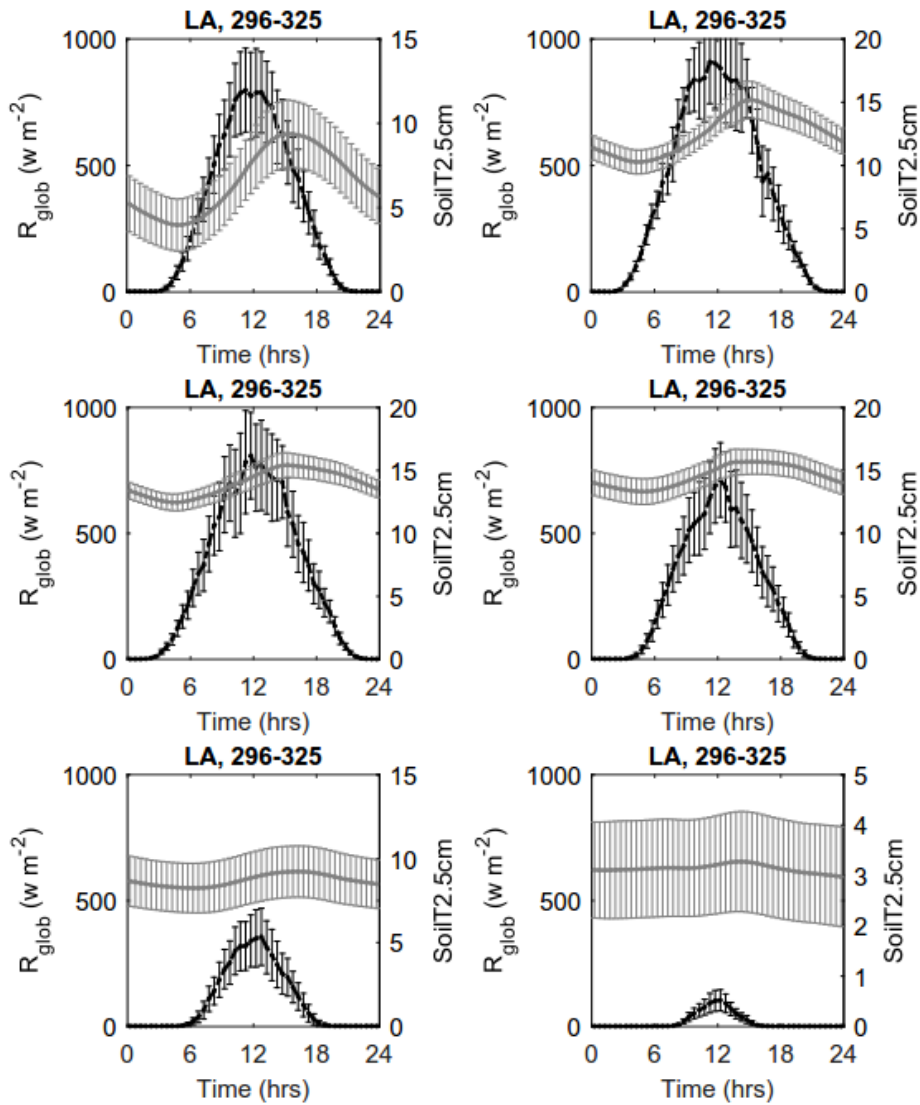


Figure 3. Diurnal cycle of half-hour mean global radiation (R_{glob} , $W m^{-2}$) (black) and soil temperature at 2.5 cm depth (grey) at the reed canary grass crop from six distinct periods during the April to November 2011. The vertical bars indicate ± 1 standard deviation of the fluxes and temperatures.

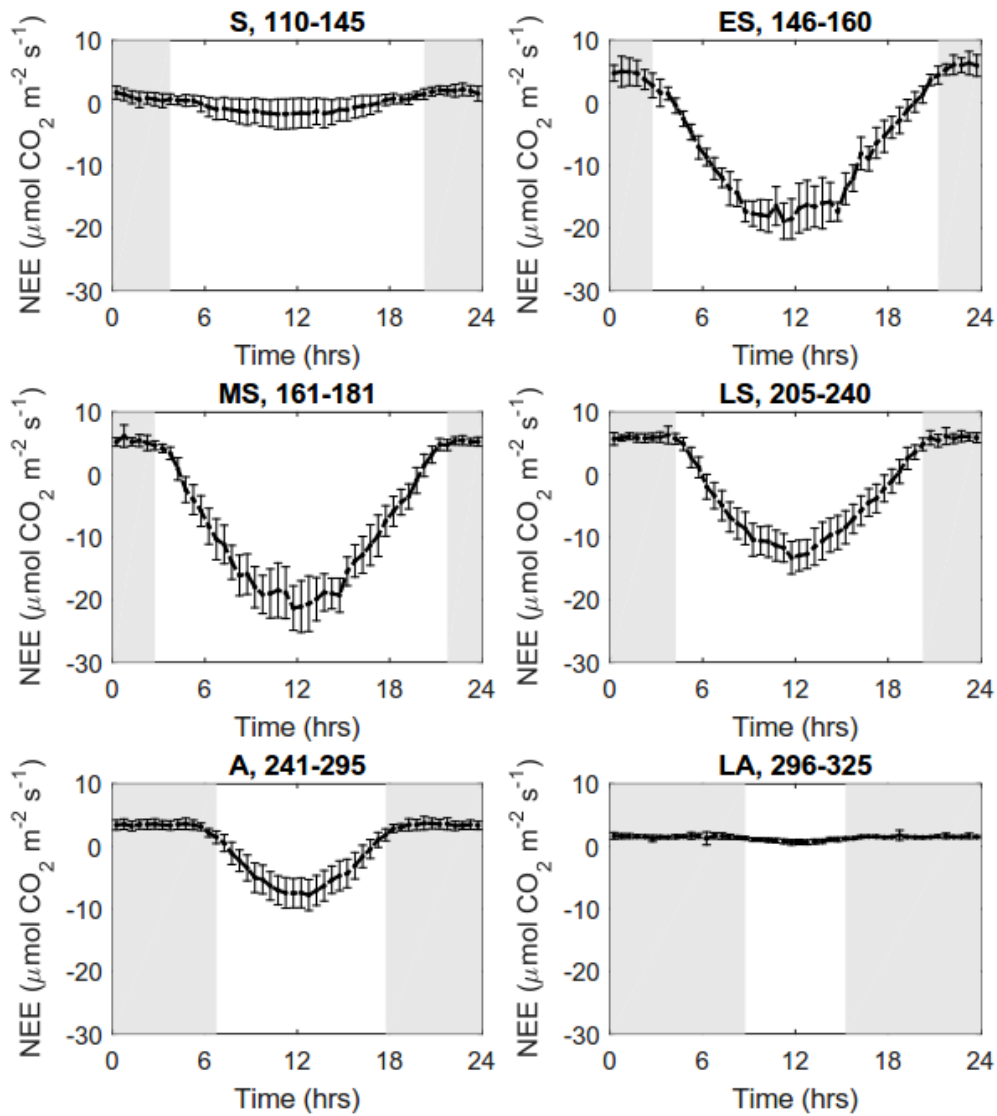


Figure 4. Diurnal cycle of half-hour mean net ecosystem exchange of CO₂ (NEE, μmol CO₂ m⁻² s⁻¹) from the reed canary grass crop from six distinct periods during the April to November 2011. Grey areas indicate the moment of sunrise and sunset, and the vertical bars indicate ±1 standard deviation of the fluxes.

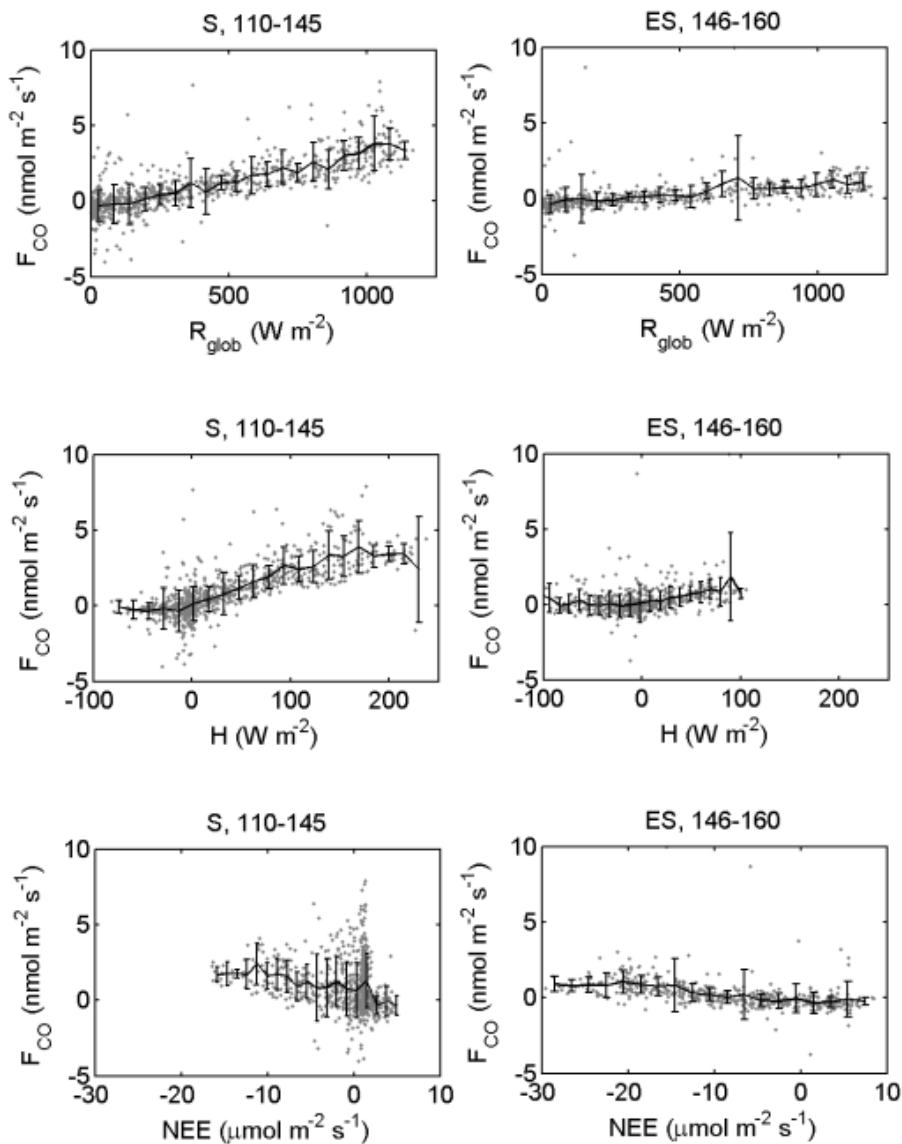


Figure 5. Daytime half-hour average CO fluxes (F_{CO}) against global radiation (R_{glob}), sensible heat flux (H) and net ecosystem exchange of CO_2 (NEE) measured over two emission periods (Spring, days 110-145, Early Summer, days 146-160) at the reed canary grass crop in Maaninka. The bin averages with ± 1 standard deviation are presented in black line.